

MASTER

JAPAN'S
NEW SUNSHINE PROJECT

1996 ANNUAL SUMMARY
OF COAL LIQUEFACTION
and GASIFICATION

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1. RESEARCH AND DEVELOPMENT OF COAL LIQUEFACTION TECHNOLOGIES

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- (2) Studies on Catalysts for Coal Liquefaction
- (3) Basic Studies on Coal Liquefaction Reaction, Reforming and Utilization of Liquefaction Products
- (4) Studies on the Mechanism of Direct Hydrogenation Reaction and Prevention of Coking
- (5) Dissolution Reaction of Coal by Hydrogen-Donating Aromatic Solvents and Development of Effective Catalyst
- (6) Mechanistic Basis of the Coal Dissolution by Hydrogen Donor Solvents: Multi-Stage Coal Liquefaction for the Better Liquid Yield under Milder Conditions

STUDIES ON THE LIQUEFACTION CHARACTERISTICS OF VARIOUS COALS AND LIQUEFACTION PROCESS DEVELOPMENT

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Objective

The main objective of this research is to conduct fundamental researches for the development of advanced coal liquefaction process. For these purposes, studies are conducted on the analysis of physical and chemical structures of coal, the analysis of interactions between coal molecules, the improvement of reaction performance by the suppression of retrogressive reaction, the development of highly active and dispersed catalyst for primary coal liquefaction, etc.

Work Program

1) Study on liquefaction characteristics of various coals

Liberation and control of non-covalent bonds in coal and its effect on liquefaction reactivity, mechanism of retrogressive reaction and the development of highly active catalyst for the primary liquefaction of coal.

2) Liquefaction test by use of 0.1 t/d BSU

Demolition studies of 0.1 t/d bench scale unit for coal liquefaction and distillation tower plant and the analysis of their materials.

Summary (1984-1996)

1. Up to FY 1995

Since 1984 the primary liquefaction of coal has been mainly studied. The analysis of coal liquefaction mechanism, the development of iron-based catalyst, the relationship between chemical structure and liquefaction reactivity of coal, the liquefaction tests of various coals by use of bench scale continuous reactor, and the analysis of flow characteristic of coal slurry in the reactor, etc. have been investigated. The coprocessing of coal/bitumen and the de-ashing of coal by oil agglomeration were also studied.

2. FY 1996

(1) Study on liquefaction characteristics of various coals

(a) Effect of intermolecular cohesion on liquefaction of bituminous coal

The elucidation of the role of non-covalent bonds in bituminous coal is very useful for the understanding of its liquefaction behavior especially at the initial stage of the reaction. In order to evaluate the effect of intermolecular cohesion on the conversion of bituminous coal, the reactivities of reductively methylated coal and o-methylated coal were tested and compared with that of raw coal by non-catalytic liquefaction reaction in tetralin solvent at 693K. The reductive methylation contributes to the release of all types of non covalent interaction (hydrogen bonds, charge transfer interaction, aromatic π - π interaction, etc.), whereas o-methylation selectively liberates only hydrogen bonds. Illinois coal was used as a sample.

Figure 1 shows the increases in oil yield and conversion of Illinois coal by the release of intermolecular cohesive force. At the nominal reaction time of 0 min, the coal conversion was drastically increased by about 35 wt% by the reductive methylation, but the increase in the conversion was limited to only 17 wt% by O-methylation. This result suggests that approximately 50 % of intermolecular cohesive force in bituminous coal can be attributable to hydrogen bonds. In addition, the increase in oil yield by the reductive methylation amounted to about 25 wt%, indicating that the release of intermolecular cohesive force especially contributes to the formaion of oil. In conclusion, the reduction of intermolecular cohesive force in coal promotes the dispersion and dissolution of coal molecules into solvents which leads to the suppression of retrogressive reaction in coal liquefaction.

(b) Characteristics of dehydrogenation and hydrogenation over carbon-supported metal catalysts

An active carbon (surface area, 1030 m²/g) from coal, supplied by Kurare Chemical Co., was used as the catalyst support. The content of metal added onto the active carbon was 3 wt%. All experiments were carried out in a downflow fixed bed reactor system. The reactor was charged with 1.5 g of catalyst and presulfurized before use. After heating to reaction temperature under 10 MPa pressure, the reaction was initiated by switching from solvent to a mixture of tetralin and anthracene in benzene solvent.

Figure 2 shows tetralin conversions against temperature for all the catalysts using the mixture of tetralin and anthracene. It is clear that metal free active carbon support itself shows some catalytic effect for the dehydrogenation of tetralin at all the temperatures. These observations support that the active carbon has the ability to abstract hydrogen atoms from aromatic hydrocarbon even at 300°C.

This figure also shows that all of the supported metal catalyst exhibited higher dehydrogenation activity than the support alone over the entire temperature range. The observed activity order was $\text{Ru} > \text{Ni} > \text{Co} \sim \text{Fe} \gg$ active carbon. Under the reaction conditions of the present work, no external hydrogen gas was supplied and much more active hydrogen atoms were formed at the active sites on the carbon surface along with the proceeding of the tetralin dehydrogenation. Therefore, a reverse-spillover process is likely to occur on all the carbon-supported metal catalysts. Namely, the metals as the gate of the reverse spillover of hydrogen promoted the hydrogen release from the carbon surface into the gas phase.

. On the other hand, when anthracene was added as hydrogen acceptor to the reaction mixture, anthracene was hydrogenated as the tetralin dehydrogenation proceeded. As shown in Figure 2, anthracene conversions strongly depended on the catalysts. With the active carbon alone, anthracene conversion increased approximately linearly with the temperature up to 380°C . This observation indicates that active carbon is also a very active catalyst for the hydrogenation of anthracene. Adding Ru and Ni onto the active carbon entirely changed the temperature-conversion profiles. In the low temperature range of $300\text{--}350^{\circ}\text{C}$, these catalysts provided much higher conversions than that obtained with the active carbon alone; whereas, in the high temperature range of $380\text{--}400^{\circ}\text{C}$, both of them showed negative catalytic behavior, giving a sharp decrease of the conversion. Co and Fe metals gave less influences on the activity of the active carbon below 350°C .

In the case of metal-free active carbon, the releasing of the hydrogen atoms occurs thermally. Its thermal desorption is relatively slow around 400°C , so more hydrogen atoms would remain on the carbon surface. On the other hand, when the supported metal catalysts were used, the hydrogen releasing process was enhanced remarkably by the reverse spillover mechanism. As a result, the concentration of surface hydrogen atoms available for hydrogenation is low. However, when the temperature is 350°C or below, hydrogen transfer on the carbon surface via the metal particles probably promotes anthracene hydrogenation. With Ru and Ni supported catalysts, higher activities were obtained at lower temperatures and this mechanism is operative. But, in the cases of Fe and Co supported catalysts, no such catalytic effect was observed. The reason of these difference is still unknown.

(c) Development of highly active hydrogenation catalyst

Two-stage liquefaction process might be one of the approaches to enhance oil

yield with minimizing the formation of radicals. This process consists of the deep hydrogenation at lower temperature and the quick hydro-cracking at higher temperatures and hence the development of new type of catalyst which has a highly hydrogenation activity at lower temperatures would be required for this process. $\text{Mn}_2\text{O}_3\text{-NiO}$ (MN) catalyst was prepared and its catalytic activity was tested for the liquefaction of coal. The content of Ru metal impregnated on these supports was 1 wt%. For a comparison, a commercial catalyst HDS-3 (NiO , 3-4%; MoO_3 , 14.5-16.0%; Cyanamid Co.) was used.

The liquefaction test was carried out by a high-pressure differential thermal and differential pressure analyzer (a high-pressure DTA/DPA) with two autoclaves which were a reference chamber and a reaction chamber. In each test, 2 g of coal sample and 3.5 g of tetralin were charged with 0.1 g of catalyst into the sample chamber and 5 g of α -alumina powder ($<149\ \mu\text{m}$) into the reference chamber. Hydrogen of 6 MPa initial pressure was charged into both chambers and then heated up to a given temperature.

Figure 3 show the liquefaction activity of Ru/MN catalyst for Yallourn brown coal and Tanito Harum coal, respectively. For a comparison, the activities of pyrite and HDS-3 (Ni-Mo) catalysts were also investigated. The activity of Ru/MN catalyst was comparable to that of HDS-3 catalyst in a temperature range of $350\sim 425^\circ\text{C}$ and the conversion of Yallourn brown coal to the THF solubles was almost 100 % beyond 375°C . Furthermore, these catalysts showed much higher activity than pyrite in every temperature range. The difference in activity between Ru/MN and pyrite was maximum around 375°C , indicating that Ru/MN catalyst is very active even at temperatures less than 400°C .

As shown in Figure 3, on the other hand, the significant difference in the activity for the liquefaction of Tanito Harum subbituminous coal was not found among these three catalysts at any temperatures, except that Ru/MN catalyst showed a little bit higher activity than others at higher temperatures. It is worthy to note that the temperature dependence of activity of pyrite was almost the same between Yallourn and Tanito Harum coals, whereas the activities of Ru/MN and HDS-3 catalysts was remarkably reduced in the liquefaction of Tanito Harum coal.

(2) Liquefaction test by use of 0.1 t/d BSU

(a) Demolition study of 0.1 t/d BSU coal liquefaction plant

The following portions of the BSU plant were sampled and analyzed by various tests.

(1) Sample

- 1) Pipe in a recycle line of weighing vessel
- 2) Pipe in a preheater for hydrogen
- 3) Inlet and outlet pipes of let-down vessel for high-temperature separation
- 4) Pipe in a recycle line of hydrogen (gas inlet portion of compressor)
- 5) Reactor (top, middle and bottom)
- 6) Let-down vessel for high-temperature separation
- 7) Valve of let-down vessel for high-temperature separation (body, port, sheet)
- 8) Slurry pump (port, sheet)
- 9) Diaphragm in the hydrogen compressor

(2) Analysis

- 1) Appearance test and liquid penetrant test
- 2) Measurement of surface roughness
- 3) Microscopic examination
- 4) 10% oxalic acid etch test
- 5) Hardness test
- 6) Tensile test
- 7) Impact test
- 8) Chemical analysis of acid ingredients
- 9) Fractography

As a result, the corrosion was observed in a preheater pipe for hydrogen, reactor and let-down vessel for high-temperature separation. Some of corrosion was assigned to grain boundary attacks. The slight erosion was also found in the slurry pipe line.

Future tasks

The present project was completed in FY 1996. The following tasks will be studied in a subsequent project for the evaluation of the NEDOL process.

- 1) Evaluation of liquefaction reactivities of various coals,
- 2) Evaluation of reactivity of coal-oil products in the hydrotreatment process and its simulation .

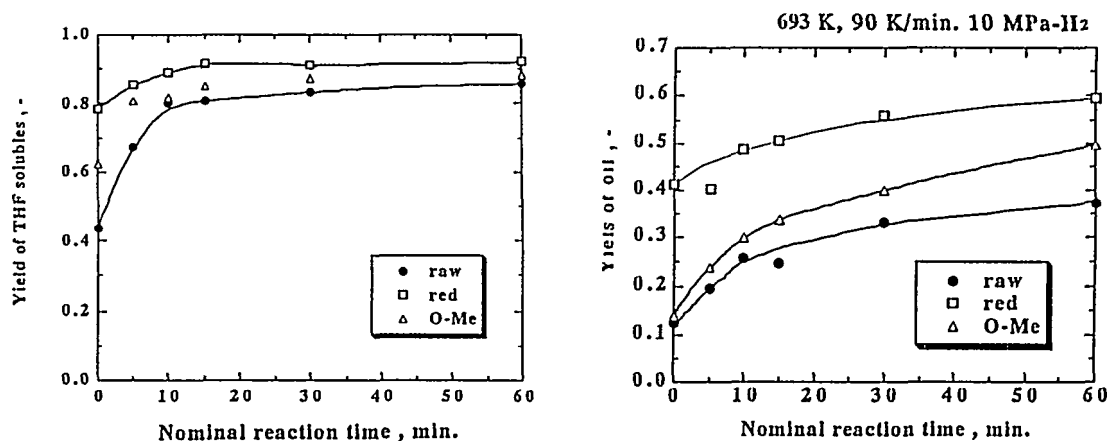


Fig. 1 Increases in oil yield and coal conversion by release of intermolecular cohesive force

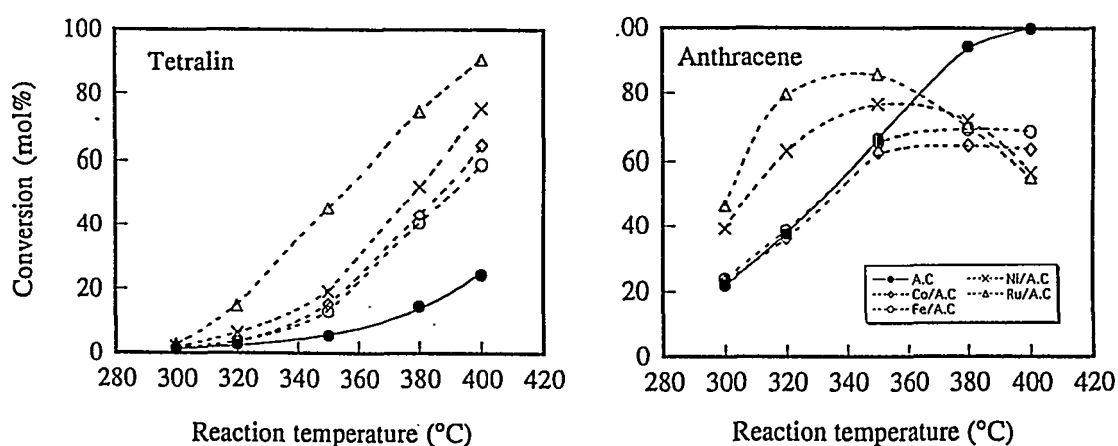


Fig. 2 Dehydrogenation of tetralin and hydrogenation of anthracene over various carbon-supported metal catalysts

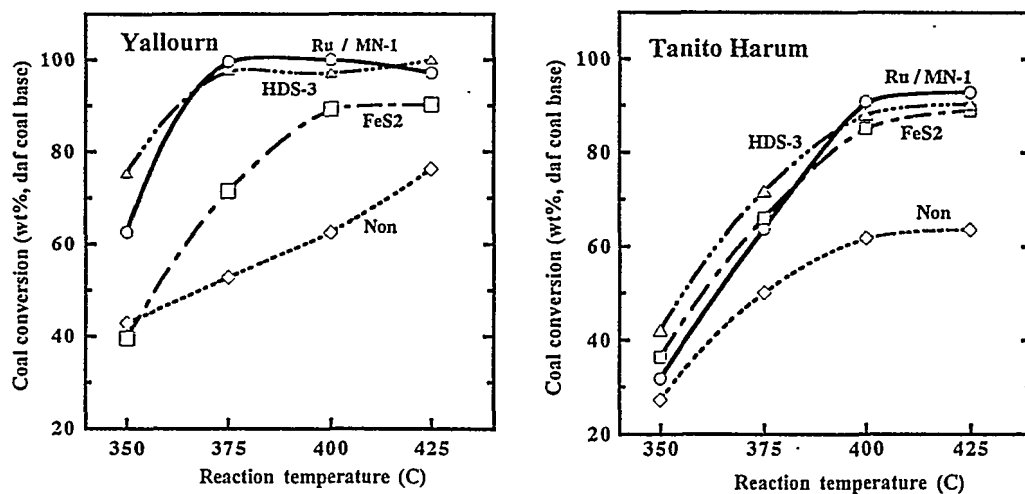


Fig. 3 Liquefaction activities of various catalysts for Yallourn brown coal and Tanito Harum bituminous coal

STUDIES ON CATALYSTS FOR COAL LIQUEFACTION

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Objectives

To support the development of coal liquefaction and coal liquid upgrading catalysts.

To establish novel and precise analytical methods of coal liquids and related compounds.

Work Program

Following the results obtained through the years up to FY 1995, the subjects described below were studied in FY1996.

(1) Design and characterization of catalysts

- a. The catalytic features of Ni-W catalysts are studied in detail. The major focus of the study is placed on the comparison of the catalytic properties of Ni-W with those of Ni-Mo.
- b. Cracking mechanisms of naphthalene-type compounds are studied to design better hydrocracking catalysts which would yield high selectivity to high-quality diesel fractions.

(2) Mechanistic studies on catalytic reactions in coal liquefaction.

- a. The activities and selectivities of unsupported Ni-W-S catalysts were investigated for hydrogenation of 1-methylnaphthalene, and some analytical techniques were evaluated to better understand the structures of nondistillable components in coal liquids.

Summary (1980-1995)

1. Up to FY 1995

(1) Design and characterization of catalysts

- a. Ni-W catalysts newly developed were more active than conventional Ni-Mo catalysts in upgrading coal-derived liquids. The activities and lives of the catalysts were improved year by year.
- b. One of the significant catalyst deactivation causes of coal-liquid upgrading catalysts was found to be structural changes of the catalysts which were accelerated by oxygen containing compounds in coal-derived liquids.
- c. The use of solid acid-based catalyst for the second-stage hydrocracking was essential to achieve high yields of high-quality transportation fuels. Among the catalysts tested, a Ni-W/HY- Al_2O_3 showed the best performance in yielding the gasoline fraction.

(2) Mechanistic studies on principal reactions for coal liquefaction

- a. Coal liquids were characterized in detail by capillary GC, GCMS and FIMS, and the role of catalyst and solvent during the conversion of coal to oil were investigated.
- b. Major compound types such as naphthalenes, phenanthrenes, and phenols in PSU recycle solvents were analyzed, and their compositional changes were clarified during 50 days operation of the plant.

2. For FY 1996

(1) Design and characterization of catalysts

As regard to the first-stage catalysts of which major roles are hydrogenation and hydrodenitrogenation, the catalytic features of Ni-W sulfide catalysts were investigated, compared with Ni-Mo sulfide catalysts. It was also investigated if it would be possible to selectively yield diesel fuels from coal-derived middle distillates over solid acid-based hydrocracking catalysts.

a. Comparison of catalytic features between Ni-W and Ni-Mo sulfide catalysts

To elucidate the superior performance of Ni-W catalysts to Ni-Mo catalysts in coal-liquid upgrading, the hydrodenitrogenation mechanisms of quinoline were investigated. Table 1 shows the comparison of the product distribution over the two catalysts. For the cleavage of the first C-N bonding yielding amino compounds (described as NH₂ in Table 1), the gaseous hydrogen plays an important role. In contrast, the effect of hydrogen pressure is quite small for the cleavage of second C-N bonding which is needed to yield denitrogenated compounds (described as DN in Table 1). As evidently observed in Table 1, the Ni-W catalyst gives higher activity than the Ni-Mo for the first C-N cleavage, though inferior to the Ni-Mo in the final hydrodenitrogenation. This indicates that the hydrocracking active sites of Ni-W function with the association of gaseous hydrogen. On the other hand, those of the Ni-Mo function with solid-acid like properties. The mild function of the active sites of the Ni-W is presumably suitable for hydrogenation and hydrodenitrogenation of coal-derived liquids which contain large amounts of catalyst poisoning components.

The catalytic properties of Ni-W and Ni-Mo sulfide catalysts with different degrees of sulfidation were investigated. Figure 1 shows the hydrogenation and hydrocracking activities of Ni-W and Ni-Mo catalysts which were sulfided under different temperatures. For both activity profiles the Ni-Mo catalyst give the maximums by sulfidation at 300-400 °C. The hydrogenation activity of Ni-W increases with raising sulfiding temperature, while the hydrocracking activity decreases. Thus, the genesis mechanisms of catalytically active sites are quite different between Ni-W and Ni-Mo sulfides. XPS analyses elucidated that the sulfidation of Ni and W in the Ni-W

Table 1 Product distribution of quinoline hydrodenitrogenation over Ni-W and Ni-Mo sulfide catalysts

Temperature (K)		613						653					
H ₂ Press. (MPa) ¹		4.9			8.8			4.9			9.8		
Products ²		HY	NH ₂	DN	HY	NH ₂	DN	HY	NH ₂	DN	HY	NH ₂	DN
Ni-Mo/Al ₂ O ₃		74.4	18.4	7.2	66.3	26.1	7.6	39.0	15.5	45.5	24.7	23.1	52.2
Ni-W/Al ₂ O ₃		67.4	28.9	3.7	55.4	40.9	3.7	20.0	37.3	42.7	5.7	52.3	42.0

1: Cold charge, 2:HY=hydrogenated quinolines, NH₂=amino-compounds, DN=denitrogenated compounds

* In all the reactions the quinoline conversions were 100%.

catalyst was much slower than Ni and Mo in the Ni-Mo catalyst. This indicates that the formation of the hydrogenation active species, "Ni-W-S" structure, in the Ni-W catalyst requires sulfidation at higher temperatures or for longer hours. On the other hand, hydrocracking active sites of the Ni-W disappeared at high temperature sulfiding in spite of the formation of Ni-W-S structure. This is in contrast to the case of Ni-Mo, in which both hydrogenation and hydrocracking activities increase with the formation of "Ni-Mo-S" structure. Thus, incomplete sulfiding of Ni-W catalysts likely results in catalysts with low hydrogenation/hydrocracking activity ratio which would tend to cause rapid deactivation of the catalyst. It is worthwhile to note that too severe sulfiding leads to aggregation of sulfide catalysts which decreases the number of the active sites. In conclusion, proper pre-sulfiding procedure is essential to achieve the maximum catalytic activity of Ni-W catalysts.

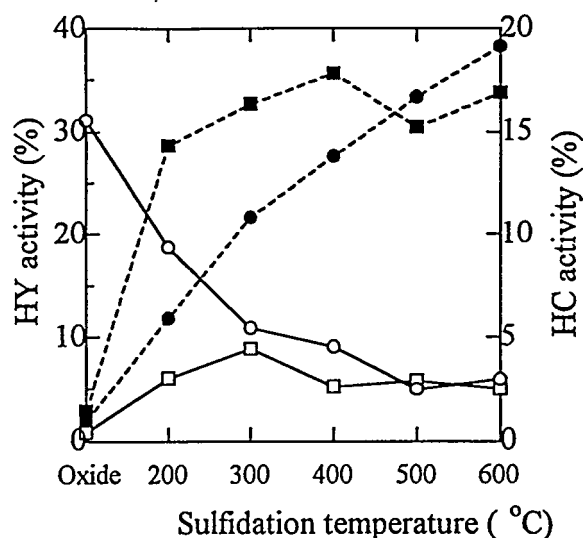


Fig. 1. Changes in hydrogenation and hydrocracking activities of alumina supported Ni-W and Ni-Mo catalysts with sulfidation temperature

b. Hydrocracking of polyaromatics over zeolite based catalyst

The production of diesel fuels with high cetane number needs conversion of polyaromatics to normal- or iso-paraffins through hydrogenation and cleavage of the naphthenic rings. Several kinds of catalysts with different ratios of hydrocracking/hydrogenation activities were prepared and used for the reactions of naphthalene-family compounds under many reaction conditions. The major reaction scheme is shown in Fig. 2. The ratio of (alkyl-) cyclohexane/(alkyl-)benzene can be controlled by hydrogenation/hydrocracking activity balance of the catalysts, however, the de-alkylation reaction precedes the cleavage of the cycloparaffin rings in any reaction conditions. Thus, benzene and cyclohexane are preferred to normal- or iso-paraffins by both thermal and catalytic cracking of alkylbenzene and alkylcyclohexane. No normal- or iso-paraffin with carbon number of eight or higher was detected in any reaction. To achieve the cetane number of 45 or higher, alkylcycloparaffins need to have alkyl groups longer than C12. This indicates that the production of diesel fuels which meet JIS is very hard, unless novel catalytic cracking routes are established.

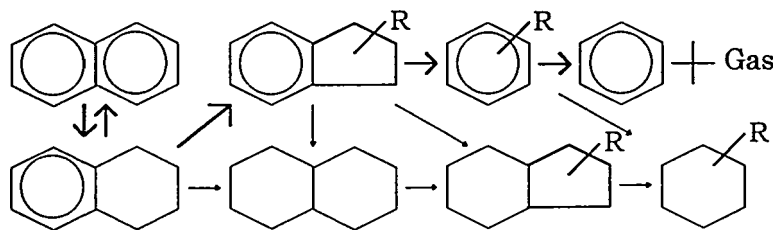


Fig. 2. Hydrocracking of diaromatic-ring compounds over solid-acid based catalysts

(2) Mechanistic studies on principal reactions for coal liquefaction

a. Activity and selectivity of unsupported nickel-tungsten sulfide

A series of nickel sulfide/tungsten sulfide catalysts for hydrogenation of coal oil was prepared, and the relation between its composition and its activity was investigated by using the hydrogenation of 1-methylnaphthalene as the test reaction. The catalysts were prepared from ammonium thiotungstate and ammonium nickel sulfate and consisted NiS_2/WS_2 ratio(mol) of 1/10, 1/5, 2/5, 8/5, 4/1, and 8/1.

The catalysts with NiS_2/WS_2 of 2/5 and 8/5 showed the highest value of activity (Fig. 3). The catalysts with NiS_2/WS_2 of 4/1 and 1/5 showed the comparable activity with tungsten sulfide catalyst(WS_2). The high tungsten catalyst($\text{NiS}_2/\text{WS}_2=1/10$) and high nickel catalyst($\text{NiS}_2/\text{WS}_2=8/1$) showed lower activity than tungsten sulfide catalyst.

The selectivity in 1-methylnaphthalene hydrogenation is explained by the value of 1-methyl-tetralin(1-MT)/5-methyltetralin(5-MT) ratio. The catalyst with $\text{NiS}_2/\text{WS}_2=2/5$ showed the value of 0.5 in selectivity which was the lowest value and was not affected by hydrogenation conversion (Fig. 4). All of the nickel sulfide/tungsten sulfide two dimensional catalysts showed lower values in selectivity than one dimensional catalysts of nickel sulfide or tungsten sulfide, which suggests that the activity site of two dimensional catalysts differ from that of the one dimensional catalysts in quantity.

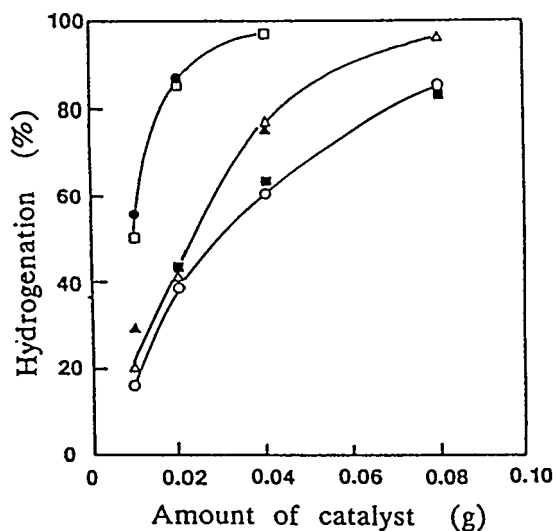


Fig. 3. Composition and activity of nickel-tungsten sulfide

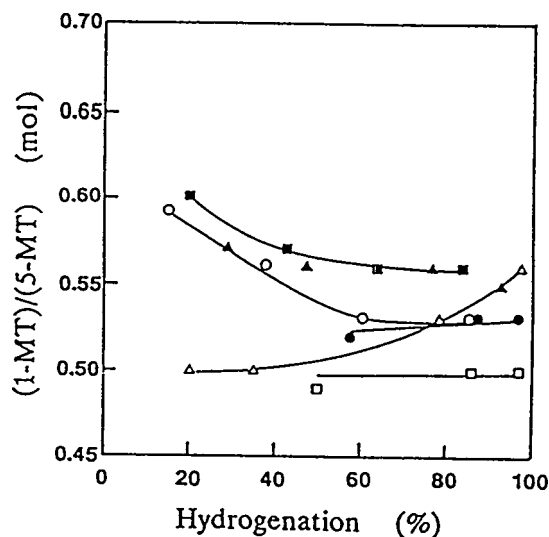


Fig. 4. Composition and selectivity of nickel-tungsten sulfide

○; Ni/W=1/10, △; Ni/W=1/5, □; Ni/W=2/5
●; Ni/W=8/5, ▲; Ni/W=4/1, ■; Ni/W=8/1

b. Characterization of residual materials in coal liquids

The residual materials from NEDOL process account for around 20wt% of the total product, and the analytical techniques of the residue were investigated to develop its utilization technology. Pyrolysis-gas chromatograph(Py-GC) was used to understand the skeletal structures of heavy components. The residue obtained from Banko coal by using a 0.1ton/day BSU of NBCL was separated into several fractions which were analyzed by Py-GC (Fig. 5). Aromatics(As), polar(Po) and asphaltene (As) were almost cracked into volatile components, whereas preasphaltene (PAs) produced a large amount of nonvolatile materials or char in a yield of 46%. The pyrograms showed that Ar, Po and

As consisted mainly of tricyclic and tetracyclic polycondensed aromatic compounds (C) with a much smaller amount of monocyclics and dicyclics (B). There was a significant amount of hydrocarbon gas(A) and mono-/di-cyclics in the pyrogram of PAs, and larger cyclic skeletons in PAs seemed to be converted to nonvolatile materials. It is shown that Py-GC technique is useful for the characterization of toluene-soluble heavy fractions(Ar, Po, As), but not for that of toluene-insolubles(PAs).

Laser-ionization mass spectrometry was tried to obtain molecular distribution of PAs. This ionization method afforded a large amount of peaks with molecular weights of more than 1000, and was shown to be superior to conventional ionization methods such as FAB and FD.

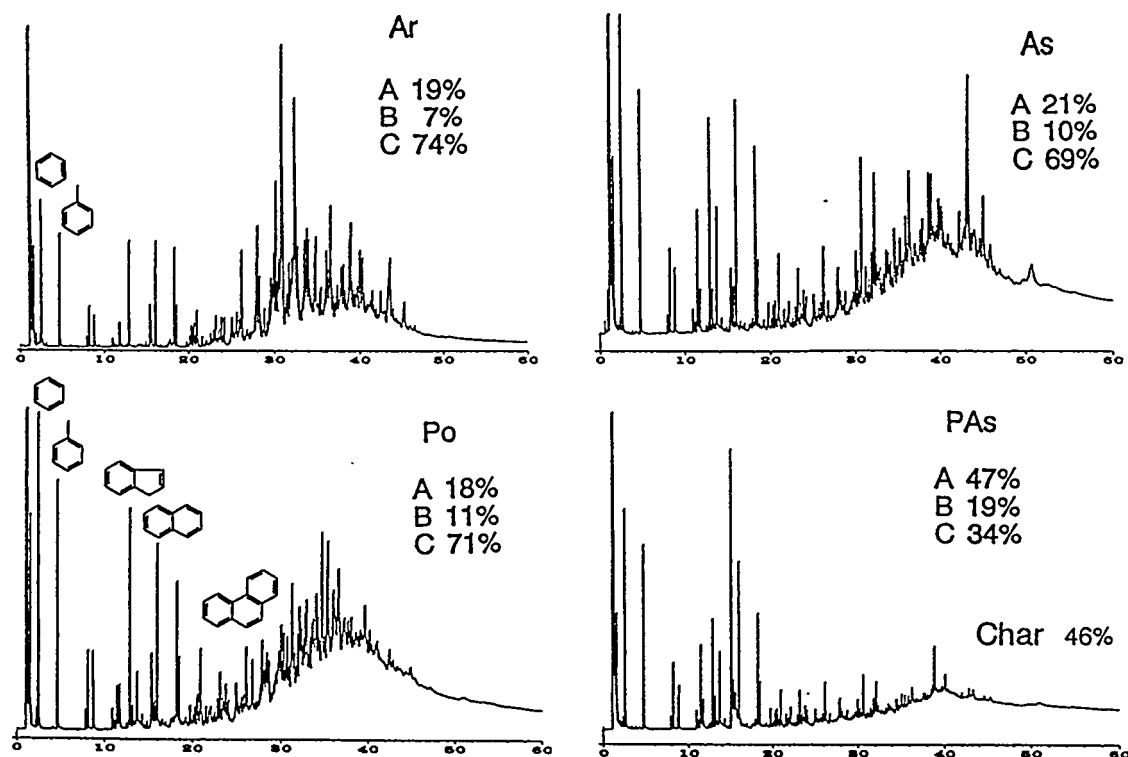


Fig.5. Pyrograms of aromatics(As), polar(Po), Asphaltene(As), and Preasphaltene (PAs). Temp. of pyrolyzer; 800°C. A; area% of hydrocarbon gas, B; area% of mono-/di-cyclics, C; area% of tri-/tetra-cyclics. The yield of char is about 0% for Ar, Po, As.

c. Preparation of metal sulfide particles and catalytic activity

We reported that catalytic activity of MoS₂ fine particle prepared by mechanical milling. Here the ultra fine particles of CoS and NiS were prepared by mechanical milling and the catalytic activities of the particles were investigated by using the hydrogenation reaction of 1-MN as a model compound and of Tanito Harum coal. Commercially available MoS₂, CoS and NiS particles were used without any pre-treatment. These materials were comminuted in a media agitating mill, which was made of zirconia.

Table 2 Hydrogenation and Liquefaction

Hydrogenation		Coal liquefaction	
reactant / 1-MN	5 g	coal / Tanito Harum	3 g
		solvent / tetralin	4.5 g
catalyst %-reactant	0.5~20 %	catalyst %-coal	2%
temperature	623 K	temperature	673K
hydrogen pressure	7.9 MPa	hydrogen pressure	7.9MPa

The catalytic activity these metal sulfide particles were examined by using model compound of 1-methylnaphthalene (1-MN) and Tanito Harum coal (<100 mesh) conducted in a stainless steel batch microautoclave (50 ml). Table 2 shows the experimental conditions of hydrogenation of 1-MN and liquefaction of coal.

The median diameter and the specific surface area of as-received and mechanically milled MoS₂, CoS and NiS are shown in Table 3. As-received particles are all a few micron in diameter, but milled particles are all submicron. MoS₂ is most fragile sulfide, probably because MoS₂ only is a layered material. The median diameter in 50 h milling was 40 nm. The milled MoS₂ was

Table 3 Results of milling

Name of	Milling	Median of	Specific area
MoS ₂	(as	2600 nm	5.8 m ² /g
MoS ₂ /10	10 hr	90	76
MoS ₂ /50	50 hr	40	119
CoS	(as	5460	0.9
CoS/10H	10 hr	170	63
NiS	(as	4980	0.8
NiS/10H	10 hr	230	47
NiS/50H	50 hr	150	52

not amorphous, but had crystal phase according to XRD profiles of the milled MoS₂, which was not depicted here. The productivity of ultra fine particles by mechanical milling was found to be pretty high.

The results of hydrogenation of 1-MN is shown in Table 4. All the reaction time is 60 min and changing the milling time of the catalysts. The conversion yields of 1-MN by using raw materials (before milling) except CoS is low, and conversion yields of the milled catalyst increased. It is because of specific surface area of the catalyst produced by milling process increased as indicated in Table 4. Among these raw materials, the activity of the NiS is the lowest and that of the CoS is the highest. After ten hours milling, the conversion yields of the MoS₂/10H increased significantly and showed the same activity as that of CoS/10H. Fig. 6 clearly indicates that reaction

Table 4 Hydrogenation of 1-MN

Name of catalyst	Conversion of 1-MN %	Yield of 1-MTL & 5-MTL %
MoS ₂	3.0	2.4
MoS ₂ /10H	70.8	68.3
MoS ₂ /50H	85.3	81.6
CoS	10.0	9.8
CoS/10H	70.9	67.2
NiS	2.1	2.1
NiS/10H	24.1	23.3
NiS/50H	19.2	18.0

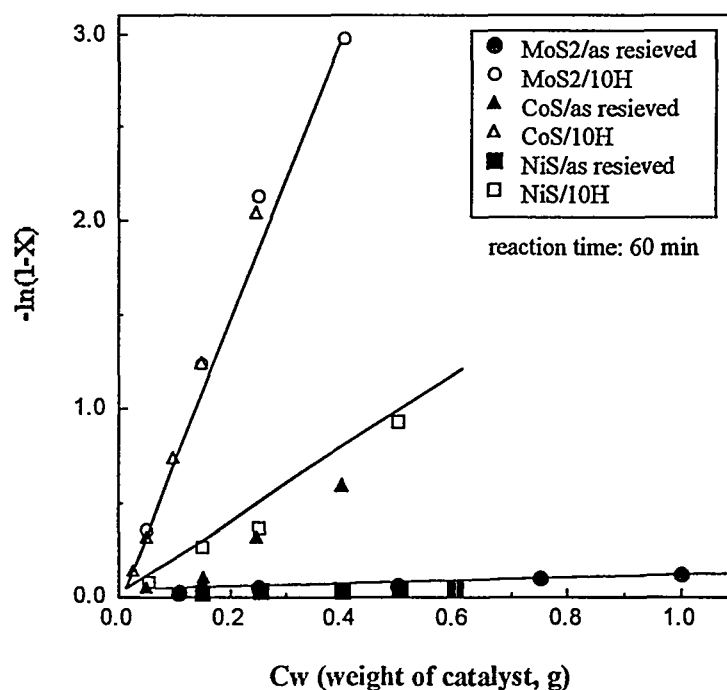


Fig.6. Results of kinetic

Table 5 Results of Liquefaction of Tanito Harum coal

Name of catalyst	Conversion	Yield			Hydrogen consumption
	THFs	PAs+As	Oil+water	Gas	
non	77.1	38.9	32.1	6.2	0.42
MoS ₂	79.9	37.8	35.4	6.6	0.71
MoS ₂ /10H	85.0	40.2	38.4	6.4	1.26
MoS ₂ /50H	84.0	36.7	40.9	6.4	1.41
CoS	81.7	39.4	35.6	6.8	0.75
CoS/10H	87.3	43.8	37.5	6.1	1.67
NiS	77.8	37.5	33.8	6.5	0.59
NiS/10H	81.9	41.3	34.4	6.2	0.94
NiS/50H	81.8	39.8	35.5	6.4	1.08

rate increase with increase of amount of catalyst and milling treatment increased catalytic activity. The activity of the milled MoS₂ significantly increased per the certain unit of the surface area compared with raw MoS₂. It means different active point of catalyst was produced by milling. We suppose that increase of the edge part of MoS₂ crystal (may be more active than plane) by milling process increase hydrogenation activity. On the other hand, concerning CoS, the catalyst activity of the raw CoS per unit surface area is higher than the milled CoS, we suppose that the catalyst activity per the certain surface unit relatively dropped by milling process.

Result of coal liquefaction experiment of Tanito Harum coal is shown in Table 5. During the coal liquefaction process, the effect of the catalyst as well as the effect of the milling process of the catalyst can be noticed, when we compare it with that process without catalyst. CoS/10H gave highest THF soluble yields and MoS₂/50H gave highest oil yields.

Future Tasks

Design of catalyst and process based on full understanding of reaction mechanism during conversion of coal to transportation fuel

Major publications in FY1996

1. Dual-functional Ni-Mo sulfide catalysts on zeolite-alumina supports for hydrotreating and hydrocracking of heavy oils, *H. Shimada, S. Yoshitomi, T. Sato, N. Matsubayashi, M. Imamura, Y. Yoshimura, A. Nishijima*, *Studies in Surface Science and Catalysis*, **106**, 115, (1997)
2. Hydrogenation and Hydrocrackin activities of Tungsten Sulfide Catalysts Supported on Alumina (Part II) Differences in Catalytic Functions between Ni-W and Ni-Mo Catalysts, *T. Kameoka, T. Sato, Y. Yoshimura, H. Shimada, N. Matsubayashi, M. Imamura, A. Nishijima*, *Sekiyu Gakkai-shi*, **39**, 87, (1996)
3. Hydrocracking of fluorene over presulfided Ni-Mo/Al₂O₃ catalysts, *Y.Miki, Y.Sugimoto*, *J. Jpn Inst. of Energy*, **75**, 817(1996).
4. Characterization of thermally decomposed cellulose and red pine at 200°C in water, *Y.Sugimoto, Y.Miki, K.Hayamizu, S.Umeda, T.Komano, K.Mashimo, T.Wainai*, *J. Jpn Inst. of Energy*, **75**, 829 (1996).

BASIC STUDIES ON COAL LIQUEFACTION REACTION, REFORMING AND UTILIZATION OF LIQUEFACTION PRODUCTS

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OBJECTIVES

The purpose of this research is to provide the fundamental data for the selection of the optimum reaction condition on the liquefaction of each of various coals and for the upgrading of coal liquid. Evaluation and utilization of products are also investigated.

WORK PROGRAM

1. Fundamental Study on Coal Liquefaction

(1) Liquefaction Coprocessing using Oil Soluble Catalyst

Effect of solvent addition and the particle size of coal on liquefaction characteristics in coprocessing of Tiheiyo coal with tarsand bitumen is studied.

(2) Coal Liquefaction with Recyclable Superacid under Mild Conditions

HF/BF₃, which has been recognized as a recyclable and reusable superacid is studied as a catalyst for coal solubilization with aromatic hydrocarbon via an ionic reaction.

(3) Research and Development of Hydropyrolysis of Coal

Reaction of coal and hydrogen atom was carried out using a differential thermal balance. Products from thermal decomposition and the reaction of coal with hydrogen atom is identified and measured.

(4) Liquefaction Behavior of Finely Pulverized Coal

The activities in cracking and hydrogen transfer of several catalysts for coal liquefaction are evaluated quantitatively by measuring the cracking rate of dibenzyl.

2. Hydrotreatment of Coal Derived Liquid

(1) Dealkylation of Substituted Phenol into Unsubstituted Phenol

Estimation and calculation of products distribution in thermal hydrodealkylation are carried out using the data of relative reactivities of methylphenols.

(2) Solvent Extraction of Phenolic Compounds from Coal Derived Liquids

Experiments are carried out to clarify the extraction behavior of nitrogen containing compounds from model solution and to establish mathematical expression for the extraction yield. The extraction of heteroatom containing compounds from naphtha fraction of Tanito Harum coal liquid is also studied.

(3) Dearomatization and Evaluation of Gas Oil from Coal Liquids

Adsorption behavior of aromatics in middle distillate of coal liquid are studied and the properties of exhaust emissions from a test diesel engine using several model fuels of coal liquid are investigated.

SUMMARY (1975-1996)

1. Up to FY 1995

(1) Fundamental Study on Coal Liquefaction

Coprocessing of coal and tarsand bitumen or shale oil vacuum residues (VRs) using iron oxide and sulfur catalyst or oil soluble molybdenum catalyst have been studied to see the availability of bitumen or VRs as solvent.

A bronsted superacid, trifluoromethanesulphonic acid, was found to desulphurize coal in the presence of hydrocarbon without gaseous hydrogen. Removal of sulphur from coal depended on the solvent, catalyst concentration and reaction temperature.

The roles of hydrogen on hydrolysis were investigated by using dibenzyl penetrated in active carbon as model. The effect of swelling by 5,6,7,8-tetrahydro quinolin was also studied.

In finely pulverized coal liquefaction, remarkable increase in liquid yield was observed and it was considered due to the intimate contact among coal-catalyst-solvent.

(2) Hydrotreatment of Coal Derived Liquids

Compositional analysis of hetero-atom containing fractions extracted from coal liquid by acid-base and methanol-water methods were studied.

The extraction behaviors were studied on phenols by methanol-mediated extraction method with naphtha and gas oil fractions of several coal liquids. The extraction behavior was also studied with heavy naphtha fraction of Tanito Harum coal liquid.

The adsorption performance and the reactivation methods were studied on several adsorbents for the separation of aromatics.

The relationship between components and the exhaust emissions on some model diesel fuels were studied using pure compounds as model fuels.

(3) Utilization of Products.

Coal derived naphtha, middle distillate, those hydrotreated oil and mixtures of those with a commercial gas oil were characterized and tested by JIS methods for the purpose to utilize coal liquid as a diesel fuel. Recovery of tars from the liquefaction residues were carried out by heat-treating up to 650 C, and the product yields were compared with the results estimated by thermo-balance experiments and with those obtained from the raw coals.

2. For FY 1996

(1) Fundamental Study on the Coal Liquefaction.

(a) Liquefaction Coprocessing using Oil Soluble Catalyst

Taiheiyo coal was ground under 100mesh or 24 mesh and liquified with mixed solvent system such as tarsand bitumen(TSB) and 1-methylnaphthalene(MN) using oil soluble MoDTC catalyst or synthetic pyrite to see the effects of addition of aromatic solvent and coal particle size. Fig.1 shows that particle size of coal affected HI, TI and THFI conversion and the smaller particle size of coal gave the higher conversion. The effect of particle size on conversion was clearer in case of synthetic pyrite than MoDTC. Fig.2 shows the effect of solvent addition in coprocessing and addition of MN was found to be very effective. In thermal cracking reaction of asphaltene obtained from TSB, addition of aromatic solvent to the reaction system caused high suppression of coke formation due to the deaggregation of asphaltene micelle structure by the solvent. In this study, addition of aromatic

solvent in coprocessing was also effective and increased each conversion.

(b) Coal Liquefaction using Recyclable Superacid under Mild Conditions

Solubilization of the treated coals are shown in Fig. 3 and average molecular weight of soluble fraction are shown in Table 1. The original Taiheiyo coal (Fig. 3 Original coal) was slightly soluble in THF (3 wt%), and soluble in pyridine (14 wt%). Addition of HF of approximately 5 g/g-coal (Run A) allowed high solubility such as 66 wt% in pyridine, 50 wt% in THF and 36 wt% in benzene (Fig. 1 Run A). It is noted that the conjugate bronsted-Lewis superacids such as HF combination with 2 mol% of BF₃ (Run B) provided high solubility. 7 mol% of BF₃ in HF (Run C) provided higher solubility. However, a further increase in BF₃ concentration to 10 mol% (Run D) did not proceed solubilization. This result suggested that HF with even small amount of BF₃ such as 2 mol% or 7 mol% drastically promoted depolymerization of constituent molecules in coal, but HF with excess amount of BF₃ is not necessary to achieve maximum solubility. The reaction with HF/7 mol% BF₃ and isopentane (Run E) resulted in lower solubility than that of the reaction with toluene, indicating that toluene played more important role to stabilize a carbonium ion produced from cleavage of coal constituent molecules and to enhance coal depolymerization than isopentane.

(c) Research and Development of Hydropyrolysis of Coal

Reaction of coal and hydrogen atom was carried out to study detail of reaction mechanism of hydrogen gas and coal on flash hydropyrolysis. In this experiment, Taiheiyo coal under 100 mesh was heated using a differential thermal balance. The products from coal were analyzed by a mass spectrometer. Hydrogen atom was produced from hydrogen by passing through a microwave discharge cavity. Rates of weight decrease of coal heated at 5 C/min under 760 Torr and 1 Torr of helium were shown in Fig. 4. Remarkable weight decreases of coal were observed at 450 C under 760 Torr of helium. Under 760 Torr of hydrogen, weight decrease caused by the reaction of coal with hydrogen gas was observed over 800 C. On the other hand, maximum rate of weight decrease was observed at 430 C under 1 Torr of helium. Shifts of the temperature, the maximum rate of weight decrease was observed, implied that transfer of products to out of coal particle was enhanced under low pressure. The weights of samples at 1000 C under 760 Torr and 1 Torr of helium were 20% and 50 % of initial weight of coal respectively. The higher conversion of coal under high pressure may indicate that volatile materials remained in coal enhanced decomposition of coal. The reaction of coal and hydrogen gas was not observed under 1 Torr of hydrogen. Mass spectra of products from thermal decomposition of coal and the reaction of coal and hydrogen atom at 200 C, 400 C, and 600 C were shown in Fig. 5. Methane, carbon monoxide, carbon dioxide, benzene, and toluene were identified by their mass number and fragment pattern. Production from thermal decomposition was maximum at 400 C. Productions of methane, carbon monoxide, and carbon dioxide from the reaction with hydrogen atom were 1- 9 times, 9-33 times, and 10 times larger than those from thermal decomposition. The large amount production implies that hydrogen atom enhanced the decomposition of coal. Production from the reaction with hydrogen atom was also maximum at 400 C.

(d) Quantitative Evaluation on Cracking and Hydrogen Transfer Activities of Catalysts for Coal

Liquefaction

The activities in cracking and hydrogen transfer of several catalysts for coal liquefaction were

evaluated quantitatively by the measurement of the liquid-phase cracking rate of dibenzyl using a small autoclave at 440 °C with tetralin, decalin and 1-methylnaphthalene under hydrogen or nitrogen atmosphere. Marked increase in rate constant was not observed in the cracking using carbon black, zinc chloride, and zeolite catalysts in the presence of tetralin and nitrogen gas, but the sulfided iron oxide can be activated by liquid-phase tetralin to show higher cracking rate. On the other hand, in the presence of hydrogen gas, all the catalytic reactions showed higher rate constants than with the thermal reaction. The rate constant for the Ni-Mo/Al₂O₃ rose drastically in the presence of hydrogen gas with decalin. (Fig. 6) The results show that the sulfided iron oxide catalyst can transfer hydrogen much more effectively from liquid-phase tetralin than from gaseous hydrogen, and Ni-Mo/Al₂O₃ can use gaseous hydrogen effectively under the reaction conditions.

(2) Hydrotreatment of Coal Derived Liquid

(a) Estimation of Products Distribution on the Thermal Hydrodealkylation of Alkylphenol Mixture from Coal Liquid.

We estimated the products distribution by the thermal hydrodealkylation of alkylphenol mixture at several temperatures and residence times. Reactant alkylphenol mixture contains 16wt% of phenol and 23wt% of cresols with about 60% of other alkylphenols including trimethylphenols. We used relative demethylation and hydroxylation rates per one equivalent methyl and hydroxyl groups measured by the previous experiments for cresols and six different dimethylphenols and estimated the activation energies of cresols and trimethylphenols assuming the same A-factor with toluene. Trimethylphenols decreased rapidly in any reaction conditions and phenol with BTX were concentrated according to the elevation of reaction temperature. Concentration of phenol at 700 °C reached to 40.6wt% with 30wt% of BTX and small amount of m-cresol as shown in Fig. 7.

(b) Solvent Extraction of Phenolic Compounds from Coal Derived Liquids

Partition coefficients (K) for phenols and nitrogen-containing compounds were measured using model compounds in order to estimate extraction ratios on methanol-mediated extraction. From the results, the extraction behavior and the limit of the extraction by this method were discussed. The model oil phase was prepared by mixing a heteroatom-containing compound with n-butylbenzene. The value of K for phenol was very low and almost constant at $X_w < 0.4$, where X_w means the ratio of water in methanol-water phase. This indicates that high extraction ratio would be expected in this X_w . However, K increased rapidly in $X_w > 0.6$, and reached about 1.5 at $X_w = 1$. The order of K for several compounds were phenol \ll cresol, ethylphenols, substituted pyridines $<$ indole, quinoline, isoquinoline $<$ acridine. From these results, this method may not be applicable for triaromatic polar compounds like acridine. The logarithms of K on X_w were almost linear having similar slope one another (Fig. 8). In addition, the mass distributions of phenol-methanol-water systems were measured using a cluster mass spectrometer.

Methanol-mediated extraction was conducted with a light naphtha fraction of Tanito Harum coal liquid. The extraction ratio of phenol was similar to other coal liquids reported before, but the selectivity was poorer. The reason was thought the high contamination of neutral fraction. However, by GC/MS analysis, it was clarified that the content of the neutral fraction was almost phenols and nitrogen

containing compounds that were not determined.

(c) Dearomatization and Estimation of the Exhaust Emissions of Gas Oil from Coal Liquids

This year, the adsorption capacity of Active Carbon-impregnated Silica-gel (ACSIL), a new commercial adsorbent, was measured, and the reactivation method was investigated. The adsorption of phenanthrene from its n-heptane solution indicated that ACSIL has almost double adsorption capacity and 30 times of the adsorption constant as much as those of Silica-gel (SIL). The order of adsorbability was phenanthrene > 1-methylnaphthalene > n-butylbenzene, indicating the higher adsorbability for the more numbers of aromatic rings (Fig. 9). The amount of adsorbed phenanthrene was closer to the adsorption capacity even in the diluted solution. This means the adsorption efficiency is excellent. The desorption of phenanthrene by a two step reactivation, the desorption of phenanthrene with acetone followed by the washing with supercritical CO₂, was succeeded within several hours. From these results, ACSIL is more efficient than Silica-gel on the adsorption capacity, and than Molecular Sieve 13X and Active Carbon on the reactivation performance.

The effects of composition of hydrocarbons on exhaust emissions were investigated using a test engine with model fuels prepared by mixing two kinds of pure compounds (aromatics or cycloalkanes)

with base oil that consisted of n-hexadecane and 2,2,4,4,6,8,8-heptamethylnonane. The concentration of smoke and mass emissions of particulate matter from the engine were linearly related to the percentage of aromatic quaternary carbons as well as the results obtained last year. In addition, The contribution of the fuel composition to the amount of emissions was independent from the engine load. Further investigation was carried out using a test engine with model coal liquids prepared from LCO and gas oil. Here, The measurement of the properties of exhaust emissions and the analysis of test fuels were performed.

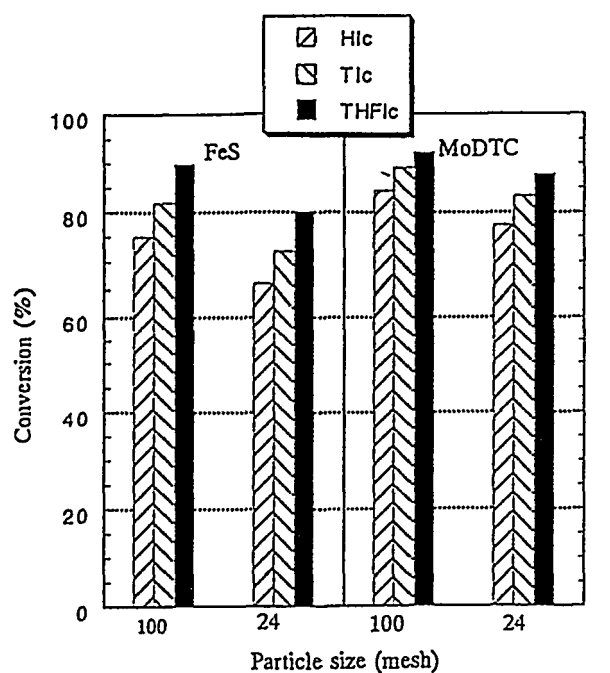
Future Tasks

1. Fundamental Study on the Coal Liquefaction

- (1) Study on the pretreatment effect of heavy oils on the behavior in liquefaction coprocessing
- (2) Study on the desulphurization behavior and coal liquefaction at mild conditions by the aid of HF/BF₃
- (3) Study on the effect of reaction conditions on the yield of liquid product in the reaction between coal and hydrogen atom
- (4) Study on the optimization of catalytic activity for coal liquefaction in relation with the design of solvent quality

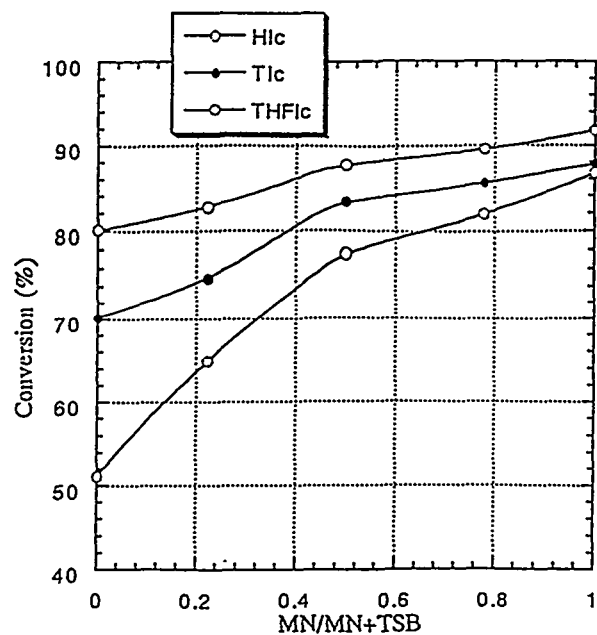
2. Hydrotreating of Coal Derived Liquids

- (1) Study on the dealkylation of alkyl-substituted phenols from coal derived liquids in comparison with the product distribution by calculation
- (2) Study on the refinement of the equation for the estimation of extraction yield and behavior of phenolic compounds in water-methanol extraction method
- (3) Study on the effect of activation methods and adsorption behavior on polyaromatics and the analysis of the relationship between the emission and the composition of fuels.



Coal:15g, Solvent: TSB 22.5g+MN 22.5g, H₂: 8.5MPa
430 °C, 60 min

Fig.1 Effect of coal particle size on coal conversion



Coal:15g, MN+TSB=45g, H₂: 8.5MPa, 430°C, 60min

Fig. 2 Coal conversion vs. MN/MN+TSB

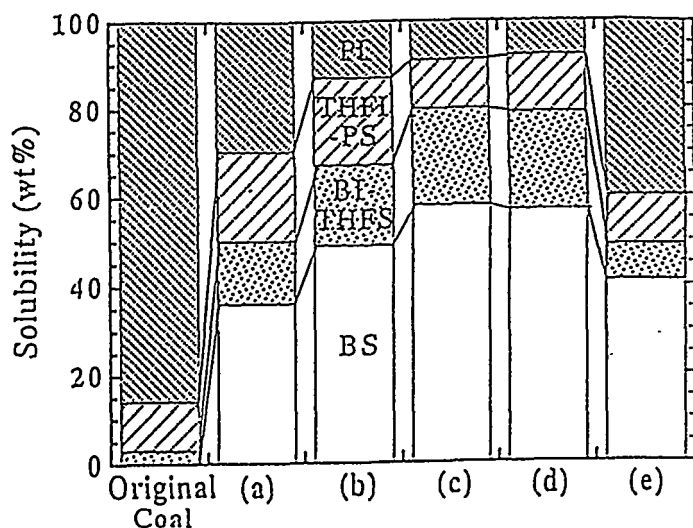


Figure 3 Coal solubilization with HF and HF/BF₃.

(a)Run A, HF/toluene (b)Run B, HF/2 mol% BF₃/toluene
(c)Run C, HF/7 mol% BF₃/toluene (d)Run D, HF/10 mol%
BF₃/toluene (e)Run E, HF/7 mol% BF₃/isopentane

BS: Benzene Soluble, BI-THFS: Benzene Insoluble - THF Soluble,
THFI-PS: THF Insoluble-Pyridine Soluble, PI: Pyridine Insoluble

Table 1 Average molecular weight of soluble fractions.

Run	molecular weight		
	BS	BI-THFS	PS
Taiheiyō	-	-	893(14*)
A	448(36)	1132(14)	-
B	302(49)	578(18)	-
C**	347(58)	876(22)	-
E	521(41)	1134(8)	-

* : content wt%, ** : THFS = 375(80 wt%)

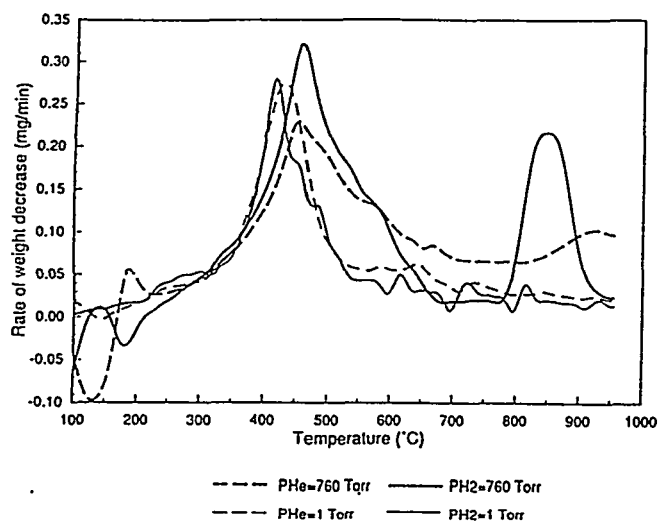


Fig. 4 Rate of weight decreases of coal (mg/min)

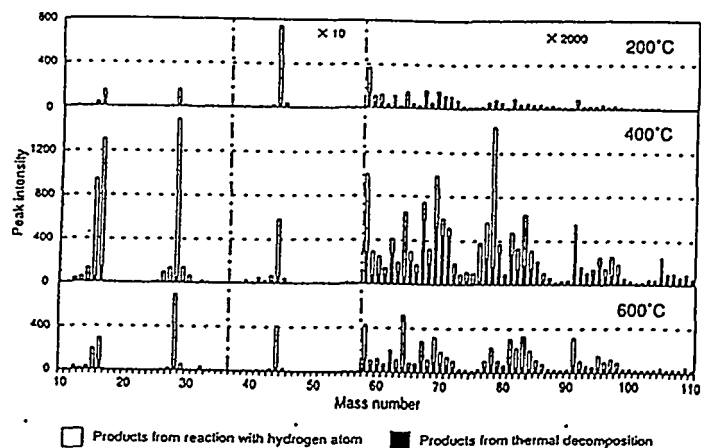


Fig. 5 Mass spectrum of products from thermal decomposition of coal and reaction with hydrogen atom

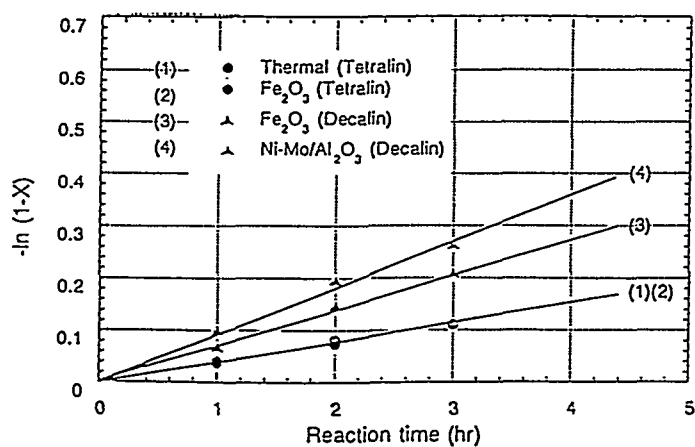


Fig. 6 First-order Plot for the Cracking of Dibenzyl (420°C, H₂)

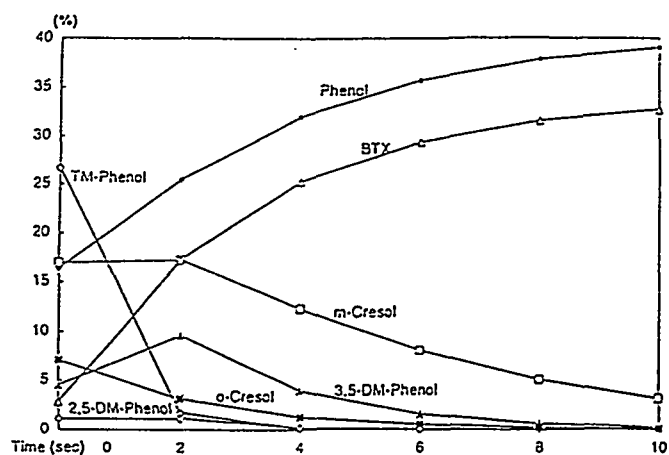


Fig. 7 Hydroalkylation of Phenol Mixture (700°C)

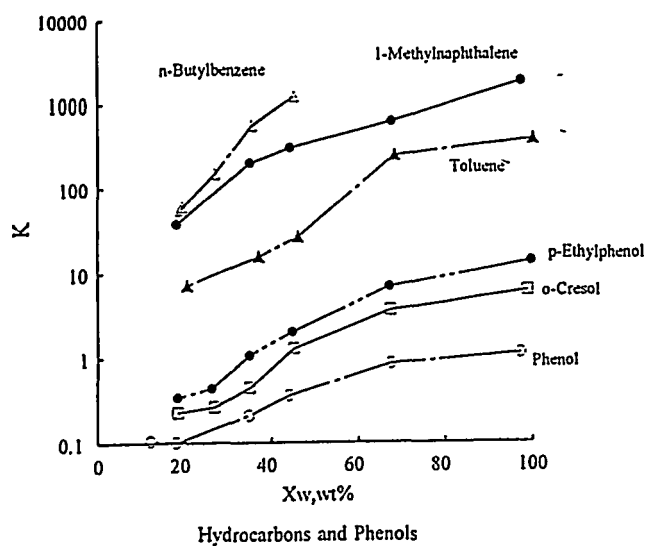


Fig.8 Partition Coefficients (K) of Several Model Compounds

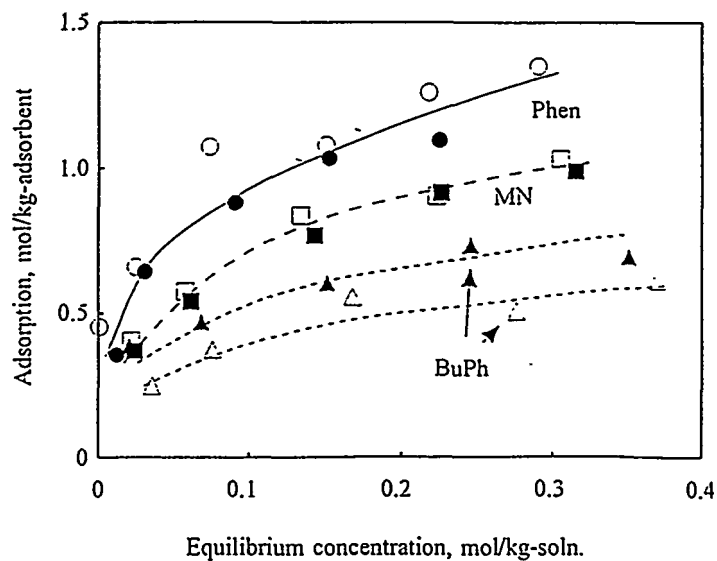


Fig. 9 Adsorption of Aromatics on Active Carbon-impregnated Silicagel

Activation Method of Adsorbent

- ■ ▲ New ACSIL was used with no activation.
- □ △ Used ACSIL was reactivated by desorbing aromatics with acetone for 1hr and drying with 2ml/min supercritical CO₂ for 1hr at 40°C, 15MPa.

Studies on the Mechanism of Direct Hydrogenation Reaction and Prevention of Coking

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Objectives

The aim of this studies is to elucidate the reaction mechanism of high pressure hydroliquefaction of coal and the prevention of coking, and to investigate the effective coal liquefaction procedure.

Work Program

1. Reaction mechanism of coal liquefaction. Hydrogenolysis of model compounds using synthetic pyrite as catalyst.
2. Upgrading of coal liquid
3. Extent of coal liquefaction at process preheating conditions

Summary (1981-1996)

1. Up to 1994

Benzyl phenyl ether as was hydrogenated using stabilized nickel and synthetic pyrite as catalysts. In the case of stabilized nickel the hydrogenated products were produced at the lower reaction temperature. In the reaction with synthetic pyrite catalyst no hydrogenated product was obtained and a significant amount of the condensed products were obtained. Toluene and phenol were also produced via benzylphenol from the reaction of benzyl phenyl ether.

A model chemical structure of Taiheiyo coal was proposed from the analyses of oil fractions by the mild hydrogenation.

The hydrogen generated in-situ from decomposition of methanol or the reaction of zinc metal with water was very effective to dissolve coal into solvent.

Coal liquids were dealkylated effectively by using hydrogen due to the decomposition of methanol. This reaction was accelerated in the presence of hydrogen gas. Alkylbenzenes were hydrodealkylated effectively in this non-catalytic thermal reaction. Hydrodefunctional reaction of alkylphenols in this reaction system was somewhat different from the reaction of alkylbenzenes because of formation of water from OH-group.

The semi-coke was shown to form from the thermally cracked fragments at the initial reaction stage without sufficient external hydrogen supply. Coking characteristics was experimentally examined for preasphaltene derived from Akabira coal liquefaction. Wandoan coal conversion at temperature of a preheater was supposed to be 80 %. Tanitoharum coal also showed the similar conversion to Wandoan coal at the condition of preheater.

2. For FY 1996

(1) Reaction mechanism of coal liquefaction: Hydrogenolysis of model compound using synthetic pyrite as catalyst (7) Formation and decomposition of condensed

products

Benzyl phenyl ether (BPE) were reacted using synthetic pyrite as catalyst to discuss the formation and decomposition of condensed products. The products obtained at 300 to 450°C in the heating step and those at 0 to 60 min at 450°C of reaction temperature were analyzed by GC and GC/MS. The result is shown in Fig. 1. BPE converted almost 100% at 375°C in the heating step. Up to about 425°C in the heating step the condensed products such as bibenzylphenol (DBP) and tribenzylphenol (TBP) were produced significantly together with toluene and phenol. At 450°C in the heating step these condensed products decreased. It is shown that these products produce in the earlier period of the reaction. Of the products after holding time at 450°C, as the longer reaction time until 30 min, as the smaller amount of the condensed products. The condensed products after holding 60 min of reaction time at 450°C were not so much change. The yield of benzylphenol (BP), which is rearrangement compound from BPE, also increased during heating step to 400°C and decreased at higher temperature then 400°C and not so much changed at any holding time at 450°C. The increase of decomposed products from BPE, toluene and phenol, at higher temperature than 400°C in the heating step and at the holding time at 450 C should be due to the decomposition of DBP, TBP and BP because no BPE were present in these conditions. It is suggested that synthetic pyrite has ability to decompose these condensed products. However, at the longer holding time at 450°C synthetic pyrite would lose the activity of decomposition and hydrogenation, so that the products based on benzyl radical such as diphenylmethane (DPM), bibenzyl (DB) and methyl diphenylmethane (MDM) increased.

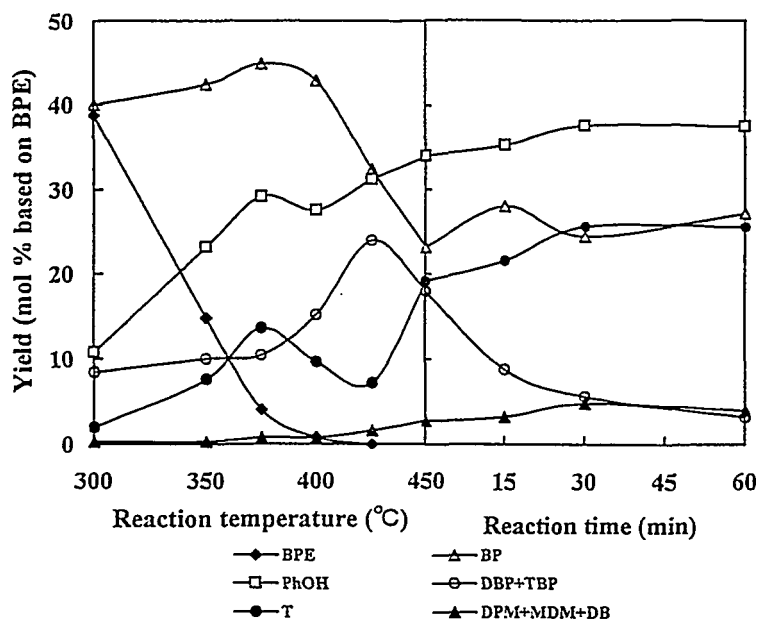


Fig.1 Effect of the reaction temperature and time on the product from benzyl phenyl ether (synthetic pyrite)

The result with stabilized nickel catalyst reported before is shown in Fig. 2. The products hydrogenated BPE, hexa-hydrogenated- (HHE) or per-hydrogenated BPE (PHE), were obtained at 200 to 350°C using this catalyst. Moreover, the hydrogenated decomposed products, such as cyclohexanol (CHL) and methylcyclohexane (MCH) also produced. Stabilized nickel has ability of hydrogenation but synthetic pyrite does hardly.

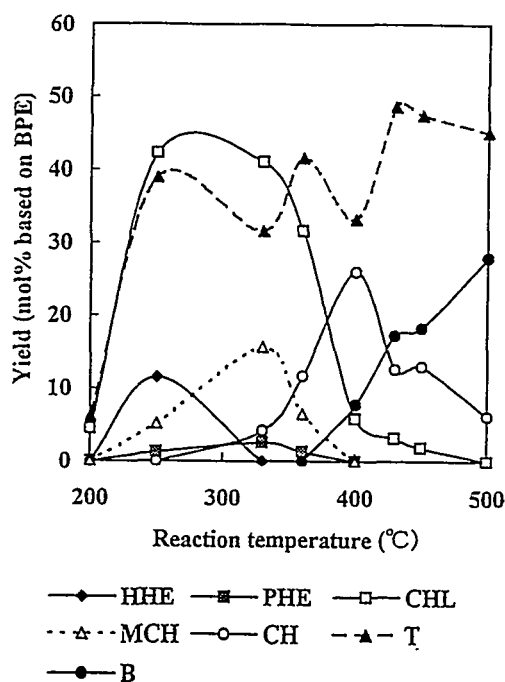


Fig.2 Effect of the reaction temperature on the product from benzyl phenyl ether (stabilized nickel)

(2) Coal liquefaction at preheater and reactor conditions

This part of the study aims to develop a comprehensive reaction model of coal liquefaction which is thought to occur in a process preheater and a reactor. Up to the last financial year data of the conversion of coal and the yields of derived liquids were accumulated for Tanitoharum and Wandoan coals (hereafter, T and W coals, respectively) in a 50cm³ micro-autoclave which was heated at a rate equivalent to that in a continuous process preheater, i.e., 50K/min for heating and 150K/min for cooling. Details of the experiment were described in our previous reports. In addition, a generalized liquefaction model was deduced which explains well the observed characteristic changes of the yield of the products. This financial year the oil fraction from the coals (See Table 1) was further

Table 1 Results of Proximate and Ultimate Analyses of Coal Used

Coal	Proximate			Ultimate				
	VM*	FC*	Ash	C	H	O	N	S
	[wt% of mf coal]			[wt% of daf coal]				
Tanitoharm	40.8	44.1	15.1	77.1	5.6	15.6	1.6	0.2
Wandoan	43.8	47.8	8.4	76.8	6.7	15.1	1.1	0.3

* VM: volatile matter, FC: fixed carbon

fractionated by a high-pressure liquid chromatography (HPLC) into the following five sub-fractions:

Fraction P (**Fr-P**); parafinic hydrocarbons
 Fraction M (**Fr-M**); mono-aromatic hydrocarbons
 Fraction D (**Fr-D**); di-aromatic hydrocarbons
 Fraction T (**Fr-T**); tri- and tetra-aromatic hydrocarbons
 Fraction PP(**Fr-PP**); poly-aromatic and polar-functional hydrocarbons

Measurements were carried out for the yield as well as the average molecular weight of each sub-fraction, MW_i , by a mass spectroscopy (MS).

Fig. 3 plots the yields of sub-fractions, y_i , against the yield of the oil and gas fraction, $y_{O\&G}$. As can be seen for W coal, the yield of **Fr-M**, y_M , increases with $y_{O\&G}$ and levels off ($y_M = 5\text{wt}\%$) for $y_{O\&G} > \text{ca.} 30\text{wt}\%$ while the yields other than **Fr-M** (y_P , y_D , y_T and y_{PP}) increases monotonously in the whole range of $y_{O\&G}$. For T coal the level-off yield is seen for **Fr-M** and **Fr-P** while the monotonous increase for the other sub-fractions.

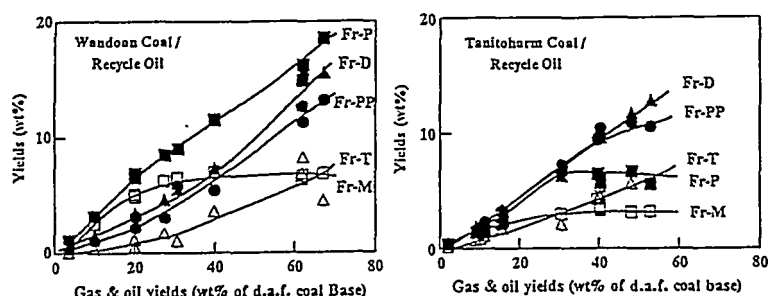


Fig. 3 Yields of HPLC fractionated oil component vs. those of Oil&Gas

The MS analysis showed that W coal has the content of partially hydrogenated aromatic hydrocarbons in the oil fraction higher than T coal. The former also exhibited a change in the oil compositions less insensitive than the latter. In Fig.4 is shown MW_i as a function of $y_{O\&G}$. For both coals MW_i is independent of $y_{O\&G}$ being about 400 for **Fr-P** and 200 for the other sub-fractions. This result would well correspond to those in the last financial year that methane becomes the major gaseous product along with the progress of liquefaction. In other words, the little variation in MW_i with $y_{O\&G}$ for each oil sub-fraction is resulted in from gradual dealkylation of all the oil sub-fractions. Further, these results are consistent with the generalized liquefaction model (Fig.5) proposed in the report in the last financial year, which assumes competitive production of each oil sub-fraction from asphaltene and volatiles in coal.

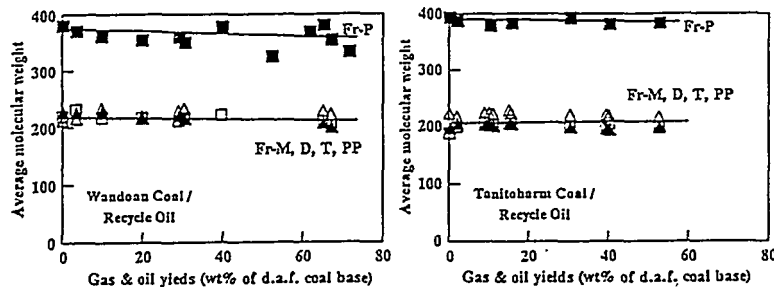


Fig. 4 Average MW of HPLC fractionated oil component vs. yields of Oil & Gas

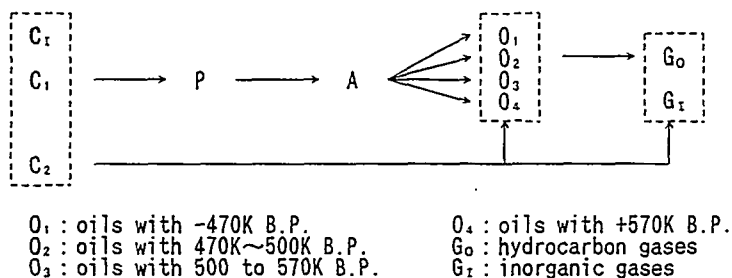


Fig. 5 Generalized coal liquefaction model

(3) Upgrading of coal liquid. Non-catalytic thermal hydrodealkylation of alkylbenzene in the presence of methanol

As reported previously, coal liquids were effectively dealkylated by using hydrogen due to the decomposition of methanol. In this report benzene, which is the product dealkylated from alkylbenzenes, and n-octylbenzene, which has a relatively longer side chain, were reacted in the presence and absence of methanol under flowing N_2 and under H_2 without methanol. As shown in Table 2 the reaction of benzene under N_2 flow without methanol at $700^\circ C$, benzene recovery was about 86%, and biphenyl and carbon also produced due to condensation reaction. At $850^\circ C$ of reaction temperature in the same reaction system, benzene was ca. 60% and condensed products such as terphenyls, triphenylene and benzo[b]-fluoranthene also produced. On the other hand in the presence of methanol under N_2 flowing, benzene recovery yield was 77% and carbon yield decreased. In the reaction of under flowing H_2 at $850^\circ C$, 86% benzene was recovered and the condensed products more decreased than the result under N_2 flowing with methanol. It is suggested that the amount of H_2 in the reaction system influences the production of condensed products.

Table 2 Yields of products from benzene.

Flow (ml/min)	N_2 (20)			H_2 (24)
Temperature ($^\circ C$)	700	850	850	850
Methanol conc. (mol%)	none	none	35	none
Carbon (wt%)	0.4	3.4	1.2	0.6
Benzene (mol%)	85.6	59.3	76.5	86.0
Naphthalene	trace	0.2	trace	0.1
Biphenyl	1.9	12.6	8.3	3.2
Acenaphthylene	-	trace	0.1	trace
Phenanthrene	-	0.1	trace	trace
o-Terphenyl	trace	0.3	trace	trace
m-Terphenyl	0.1	1.5	0.6	0.1
p-Terphenyl	trace	0.6	0.2	trace
Triphenylene	-	0.2	0.1	trace
Benzo [e] fluoranthene	-	1.0	trace	-
Others	trace	1.0	trace	trace
Total aromatics (mol%)	87.6	76.0	85.9	89.4

In the reaction of n-octylbenzene (Table 3), the yield of benzene in the presence of methanol more increased slightly than the reaction without methanol. However, the yield of benzene was less than the other alkylbenzene having a shorter alkyl side chain. The condensed aromatic products would be also produced by the reaction of longer alkyl side chain during thermal cracking reaction.

Table 3 Effect of methanol coccentration on yields of products from n-octylbenzene

Methanol conc. (vol%)	none	50
Carbon (wt%)	0.7	0.3
CH ₄ (wt%)	25.9	24.2
C ₂ H ₄	13.2	20.9
C ₂ H ₆	7.2	12.7
C ₃ ~	0.1	0.4
Benzene (mol%)	70.7	73.5
Toluene	4.9	8.4
Ethylbenzene	0.1	trace
Styrene	1.9	1.9
Indene	1.8	3.2
Naphthalene	12.1	8.8
2-Methylnaphthalene	0.2	0.2
Biphenyl	0.9	0.7
Diphenylmethane	0.2	0.1
Acenaphthylene	1.1	0.6
Fluorene	0.5	0.4
Phenanthrene	1.8	1.2
Anthracene	0.4	0.3
1-Phenylnaphthalene	0.1	trace
2-Phenylnaphthalene	0.2	0.1
Fluoranthene	0.4	0.2
Pyrene	0.3	0.1
Benz [a] anthracene	0.2	0.1
Chrysene	0.2	0.1
Benzo [b] fluoranthene	0.1	trace
Others	0.6	0.1
Total aromatics (mol%)	98.6	100.0

* at 800°C, 24ml/min of H₂ flow

Future Tasks

1. Reaction mechanism of coal liquefaction
2. Kinetic data for coal liquefaction
3. Non-catalytic reforming of coal-liquid

Dissolution Reaction of Coal by Hydrogen-Donating Aromatic Solvents and Development of Effective Catalyst

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Objectives

Coal liquefaction process must be applicable to the liquefaction of various coals which are different in coal rank and storage conditions. The main purpose of this investigation is the fundamental research into liquefaction reaction of various coals in the presence of hydrogen-donating hydroaromatic solvents and the development of effective catalysts. This year, our objectives were to investigate five work programs in basic research of the additive effects of sulfur to the catalyses on hydroconversion of 1-methylnaphthalene (1-MN) and the crystal structure of iron sulfates on 1-MN hydroconversion as a basic reaction of coal hydroliquefaction in the NEDOL Process which started to demonstrate the scale of 150 tons/day pilot plant of coal liquefaction as a Japanese national project .

Work Program

- (1) Additive effects of elemental sulfur to hydroconversion of 1-methylnaphthalene (1-MN) with ferrous sulfate and ferric sulfate catalysts.
- (2) Effects of reaction temperature and presulfiding temperature of iron sulfates on hydroconversion of 1-MN with iron sulfates catalysts.
- (3) Analysis of iron catalyst structure before and after the reaction of 1-MN hydroconversion and the thermal pretreatment under air with X-ray diffraction.
- (4) Effects of additive amount of sulfur to the catalyses of iron sulfates and the change of the sulfates structure.
- (5) Additive effects of concentrated sulfuric acid(96 wt%) to the 1-MN hydroconversion system with ferrous sulfate and pyrrhotite catalysts.

Summary (1974 - 1996)

1. Up to FY 1995

Liquefaction of various coal ranks such as Ohyubari, Akabira, Taiheiyo, Liddell, Wandoan and Yallourn, and a number of solvents has been evaluated as well as the effect of several sorts of additives such as phenols. Effects of mineral matters included in the coal was studied for both coal liquefaction and hydropyrolysis of coal-model compounds. Catalytic effect of many types of iron compounds on coal liquefaction was compared to find out the most effective form of catalyst. Some organic

compounds related to the coal structure such as aromatic ethers and polycyclic aromatic compounds were treated under coal liquefaction conditions, and the products as well as the effect of catalysts were also investigated. Strong hydrogen donor compounds were confirmed to be more reactive than tetralin toward free radicals. It has been shown that SRC promotes the hydropyrolysis of diarylmethanes and that SRC acts not only as a hydrogen donor but also as a hydrogen shuttler. It has been shown that reduced Fe and pyrrhotite are highly active catalysts in the liquefaction of Yallourn coal and in the hydropyrolysis of Wandoan coal-derived SRC. Some different rank coals were liquefied in the presence of the active and inexpensive iron ores. Partial oxidation of coal has a negative effect on coal liquefaction. It has been shown that the catalytic activity of pyrrhotite is greatly affected by its precursor and reaction temperature. Sulfur addition remarkably increases the catalytic activities of Fe and Ni-Mo catalysts for the hydroconversion of arylalkanes. It was clearly showed that catalytic activity of pyrite decreased by the oxidation under air. However, the deactivated pyrites were reactivated by using of enough sulfur(S). Last year, it was clearly showed that thermolysis of some diarylalkanes proceeded slowly by the radical chain reaction. Metallic Fe catalyst accelerated the hydrogenation of aromatic-rings. FeS_2 catalysts, which is easily transformed to pyrrhotite Fe_{1-x}S under reaction conditions, promoted $\text{C}_{ar}\text{-C}_{alk}$ bond cleavage of diarylmethanes only, and also promoted the hydrogenation of diarylethanes and diarylpropanes, especially bicyclic-rings, more than that of monocyclic-rings. C-C bond cleavage of arylalkanes was related to the hydrogen-accepting ability, C-C bond dissociation energy and resonance energy of the species after C-C bond scission.

2. For FY 1996

We took notice of iron sulfates catalyst because the iron sulfates were easily produced by the reaction between sulfuric acid and many kinds of iron resources, such as iron ores, scraps and waste recycle materials containing iron. The first stage of reactor in direct coal liquefaction requires a catalyst which is both inexpensive and disposable in order to develop an economically viable technology. Iron catalyst is one of cheapest transition metal catalyst and the catalyst has highly activity to the hydroconversion of polycyclic aromatics, arylalkanes and diarylalkanes. This year, our project investigated five topics on the hydroconversion of 1-methylnaphthalene (1-MN) as a coal model compound in the various reaction conditions.

Experimental: *Materials:* 1-Methylnaphthalene(1-MN), decalin(DHN), ferrous sulfate($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and ferric sulfate($\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$) for catalysts and catalyst precursors and elemental sulfur(S) were commercial reagents. *Batch Reaction Conditions:* In one typical reaction, 1.0 g(7.1 mmol) of 1-MN, prescribed amounts of iron sulfates(ab. Fe 2.2 mg-atom) and S(ab. 6.0 mg-atom) and 30 ml(ab. 191 mmol) of DHN were put into a 150 ml stainless steel(SUS 316), magnetically-stirred autoclave. After the reactor was pressurized with hydrogen to 10 MPa at room temperature, the autoclave was heated up to the prescribed temperature(usually 350°C) within 20 min and kept at the temperature for a prescribed time. After the reaction, the hot reactor was immediately quenched in an ice-water bath. Another method is the hydroconversion with presulfided catalysts at various temperatures before the 1-MN hydroconversion reaction. *Products Analyses:* Liquid products were

identified by GC-MS and quantified by GC. Structure of iron catalysts was analyzed by XRD method.

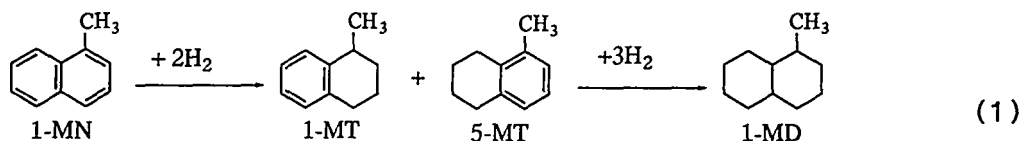
(1) Additive effects of elemental sulfur to hydroconversion of 1-methylnaphthalene (1-MN) with ferrous sulfate and ferric sulfate catalysts.

Table 1 summarizes typical results of additive effects of S at 2.5 of S/Fe atomic ratio on the hydroconversion of 1-MN at 350°C for 1 hr in the presence of ferrous sulfates catalysts roughly powdered with a ceramics mortar. Ferrous sulfate and its dried sulfates were very low activities in the absence of S. Hydrogenation activity of ferrous sulfates, however, dramatically improved with addition of enough S(S/Fe = 2.5). Added S was stoichiometrically in excess of amounts needed for formation of troilite(FeS), pyrrhotites(Fe_{1-x}S) and pyrite (FeS₂), but the amounts of S are not enough to form pyrite, according to the phase diagram of Fe - H₂ - H₂S system in references.

Table 1 Hydroconversion of 1-MN with iron sulfate catalysts at 350 °C for 1 hr.

Catalyst ¹	Grind ²	Dry ³	S-add.	Conv.(%)	4H-select.(%) ⁴	5-MT/1-MT
FeSO ₄	yes	no	no	1.4	~	~
	yes	yes	no	2.0	20	~
	no	yes	yes ⁵	36.0	86	1.11
	yes	yes	yes ⁵	43.5	84	1.10
	yes	yes	yes ⁵	42.5	90	1.11
Fe ₂ (SO ₄) ₃	yes	no	no	7.0	3.2	1.57
	yes	no	no	5.9	6.4	1.56
	yes	no	yes ⁵	6.1	8.1	1.71
	yes	yes	yes ⁵	6.0	7.2	1.59

1: 2.2 Fe g-atom; 2: grind of iron sulfate; 3: at 150 °C for 1 hr; 4: selectivity to methyltetralins; 5: S/Fe = 2.5.



Hydrogenation of 1-MN proceeded as in eq. (1). Major products from 1-MN hydroconversion were 1-methyltetralin(1-MT) and 5-methyltetralin(5-MT), and 1-methyldecalins(1-MDs) were also produced a little. Ratios of 5-MT/1-MT in the products from 1-MN hydrogenation with ferrous sulfate catalyst were always about 1.1 in the presence of enough S. These results indicate that 1-MN hydrogenation proceeds with consecutive hydrogenation and hydrogenation of methyltetralins(MTs) as a second step is very slow. Further, hydrogenation rate of aromatic-ring bonded with a methyl group is slightly slow compared with the other ring in 1-MN. The activity of catalyst formed during the reaction with ferrous sulfate was a little low to compare with that of synthetic pyrite developed by Asahi Chemical Industry Co. Ltd. as a consignment from Japanese national project.

Catalysis of ferric sulfates and additive effects of S on the hydroconversion of 1-MN are also shown in Table 1. Conversions of 1-MN with ferric sulfates in the absence of S were also low level between 6 % and 7 %. These conversions were a little higher than those in the case of ferrous sulfates. Selectivities of 1-MT and 5-MT were very low, as same as the case of ferrous sulfates in the

absence of S. Conversion of 1-MN did not increase a little by S addition when the S/Fe atomic ratio is 2.5. The major product was naphthalene and a very little tetralin was produced. Recovered liquids after the 1-MN reaction in the presence of ferric sulfates catalysts were always light yellow. These phenomena suggest that some complicated reactions occurs.

(2) Effects of reaction temperature and presulfiding temperature of iron sulfates on the hydroconversion of 1-MN with iron sulfate catalysts.

Hydroconversion of 1-MN in the presence of S such as S/Fe ratio is 2.5 were carried out from 200°C to 400°C as shown in Fig. 1. Conversions of 1-MN were very low below 300°C. In the case of ferrous sulfate catalyst, conversion of 1-MN increased with raising of temperature. The conversions were 3.3 %, 43 % and 55 % at 320°C, 350°C and 380°C, respectively. But the value at 400 °C was only a little increase from the value of 380°C. This result suggests contributions of decreasing of surface area with sintering of catalysts and the reaction beyond critical temperature of solvent decalin. In all reaction cases above 320°C, hydrogenation of 1-MN was mainly proceeded and the MTs selectivities were over 98 %.

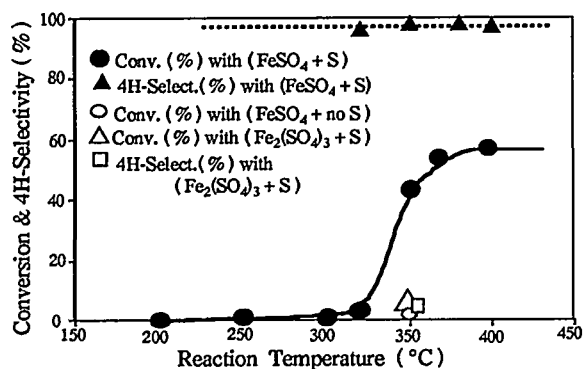


Fig. 1 Effects of reaction temperature to the conversion and tetrahydro-derivatives on 1-MN hydroconversion with iron sulfates.

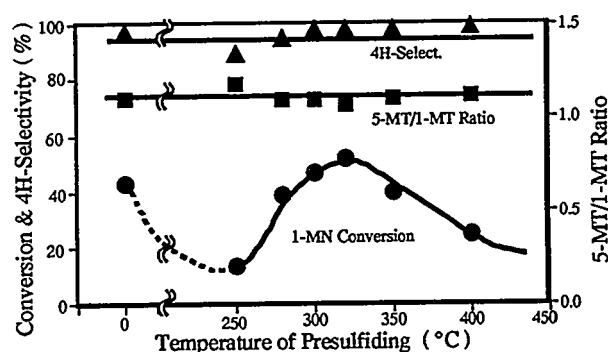


Fig. 2 Effects of Presulfiding temperature on the hydroconversion of 1-MN with ferrous sulfate catalyst (S/Fe = 2.5).

Results in Fig. 1 are the overall results including three possibilities at least, pyrrhotite formation with reaction between ferrous sulfate and elemental S or hydrogen sulfide (H_2S) formed from S, catalytic activity with pyrrhotites produced early stage of the reaction and possibility with extraordinarily active sites formation during pyrrhotites formation from the iron sulfates. We can evaluate the real catalytic activity by using previously presulfiding of sulfates before the 1-MN hydroconversion. Figure 2 shows the temperature effects of presulfiding of ferrous sulfate with S addition on the 1-MN hydroconversion. The activities of iron catalysts presulfided at 300°C and 320°C increased a little to compare with those of original sulfate. Decrease of the activity of catalyst presulfided at 400°C will be attributable to decrease of surface area with the sintering of pyrrhotites.

(3) Analysis of iron catalyst structure before and after the reaction of 1-MN hydroconversion and the thermal pretreatment under air with X-ray diffraction.

Figure 3 summarizes typical XRD patterns of ferrous sulfates. Original authentic reagent ferrous sulfate $FeSO_4 \cdot 7H_2O$ was transformed to the mixture of Butlerite ($Fe(OH)SO_4 \cdot 2H_2O$) and Szomolnokite ($FeSO_4 \cdot H_2O$) structures by heating at 150°C for 10 hr under air, and to the mixture of

$\text{FeSO}_4 \cdot \text{H}_2\text{O}$, $\text{Fe}(\text{OH})\text{SO}_4$ and $\text{Fe}_2\text{S}_2\text{O}_9 \cdot x\text{H}_2\text{O}$ and to light yellow solid by heating at 200°C for 10 hr. The catalyst recovered after the reaction of 1-MN in decalin with ferrous sulfate in the absence of S at 350°C was low crystallographic solid and we could not recognize any confirmed structure. Ferrous sulfate, however, was transformed to pyrrhotites Fe_{1-x}S structure and a little of Szomolnokite in the presence of excess S ($\text{S}/\text{Fe} = 2.5$) at 350°C , as shown in eq. (2). As shown in Fig. 4, formation of Fe_{1-x}S was certainly detected at 300°C from XRD patterns. The crystal structure of Fe_{1-x}S structures was grown with the raising of temperature. Catalyst recovered after the reaction at 400°C was completely pyrrhotites structure.

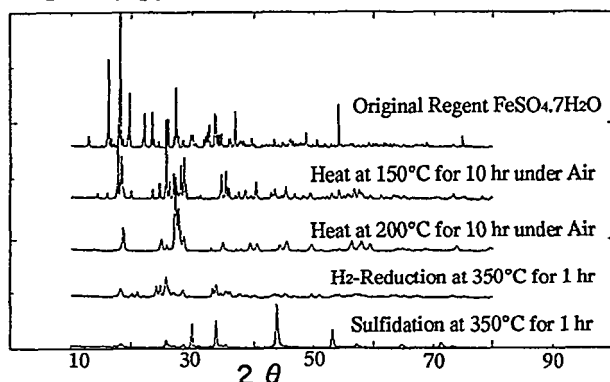


Fig. 3 XRD patterns of original ferrous sulfate, dried ferrous sulfates at 150°C and 200°C for 10 hr, and ferrous sulfate catalysts recovered after reaction in the absence and presence ($\text{S}/\text{Fe} = 2.5$) of elemental sulfur.

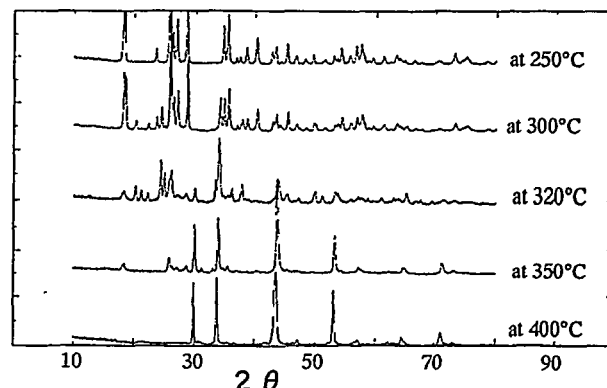
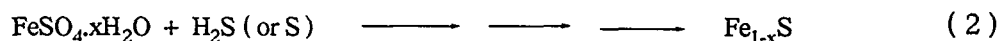


Fig. 4 Effect of reaction temperature to XRD patterns of iron catalysts after 1-methylnaphthalene hydroconversion with ferrous sulfate in the presence of elemental sulfur ($\text{S}/\text{Fe} = 2.5$).



On the other hand, original regent ferric sulfate was found to be almost $n = 8$ in $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ formula by means of XRD and from weight loss measurements. The ferric sulfate was changed to $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ by heating at 150°C for 10 hr. In contrast to the case of ferrous sulfate, formation of pyrrhotites from ferric sulfate was not confirmed from the reaction condition in the presence of S ($\text{S}/\text{Fe} = 2.5$) at 350°C for 1 hr, by means of XRD analysis as shown in Fig. 5.



(4) Effects of additive amount of sulfur in the catalyses of iron sulfates and the change of sulfates structure.

Structures of ferrous sulfate and ferric sulfate recovered after the reaction were strongly affected by the amounts of S added to the reaction system at 350°C for 1 hr, as shown in Figs. 6 and 7. Catalytic activity for 1-MN hydroconversion was also determined as shown in Fig. 8. Partial pressures of H_2S at S/Fe atomic ratios of 15 and 30 are estimated to be about 0.5 MPa and 1.0 MPa at room temperature, respectively. In the case of ferrous sulfate, pyrrhotites formation was confirmed at S/Fe atomic ratios over 1.1 in the reaction system from XRD patterns analysis. The crystallinity of pyrrhotites structure was enhanced with increase of S addition amount. The catalytic activity for 1-MN hydroconversion increased with the amounts of S added until S/Fe ratios around 6. Addition of a huge excess S, such as S/Fe ratio of 15 or 30, slightly decreased the rate and the selectivity of methyltetralins formation from 1-MN hydrogenation. In the cases of ferric sulfates as a iron catalyst precursor, however, pyrrhotites formation was not observed below 2.5 of S/Fe ratio from

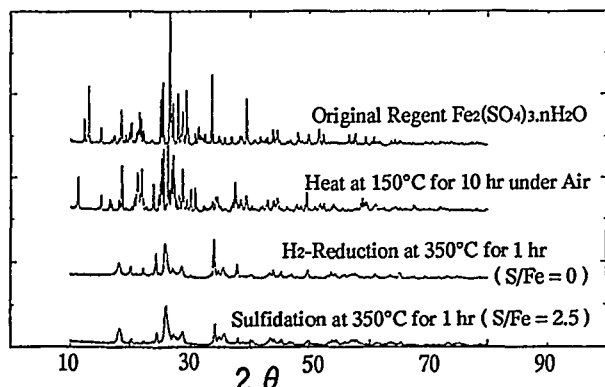


Fig. 5 XRD patterns of original ferric sulfate, dried ferric sulfate at 150°C for 10 hr, and iron catalysts recovered after reaction with ferric sulfate in the absence and presence ($\text{S}/\text{Fe} = 2.5$).

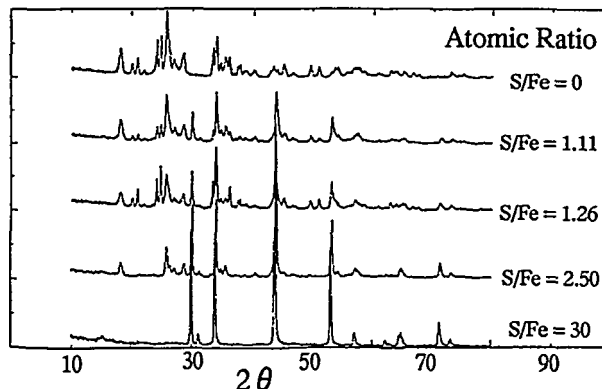


Fig. 6 Additive effect of S on XRD patterns of catalysts recovered after 1-MN hydroconversion in the presence of FeSO_4 at 350°C for 1 hr.

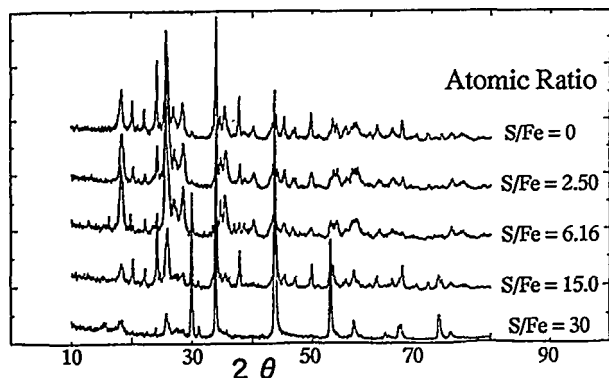


Fig. 7 Additive effect of elemental sulfur on XRD patterns of catalysts recovered after the 1-methylnaphthalene hydroconversion in the presence of ferric sulfate at 350°C for 1 hr.

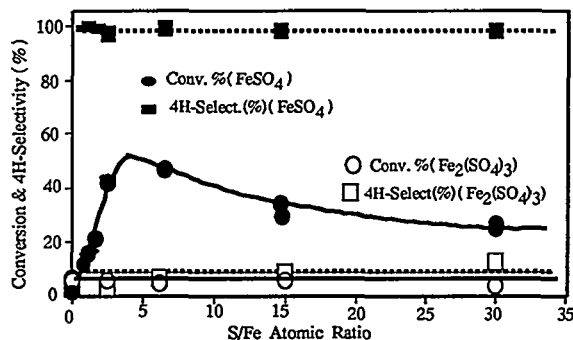
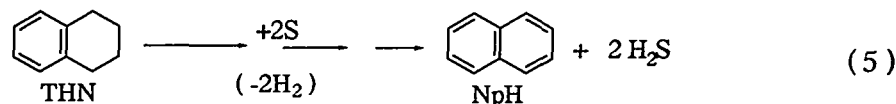
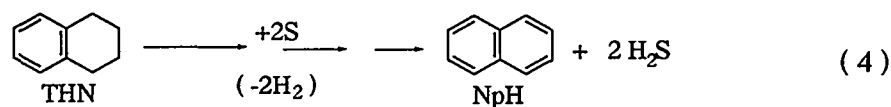


Fig. 8 Additive effects of S to the 1-MN conversion and tetrahydro-derivatives selectivity in the presence of iron-sulfates under 10 MPa of hydrogen at 350°C .

XRD patterns. Pyrrhotites formation from ferric sulfate was detected a little at 6.0 of S/Fe ratio, and ferric sulfate was almost completely transformed to pyrrhotites structures at 30 of S/Fe ratio. Although the formation of pyrrhotites structure from ferric sulfate in the presence of huge amount S was confirmed, the catalytic activity of 1-MN hydrogenation rate did not increase.

On the other hand, reaction of decalin was independently performed to compare with that in the presence of 1-MN. Yields of tetralin and naphthalene were actually increased with increase of added S as shown in eqs. (4) and (5), that is, dehydrogenation of DHN was promoted by addition of S.



Analyses of solution recovered after reaction suggested that the S charged to reaction system was mainly consumed for the formation of tetralin and naphthalene with dehydrogenation reaction of solvent decalin and for H_2S formation with molecular H_2 . The H_2S formation with H_2 and S was decreased with increase of S addition. Further, increase of *trans*-/*cis*- ratio of solvent DHN was observed with increase of S addition.

(5) Additive effects of concentrated sulfuric acid (96 wt% H_2SO_4) to the 1-MN hydroconversion system with ferrous sulfate and pyrrhotite catalysts.

It is understandable on two big differences between ferrous sulfate and ferric sulfate, that is, the oxidation state of iron and the content of sulfuric anion in the reaction system. Oxidation states and SO_4^{2-} ion/Fe ratios of ferrous sulfate and ferric sulfate are Fe^{2+} and 1.0 and Fe^{3+} and 1.5, respectively. Additive effects of concentrated sulfuric acid (96wt% H_2SO_4) were tested to the two reaction cases in the presence of ferrous sulfate as a catalyst precursor. In one case, conversion of 1-MN with ferrous sulfate in the presence of S was dramatically decreased from 44 % to 4 % by the addition of H_2SO_4 the same as the amount of ferric sulfate from initial stage, and hydrogenation activity became to very low. In the case of the reaction system with pyrrhotites catalyst transformed from ferrous sulfate in the presence of S ($\text{S/Fe} = 2.5$) at 350°C , the additive effect of H_2SO_4 was only a little decrease from 40 % to 39 %. This difference is within experimental error. We can presume that sulfuric anion affects to active site of iron catalysts and the large effects are attributable to a process of transformation from ferrous sulfate to active site formation of pyrrhotite.

We can note next things as concluding remarks from this years results. Catalysis of iron sulfates in the 1-MN hydroconversion was investigated in the development of hydroconversion catalysts of heavy hydrocarbon materials. The catalytic activities of iron sulfates in the absence of S in the reaction system were very low. Hydrogenation activity of ferrous sulfate dramatically increased with addition of enough S. The hydrogenation activity of ferric sulfate, however, did not increase with addition of S. The XRD analysis of iron catalysts recovered after the reaction indicated that ferrous sulfate was transformed to active pyrrhotites above 350°C in the presence of enough S in the stoichiometry. Ferric sulfate was not easily transformed to pyrrhotites, and was not transformed to active catalyst. Ferrous sulfates was proved excellent one of catalyst precursors for hydroconversion of heavy materials resources which includes a lot of sulfur and mineral matters.

Future Tasks

Next three points to future tasks are very important in development view of a highly available catalyst which is one of the most important element for commercial coal liquefaction industry.

- (1) Development of higher active iron catalysts, the inexpensive and simple production methods from many kinds of the iron resources for huge commercial size coal liquefaction.
- (2) Research of the most optimized condition in multi-stage coal liquefaction for the highest heat efficient process and the highest oil yield with the lowest cost.
- (3) Development of the advantageous co-process between coal and oil residues or oil sand bitumens and other heavy hydrocarbon resources.

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'96 SUNSHINE PROJECT REPORT
MECHANISTIC BASIS OF THE COAL DISSOLUTION BY HYDROGEN
DONOR SOLVENTS: MULTI-STAGE COAL LIQUEFACTION FOR
THE BETTER LIQUID YIELD UNDER MILDER CONDITIONS

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Objectives

A multi-stage coal liquefaction which consists of pretreatment of coal to enhance the depolymerization, the dissolution of coal into light asphaltene under lower pressure and catalytic upgrading of the asphaltene, can be an improved technology of coal liquefaction. Such processes offer the potential for reducing hydrogen consumption, increasing liquid yield by suppressing gas formation and retrogressive reactions, and give flexibility with respect to product slate, the latter being desirable to meet changes in demand patterns. Highly active catalysts with functions for their recovery are another target for the improvement of coal liquefaction process. The catalyst used in the upgrading second stage can provide a high degree of desulfurization and denitrogenation to the product as well as hydrogen donating ability to the recycle solvent. Multi-stage liquefaction processes are critically dependent on the efficiency of the first stage in producing light asphaltene. This facilitates effective deashing of the feedstock for the subsequent stages and decreases coking reactivity, thereby increasing the catalyst life. The activity, selectivity and durability of the catalyst should be as high as possible. Furthermore, the conditions of all stages should be as mild as possible to minimize costs. Satisfactory high efficiencies of the liquefaction stage can be achieved by the careful selection of the coal, liquefaction solvent, and the liquefaction conditions. The efficient pretreatment of coal before the liquefaction can be achieved by the detail understanding of coal structure. The detail analyses of coal liquids in terms of heterocyclic structure and reactivity may reveal the effective two-stage procedure for the refining process.

Work Programs

- (1) Designs of coal pretreatment, liquefaction solvent for the acceleration of coal dissolution
- (2) Design of highly active catalysts with functions for their recovery to economize the coal liquefaction as well as to achieve highest distillate yield
- (3) Structural analyses of coal liquids, especially N- and S-containing heavy products and development of catalysts for the effective heteroatom removal and hydrocracking in the secondary catalytic upgrading stage

Summary(1975-1996)

1. Up to FY 1995

- (1) Lignite, brown and subbituminous coals were effectively liquefied into oil and asphaltene under rapid heating rate and high temperature-short contact time conditions using a tube bomb

and molten tin bath.

- (2) Four ring hydroaromatic compounds such as hydropyrenes (especially tetrahydropyrene) and tetrahydrofluoranthene (4HFL) were found effective in liquefying the low rank and bituminous coals with the high yields of oil and asphaltene.
- (3) Pretreatments of coals (demineralization and preheattreatment) were found effective to enhance the liquefaction reactivity of brown coals through the removal of divalent alkali earth cations which bridge the coal macromolecules through oxygen-containing functional groups.
- (4) Influences of donor amount and concentration in solvent on the hydrogen-transferring liquefaction of Morwell brown coal were investigated in terms of the roles of donor and non-donor solvents, and the liquefaction mechanism.
- (5) Effective denitrogenation and hydrocracking of the heavy distillate including long-chain paraffins and vacuum residue in coal liquids were achieved by the two-stage hydrotreatment consisting of extensive hydrogenation at $<400^{\circ}\text{C}$ and effective hydrocracking at $\sim 430^{\circ}\text{C}$.
- (6) The comparative reactivities of several subbituminous coals in the hydrogen transferring liquefaction were examined in terms of microscopic and structural analyses.
- (7) Structural analyses, thermal stability, and reactivity of coal liquid vacuum residues produced from Australian brown and subbituminous coals were investigated before and after the heattreatment, and single- and two-stage hydrotreatments.
- (8) The liquefaction ability of a mixed donor of tetrahydrofluoranthene (4HFL) and 8HAN (octahydroanthracene) was examined to reveal the roles of donors with different qualities and reactivities of transferable hydrogens, the components being applied in the same pot at once (single stage) or consecutively (two stages) for the liquefaction of Morwell coal and its hexane insoluble products.
- (9) The two-stage hydrotreatment of Morwell coal liquid vacuum residue (CLVR) were examined before and after the solvent fractionation with THF or the pretreatment with HCl/THF solution.
- (10) Roles of solvent and catalyst in the two-step liquefaction were optimized in terms of solvent/coal ratio, heating rate, product distribution and suppression of retrogressive reactions.
- (11) Complete conversion of Australian brown coal was achieved by the multi stages of deashing pretreatment, hydrogen transfer, and catalysis.
- (12) The liquefaction catalysts can be recovered from the liquefaction residues by designing functional supports such as ferromagnetic particles and extremely light carbon blacks of hollow sphere.

2. For FY 1996

(1) Iron-Based Catalysts Supported on Carbon Nanoparticles for Coal Liquefaction **Introduction**

Coal liquefaction to produce synthetic crudes is anticipated to be necessary early in the next century in some particular countries as the supply of conventional petroleum crudes will become limited and the world-wide demand for crude is continually growing in the developing countries including China

and India because of their drastic motorization. However, the cost of the coal liquefaction processes developed so far is still too high for commercialization. To lower these costs, improvements are needed in the yield of oil from coal, the quality of distillate products, catalyst activity and stability for recycle, the amount of solvent required and the use of milder reaction conditions.

The present authors have proposed the use of NiMo catalysts supported on a particular carbon black of Ketjen Black(KB) which consists of very fine hollow particles, around 30 nm, which provides a large surface for supporting Ni and Mo. These catalysts, being hollow, have a very low specific gravity and can potentially be recovered from the coal liquefaction products by gravimetric separation methods.

Such catalysts were found to have excellent activity for the liquefaction of subbituminous coals and were indeed separable by floatation. Effective dispersion in slurry in the liquefaction reactor was achieved by high stirring speeds and oil yields higher than 70% were obtained. Such catalysts, though appearing promising, still require high efficiency for catalyst recovery and recycle as any loss of the catalyst even in a small quantity may increase the cost of the overall process.

Iron-based catalysts were preferentially developed and utilized in the Bergius process in the very early coal liquefaction processes even though they were known to have lower catalytic activities than those of NiMo/Al₂O₃. This choice was made because of the limited availability and high cost of Mo and iron-based catalysts were cheap enough to be considered disposable in spite of their lower catalytic activity. Pyrrhotite has been reported to be active species. Grinding it to finer particles, impregnation of iron species directly into coal macro-molecules, preparation of nanoparticle iron catalysts, and combination use of iron- and Mo-based catalysts have been reported to increase the activity of the iron-based catalysts.

In the present study, iron-based catalysts were supported on carbon nanoparticles in an attempt to provide a high dispersion of active iron species which should exhibit higher liquefaction yields with a smaller amount of iron than fine pyrite particles and in addition provide a means of more facile catalyst recovery. Other metals such as Ni and Mo were also co-impregnated with Fe on the Ketjen Black to promote the hydro-genation and hydrocracking activities to give higher yields of liquid products.

Experimental Section

Some properties of Ketjen Black(KB) carbon nanoparticles are shown in Table 1. Three kinds of iron salts of Fe(II) fumarate(Fe-FM), Fe(III) acetylacetonate(Fe-AA), and Fe(II) sulfate (Fe-SL) were used as iron precursors in the present study. The catalysts prepared in the present study are listed in Table 2. The prescribed amount of KB was dispersed in methanol by ultrasonic irradiation, and an iron salt dissolved in methanol was added to the KB-methanol slurry with a small amount of nitric acid(1vol%) as an additive. After the iron salt was completely dissolved, the slurry was well dispersed by ultrasonic irradiation, the slurry was then dried to obtain iron supported on KB. Combination metal catalysts, Fe/Mo, Fe/Ni, and Ni/Mo-supported KB catalysts were prepared by simultaneous impregnation of the two salts using methanol as the solvent: Fe-FM and Mo dioxycetylacetonate (MoO₂-AA), Fe-FM and Ni(NO₃)₂ (Ni-Nt), and Ni-Ac and MoO₂-AA, respectively. The catalyst precursors were dried at 120 °C for 12 h in vacuo. The catalysts were

Table 1. Some properties of Ketjen Black

	KB EC600JD
Surface area(m ² /g)	1270
Volatile matter (%)	0.7
pH	9.0
Particle size (nm)	30
Apparent density (g/l)	115
Ash (%)	0.1
Ni (ppm)	1.5
V (ppm)	30
Fe (ppm)	100
Cu (ppm)	1
Mn (ppm)	1

Table 2. Catalysts and salts

Catalysts*	Fe salts	Ni salt	Mo salt
1, Fe(15)/KB	Fe(III)-AA		
2, Fe(15)/KB	FeSO ₄		
3, Fe(15)/KB	FeC ₄ H ₂ O ₄		
4, Fe(10)/KB	"		
5, Fe(5)/KB	"		
6, Ni(2)Fe(10)/KB	"	Ni(NO ₂) ₃	
7, Ni(5)Fe(10)/KB	"	"	
8, Ni(10)Fe(10)/KB	"	"	
9, Mo(2)Fe(10)/KB	"		MoO ₂ (II)-AA
10, Ni(2)Mo(10)/KB		Ni(OAc) ₂	MoO ₂ (II)-AA
11, Synthetic pyrite	FeS ₂		

* Numbers in parenthesis indicates the wt% of metals

Table 4. Hydrogenation of 1-methylnaphthalene* over Fe/KB and Mo/KB catalysts

Table 3. Elemental analyses of Tanitoharum coal

C	H	N	S	O*	Ash
(wt%, d.a.f.)					(wt%)
71.6	5.6	1.6	0.23	21.0	3.9

* Difference

catalysts	conv.(%)
Fe(15)/KB	2
Ni(2)Fe(10)/KB	4
Mo(2)Fe(10)/KB	7
Ni(2)Mo(10)/KB	50

* Reaction conditions;
catalyst 10 mg
1-methylnaphthalene 1 g
decalin(solvent) 9 g
reaction temp. :400 °C
reaction pressure :9 MPa
reaction time :60 min.

presulfided in flowing 5% H₂S/H₂ at 360 °C for 2 h prior to the reaction. Synthetic pyrite powder provided by NEDO(New Energy and Industrial Technology Development Organization, Japan) was used as a reference catalyst for comparison. The elemental analysis of Tanitoharum coal, an Indonesian subbituminous coal, is summarized in Table 3. Commercially guaranteed grade tetralin (TL) was used as a liquefaction (hydrogen donating) solvent.

The liquefaction was carried out using a magnetically-stirred 50cc autoclave at 450 °C. The stirring speed was varied in the range of 500~1300 rpm. The coal(3.0 g), the solvent (4.5 g) and catalyst (0.1 g) were charged into the autoclave, which was then pressurized with hydrogen to 9.3 - 11 MPa at room temperature after replacing the air with nitrogen gas. The heating rate to the reaction temperature was ca.20 °C/min. After the reaction, the product remaining in the autoclave was recovered with THF, and extracted in sequence with n-hexane, acetone and THF after the evaporation of THF. The n-hexane soluble(HS), n-hexane insoluble-acetone soluble(HI-AcS), acetone insoluble-THF soluble(AcI-THFS), and THF insoluble(THFI) substances were defined as oil(O), asphaltene(A), preasphaltene(PA), and residue(R), respectively. The gas yield(G) was calculated by the difference between weights of the initial raw materials and the recovered products. The reactions under the same conditions were repeated three times to minimize the experimental errors.

Results

Figure 1 illustrates the liquefaction yields of Tanitoharum coal at 450 °C, 15 MPa H₂, and 60 min, and 1300 rpm of high stirring speed with Fe(15 wt%) /KB catalysts prepared from different iron salts and synthetic pyrite. The Fe/KB catalyst prepared from Fe(II) fumarate gave the highest oil yield (58.3 %) among the Fe/KB catalysts. This compares favorably with the oil yield obtained with the synthetic pyrite (59.8 %). However, the amount of iron needed in the Fe/KB catalysts was only one-twelfth of the amount of iron in the synthetic pyrite. A high dispersion of iron species supported on KB is suggested.

Figure 2 shows the effect of different Fe loadings from Fe(II) fumarate catalyst preparations on the liquefaction of Tanitoharum coal. The oil yield gradually decreased from 58.3 % to 53.9 % with decreasing loading of iron from 15 % to 5 %. Higher loadings of iron on the KB resulted in the reduced activity per mole of iron, however, the yields did increase with higher amounts of iron.

Figure 3 illustrates the liquefaction yields of Tanitoharum coal with different catalyst/coal ratios using Fe(15 wt%)/KB catalysts prepared from Fe(II) fumarate. The oil yield significantly increased from 58.3 % to 69.3 % by increasing the amount of catalyst amount added from 3.3 wt% to 9.9 wt% based on the coal. It should be noted that the higher amount of added Fe/KB catalyst converted the asphaltene selectively to the oil without increasing the gas yield. This suggests that improved contact of the Fe/KB nanoparticle catalysts with the heavy products in the reaction slurry may enhance the efficient conversion of the asphaltene.

Figure 4 shows the effect of Ni or Mo addition to the Fe (10 wt%)/KB catalyst on the liquefaction of Tanitoharum coal. The addition of 2 wt % of Ni or Mo to the Fe/KB significantly increased the oil yield, especially Mo(2)Fe(10)/KB catalyst which produced a 67.9 % of oil yield, although the Mo(2)/KB gave the similar yield to that with the Fe(10)/KB catalyst. It is noted that the oil yield with the Mo(2)Fe(10)/KB catalyst is as high as the yield obtained with Ni(2)Mo(10)/KB

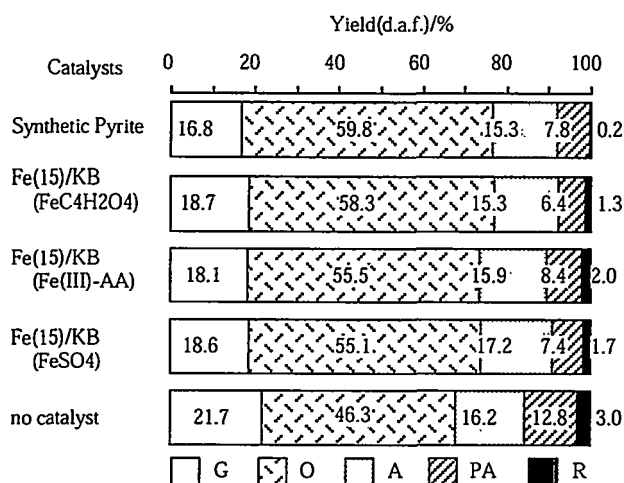


Figure 1 Effect of iron salt species on the liquefaction of Tanitoharum coal

Reaction conditions;
catalyst : Iron precursors; FeC4H2O4
Fe(III)-AA
FeSO4
catalyst/solvent/coal=0.03/1.5/1.0
reaction temp. :450°C
reaction pressure :15 MPa
reaction time :60 min.
heating rate :20 °C/min.
stirring speed :1300 rpm

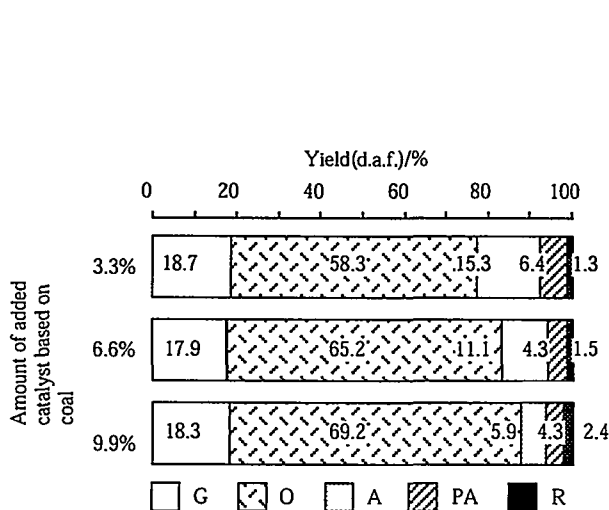


Figure 3 Influence of added amount of Fe(15)/KB catalyst on the liquefaction of Tanitoharum coal

Reaction conditions;
catalysts : Fe(15)/KB
iron precursor : FeC4H2O4
solvent/coal=1.5/1.0
reaction temp. :450 °C
reaction pressure :15 MPa
reaction time :60 min.
heating rate :20 °C/min.
stirring speed :1300 rpm

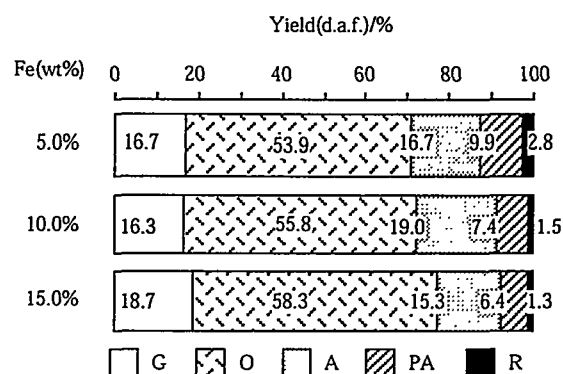


Figure 2. Effect of loading amount of iron supported on carbon on the liquefaction of Tanitoharum coal

Reaction conditions;
catalysts : Fe(X wt%)/KB, X=5, 10, 15
iron precursor : FeC4H2O4
catalyst/solvent/coal=0.03/1.5/1.0
reaction temp. :450 °C
reaction pressure :15 MPa
reaction time :60 min.
heating rate :20 °C/min.
stirring speed :1300 rpm

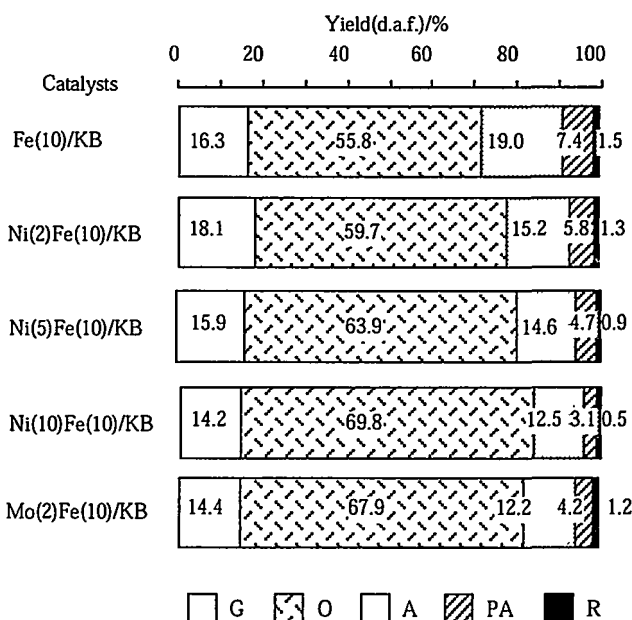


Figure 4 Effect of Ni or Mo addition to Fe(10)/KB catalyst on the liquefaction of Tanitoharum coal

Reaction conditions;
catalysts : Fe(10), Ni(2, 5, 10)Fe(10), Mo(2)Fe(10)/KB
Fe precursor: FeC4H2O4
Ni precursor: Ni(NO3)2
Mo precursor : MoO2-AA
catalyst/solvent/coal=0.03/1.5/1.0
reaction temp. :450 °C
reaction pressure :15 MPa
reaction time :60 min.
heating rate :20 °C/min.
stirring speed :1300 rpm

catalysts. Figure 4 also illustrates the effect of Ni concentration on the liquefaction yield of Tanitoharum coal at 450 °C, 15 MPa H₂, and 60 min for Ni-Fe/KB catalysts. The oil yield increased substantially with the higher amounts of added Ni. The Ni(10)Fe(10)/KB catalyst yielded 69.8 % of oil, again comparable to the yield obtained with the Ni(2) Mo(10)/KB catalyst.

Table 4 summarizes the activity of the catalysts examined in the present study for the hydrogenation of 1-methylnaphthalene at 400 °C, 9 MPa H₂, and 60 min. The hydrogenation reactions were performed at a lower temperature and a lower pressure, because the hydrogenation conversion at 450°C was above 90% with a significant amount of hydrocracked products on the NiMo/KB catalyst. The NiMo/ KB exhibited the highest hydrogenation activity among these catalysts, while all of the Fe-based catalysts exhibited low hydrogenation activities, even those in which Ni or Mo was added. This contrasts with the observed improvement of the liquefaction activity for Fe/KB catalysts with added Ni or Mo.

Discussion

The present authors reported that carbon nanoparticles such as Ketjen Black (KB) are promising catalyst supports because they have extremely high surface area and low density, which enables the high dispersion of active metal species on their surfaces and provides a means for facile catalyst recovery, respectively. The demonstration of high activity and a recovery procedure for NiMo/KB catalysts has been previously reported.

The present study revealed that Fe-based catalyst supported on KB gave much higher oil yield in the liquefaction of Tanitoharum coal than that with synthetic pyrite catalyst for the same number of moles of Fe. This high activity is attributed to the high dispersion of active metals on the KB carbon nanoparticles. Fe(II) fumarate was found to be the best catalyst precursor among the iron salts examined in the present study, probably due to its high solubility in methanol and facile decomposition during the presulfiding treatment which maintains high dispersion.

The addition of Ni or Mo to Fe/KB catalyst substantially improved the yield of oil in the liquefaction of Tanitoharum coal, reaching the level in the oil yield comparable to that obtained with NiMo/KB catalysts. On the other hand, the hydrogenation activity for two membered aromatic rings was quite low with these Fe-based/KB catalysts and was not enhanced significantly by the addition of Ni or Mo. It is suggested that high hydrogenation activity for two membered aromatic rings may not be essential in coal liquefaction reactions. Hydrogenolysis or hydrogenative capping of the fragments from coal molecules enhanced by the addition of Ni or Mo appears to accelerate oil production without excess gas production.

Future Tasks

- 1) Higher dispersion of active metals supported on Ketjen blacks to reduce the amounts of catalyst and solvent required for the high distillate yield
- 2) Design of recovery and regeneration of carbon-supported catalysts in the multi-stage liquefaction process
- 3) Design of carbon-supported catalysts for upgrading of coal liquids

2. RESEARCH AND DEVELOPMENT OF COAL GASIFICATION TECHNOLOGIES

(1) Fundamental Studies on Eco-Technology Oriented Coal Gasification

(2) The Research on Technology for Advanced Coal Gasification Process

FUNDAMENTAL STUDIES ON ECO-TECHNOLOGY ORIENTED COAL GASIFICATION

Koji Ukegawa
National Institute for Resources and Environment

Objectives

The purpose of this work is to search for the reaction conditions to improve the efficiency of coal gasification. Highly efficient and entirely clean use of coal should be attained when coal gasification process is combined with an advanced system such as fuel cell or integrated gasification combined cycle power generation in order to raise the environmental acceptability in the future. Based on the results obtained by the operation of HYCOL, gasification reaction and operation conditions are studied to establish an eco-technology oriented coal gasification.

Work Program

Mechanism of pyrolysis and hydrolysis under various conditions is studied using small scale batch type test apparatus newly constructed for hydrogasification experiment. For the fundamental studies of gasification reactions, step scan FT-IR/photoacoustic spectroscopy(PAS) was applied to depth profiling analyses of coal and gasification chars. Methanol sorption on coal was also investigated to elucidate structure and surface reactivity of raw coal and gasification chars. For improvement of gasification efficiency, investigation into the mechanism of formation of sulfur compounds during pyrolysis under hydrogen pressure was also performed.

Summary

1 Up to FY 1995

(1) Studies on the hydrogasification of coal were carried out using a small scale gasification apparatus. It was found that rate of methane formation in hydrogasification of coal is considerably affected by hydrogen pressure, height of coal bed, and feed rate of hydrogen into gasifier. Hydrogasification of Taiheiyo, Wandoan, Biduri, and Yallourn coals were investigated.

(2) Thermoplasticity and dilatation which were important properties of coal for hydrogasification were measured in the atmosphere of inert gases and hydrogen under pressure up to 50atm.

(3) Coal liquefaction residue was tested as a raw material for gasification. Properties of the residue was investigated for gasification use. High fluidity of coal

liquefaction residue, which caused serious troubles when fed to gasifier, was successfully reduced by air oxidation at low temperature.

(4) A gas producer with a capacity of 10kg/h which could conduct gasification at a temperature around melting point of ash was constructed. Gasification of Blair Athol and Kitadin coals were performed using air and steam as gasifying agents at 1000~1300°C. Equations describing mass and heat balances of coal gasification was derived by theoretical treatment of the relationship found in experimental results.

(5) Equilibrium relationship between gasifying conditions and results were estimated using free energy minimizing method.

(6) Material and thermal balances of coal gasification was investigated theoretically and an equation for cold gas efficiency was derived from the stoichiometry in general reaction formula. The published results collected from the operation of various gasifier were accumulated and treated using the equations to construct a data base for gasification process.

(7) Hot coal gas desulfurization was investigated using a high temperature reactor. Chemical composition and physical properties required for sorbents which show high desulfurization ability has been studied. Several kinds of ocher were found to be excellent for hot gas desulfurization.

(8) Gasification with simultaneous desulfurization was investigated using an air blown entrained/spouted bed gasifier. CaCO_3 and CaO with several particle size were fed into gasifier as desulfurization agents. Desulfurization efficiency indicated by the concentration of H_2S was measured under various gasification conditions. The pore structure and the rate of the sulfurization reaction for the twenty-two kinds of natural limestone were investigated.

(9) Step scan FT-IR/photoacoustic spectroscopy is used for the depth profiling of coal and gasification char particles.

2 For FY 1996

Studies on the mechanism of hydrogasification

A small scale batch type test apparatus for hydrogasification was constructed during this fiscal year. Test runs were successfully performed to obtain standard parameters for the operation.

For evaluating the properties of coal and chars, sorption of methanol on coal was investigated. Taiheiyo coal, crushed and sieved to 60-100 mesh, was dried under vacuum at 60°C. A part of the coal was heated under a nitrogen atmosphere at 125°C for 5 days to form sample C. Sample C' was produced by sorbing methanol to sample A, desorbing methanol at 25°C for 3 days, followed by heat treatment at 125°C under vacuum for 1 day. Sample D was generated by sorbing methanol to

sample C', desorbing methanol at 25°C for 3 days, followed by heat treatment at 70°C under vacuum for 5 days. Figure 1 shows the sorption isotherms for the coal heat treated at 70°C (sample D). The results of the coal heat treated at 125°C (sample C') are also shown for the comparison. The amount of methanol sorbed in run 1 of sample D is greater than those in run 1 and run 2 of sample C'. The shape of isotherm in run 1 of sample D is similar to that in run 2 of sample C'. By comparing run 1 and run 2 of sample D, almost identical shapes of isotherm were observed. The amount of methanol sorbed in run 1 is slightly greater than that sorbed in run 2 in the entire relative vapor pressure region studied. When sample C', sorbing methanol and desorbing at 25°C, was heat treated at 70°C to form sample D, pressure in the system increased. The gas released from the coal sample was proved to be methanol by mass spectrometer. Some portion of sorbed methanol was released to gas phase when coal was heated at 70°C. From the pressure increase, the amount of methanol desorbed at 70°C was smaller than that desorbed during heat treatment at 125°C. It is concluded that a small amount of methanol which desorbed at 70°C had remained in the coal during desorption at 25°C. The shape of isotherm was not affected by the release of methanol at 70°C.

The differential heat of sorption measured for sample D are illustrated in Figure 2. The results for sample C' are also shown in Figure 2. The difference between run 1 and run 2 of sample C' is not obvious in sample D. The value of the differential heat of sorption both in run 1 and in run 2 of sample D is similar to that in run 2 of sample C'. From the differential heat of sorption, it is concluded that a small amount of methanol which remained on a certain site in the coal with strong interaction after desorbed at 25°C could not be desorbed at 70°C. Methanol which has strong interaction with coal desorbes when heat treated at 125°C.

For analyses of gasification chars obtained under hydrogasification conditions, step scan FT-IR with photoacoustic(PA) detector was used. A Biorad FTS-60A/896 step scan FT-IR spectrometer was used for all spectral measurements. Spectra were recorded at resolution of 8cm⁻¹ using an MTEC model 100 PA cell with its accompanying preamplifier/power supply. Helium was used as the carrier gas in the PA cell. Stanford Research Systems SR510 lock-in amplifier was used when phase modulation was applied. Step scan speed/phase modulation frequency of 10/100Hz and 50/400Hz was used for the FT-IR measurement. A subbituminous coal char produced by hydrogasification was used for the IR measurement. In Figure 3, depth profiling FT-IR/PA spectra are shown. Carbon black was used for baseline correction. No obvious absorbance peaks could be detected on the surface by the step scan FT-IR/PAS using high modulation frequency(A). Using lower modulation frequency of 100Hz to allow IR beam to penetrate deeply inside char, peaks at 2900cm⁻¹, attributed to CH, and peaks at 1600-1700cm⁻¹, attributable to C=O or C=C, and a broad peak around 3400cm⁻¹, attributed to OH, could be clearly

detected(B). These peaks directly indicate that some organic part including oxygen containing functional groups still remain inside the char particle after being processed at high temperature hydrogasification. Difference in the spectrum obtained altering phase angles showed typical depth profile. It is demonstrated that heterogeneity and trace of reactions inside hydrogasification char particle can be detected by the FT-IR/PAS.

Sulfur compounds evolution during coal pyrolysis in hydrogen atmosphere

Sulfur in coal, which exist in inorganic minerals and organic functional groups, is evolved as mainly H_2S into gas phase during pyrolysis in hydrogen atmosphere. While the inorganic sulfur compounds can be almost eliminated from coal before it is used by the chemical or physical treatment, the organic sulfur is quite difficult to remove without severe treatment. Therefore, the understanding on the behavior of organic sulfur in coal during pyrolysis is quite important. In this study, the evolution of sulfur compounds during pyrolysis in hydrogen atmosphere was pursued for deashed coal which prepared by acid treatment on coal.

To eliminate the inorganic sulfur from coal, coal samples were immersed in 7.7% HNO_3 solution for 1 day at room temperature. Then, samples were washed by distilled water and dried under vacuum at 80°C . While the inorganic sulfur and a part of minerals were eliminated after HNO_3 treatment, the nitrogen and oxygen content in samples were slightly increased which implied the oxidation or nitration of samples. To prepare the complete deashed samples, 47% HF solution was used instead of HNO_3 solution. Because a part of minerals seemed to be remained as a fluoride compounds, samples were subsequently treated by 18% HCl solution at room temperature with stirring for 1 day. By HF treatment on coal, no oxidation was occurred. These raw and acid treated coal samples were pyrolyzed using fixed bed reactor with heating rate of $5^\circ\text{C}/\text{min}$ in H_2 atmosphere (flow rate of $1\text{L}/\text{min}$). During the pyrolysis, small amount of out-gas was sampled and analyzed by GC-MS system to evaluate the sulfur containing species.

The effect of acid treatment on H_2S evolution from Taiheiyo coal during pyrolysis is shown in Fig. 1. Although the maximum around 450°C on H_2S evolution curves of HF treated coal (TC-HFHCl) was almost the same as that of raw TC, the maximum of HNO_3 treated coal (TC- HNO_3) was decreased. In this temperature region, the evolution of COS from TC- HNO_3 , which amount was two order of magnitude smaller than H_2S , was increased about two times compare to the other two samples. Because the production of COS is considered to be the result of the reaction between sulfur and oxygen containing functional groups in coal, these changes in the evolution of sulfur compounds from TC- HNO_3 suggests the oxidation of organic part of coal.

On the other hand, TC-HF HCl showed large amount of H_2S evolution above 600°C , while TC and TC- HNO_3 released quite small amount of H_2S . The X-ray diffraction analysis of residue (char) from pyrolysis of TC and TC- HNO_3 exhibited the existence of gypsum. This fact indicates that the sulfur in TC and TC- HNO_3 reacts with calcium in the samples at high temperature region. Therefore, the sulfur in these two samples were fixed into the solid phase and could not evolved in the gas phase. Using several kinds of coal samples, it is confirmed that the effect of acid treatment on the H_2S evolution during pyrolysis was depended on the ratio of Ca/S which was determined by X-ray fluorescence analysis. From this study, it is clear that the HF treated coal sample includes only organic sulfur without oxidation of organic part of coal and shows essential behavior of organic sulfur in coal during pyrolysis in hydrogen atmosphere.

Future tasks

- (1) Adding gasification data using various kinds of coal to the database in order to clarify the effect of coal properties on gasification efficiency and the mechanism of pyrolysis and hydropyrolysis.
- (2) Analyses of coal and gasification chars formed under various conditions using a step scan FT-IR/PA spectroscopy, methanol sorption and other characterization methods.

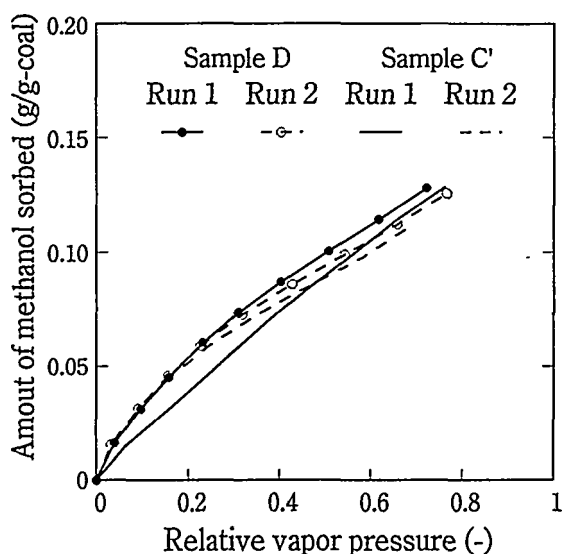


Figure 1 Sorption isotherm of methanol on the coal heat treated at 70°C (sample D) and the coal heat treated at 125°C (sample C').

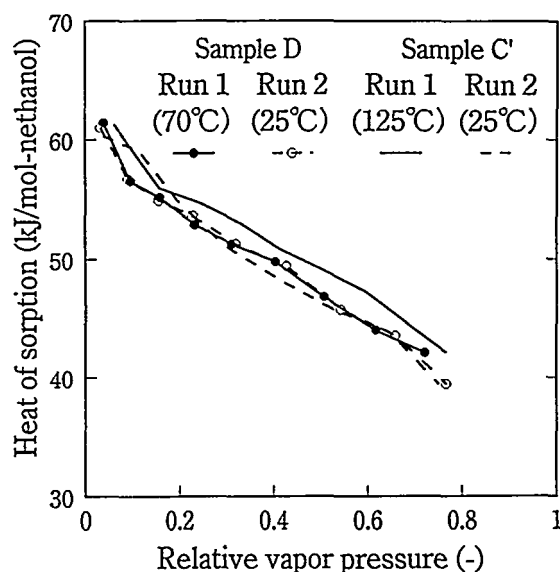


Figure 2 Differential heat of sorption of methanol on sample D and C'. (Temperature during desorption before each experiment is shown.)

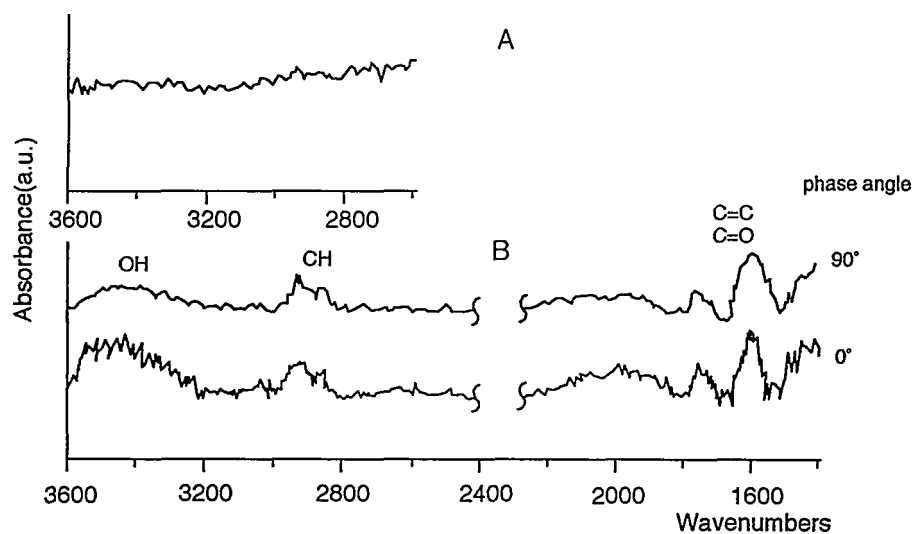


Figure 3 Depth profile of hydrogasification char obtained by step scan FT-IR/PAS. A: surface(modulation frequency 400Hz, phase angle 90°), B: inside(modulation frequency 100Hz).

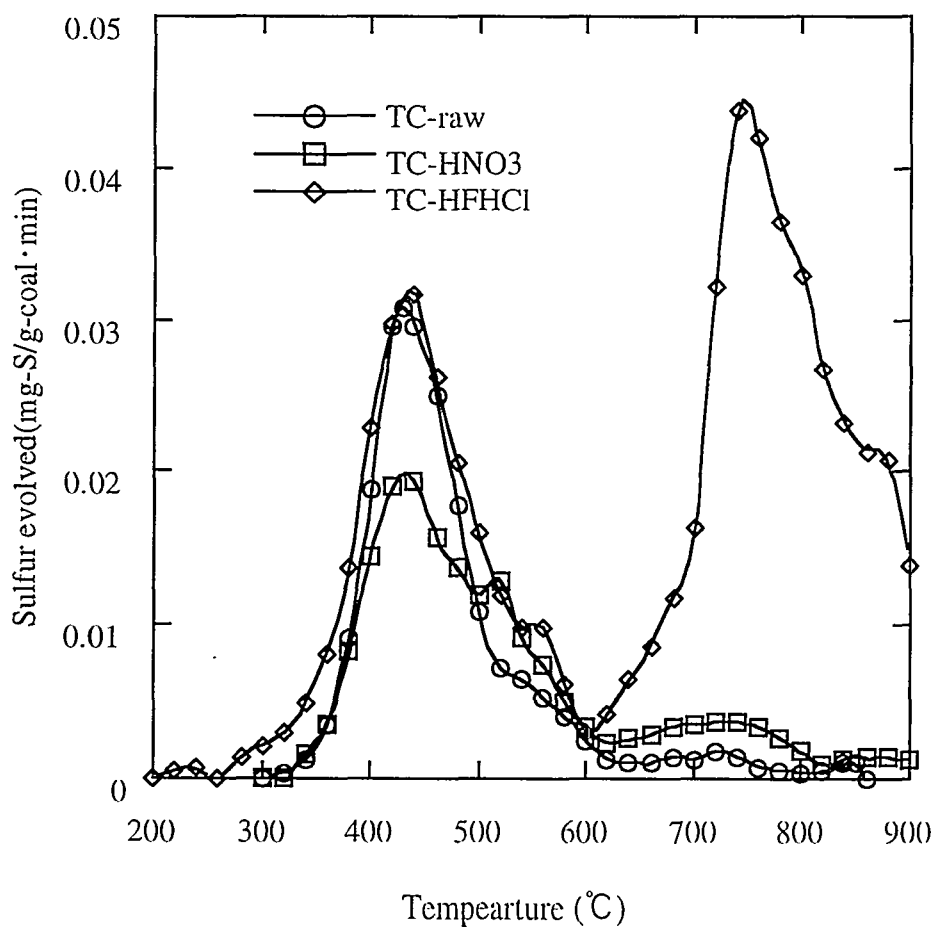


Figure 4 H₂S evolution from Taiheiyo coal.

THE RESEARCH ON TECHNOLOGY FOR ADVANCED COAL GASIFICATION PROCESS

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OBJECTIVES

There is no doubt that the coal is important resources alternative petroleum. However, the coal shows the wide varieties of characteristics. And the apparent properties of coal depend on the treatment in process. This research aims to develop the active pre-treatment of coals for certain gasification process. The properties of various coals, such as gasification reactivities and ash melting behavior, will be modified by thermal and chemical treatment. Also the control of the pollutant for the environment will be the research subject. Consequently, the clean and efficient utilization of wide variety of coals may be the major objectives in this research.

WORK PROGRAM

(1) Reactivity control of coal by means of modification of coal.

Very fine grinding, oil treatment, flash heat treatment and acid/base chemical treatment will be investigated for modify or control the surface structure, amount of surface complex and catalytic effect of chemicals. This may provide the principle in the way of lowering the operation temperature of gasifier and minimize the dispersion of characteristics of coals.

(2) The improvement of gasification process for the protection of the environment.

The one of important technology for coal gasification process is desulfurization. The reaction mechanism of desulfurization under pressurized gasification atmosphere will be studied. The reaction rate formula for the process development will present.

SUMMARY(1975-1996)

1. Up to FY 1995

This research has started at this year. However, some subjects related with coal gasification were studied in former project "Basic research on gasification characteristics of various coals."

The multi-stages pressurized fluidized bed was developed from 1975 to 1985. The gasification reactivities and ash properties of various coals and their derivatives, such as liquefaction residues and low grade coal, were investigated during 1984 to 1995. It has become apparent that the some important characteristics of coal char strongly affect gasification reactivity. These are surface area, the number of active sites, carbon structure, contained metal components and maceral components. The mineral components of ash and interaction of minerals are important to determine the ash fusion behavior. Also, the possibility of change of these properties was shown with the types of reactors.

2. For FY 1996

(1) Reactivity control of coal by means of modification of coal.

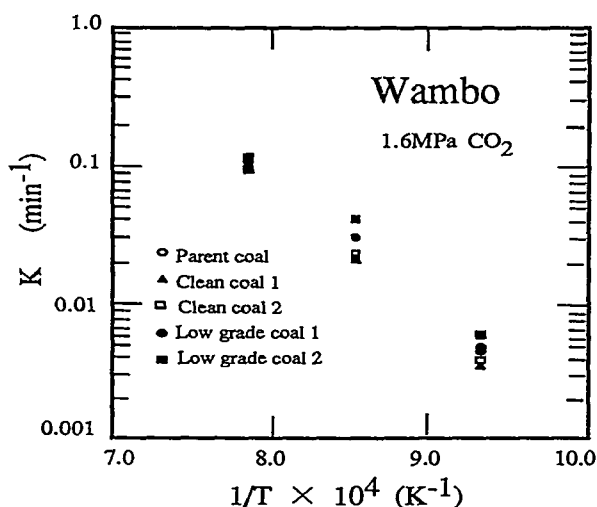


Figure 1 The reactivities of Wambo coal samples

The de-ash is the one of "active pre-treatment." There are two ideas for the advantage of de-ash. One is the application of clean coal, low ash coal, to reduce the load to gasifier. Another is the utilization of high ash coal to improve the total efficiency of coal conversion process. Under the former project "Basic research on gasification characteristics of various coal", the different ash contents coal samples from density separation as well as oil agglomeration treatment are tested for reaction rates. Figure 1 shows the Arrhenius plot of initial gasification rate for Wambo coal samples that includes two clean coals, two low grade coals and a parent coal.

The reaction rate increases with temperature and the differences between each sample become small at high temperature. However, the reaction rates' difference of each sample at lower temperature in which may be reaction control condition shows the following order.

low grade 2 > low grade 1 > parent coal > clean coal 1 = clean coal 2

This results seems to contrary to the general idea that the low grade coal has low reactivities.

Figure 2 summarizes the obtained results of reactivity measurement of other coals using high pressure TG under the conditions of 1127K and 1.6MPa. According to these experimental results, it may be summarized that the low grade coal has higher reactivity than parent coal in the case of Wambo, Montana and Illinois coal. And the differences of reactivities among low grade coal and parent coal samples of Taiheiyo coal and Wandoan coal are small. The samples from oil agglomeration treatment were also tested. These samples were low ash contents coals. The Montana and Wyoming coal samples show higher reactivities than their parents coals. Illinois coal has almost same order of reactivity with its parent coal. The phenomena of reactivities change due to de-ash

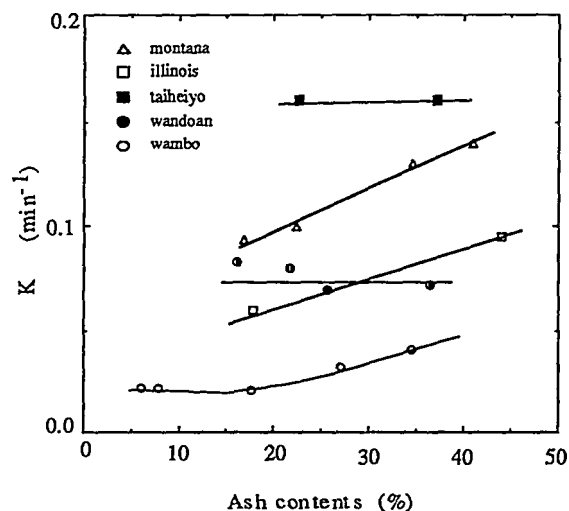


Figure 2 The effect of ash content on reaction rate constants

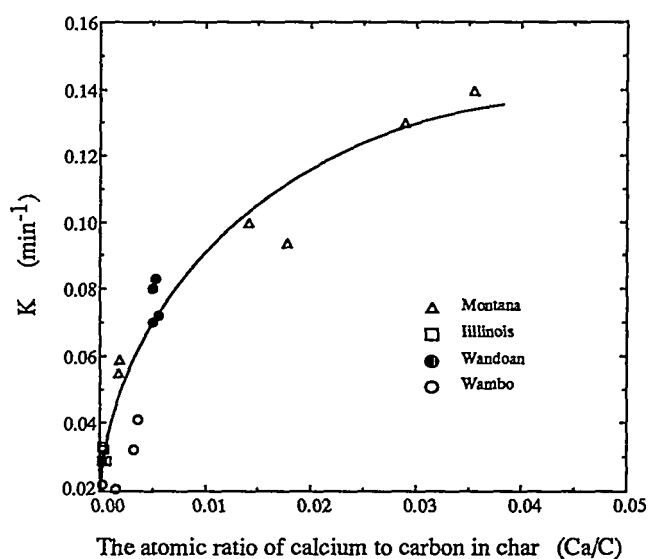


Figure 3 The relationship between reaction rate constants of char and Ca/C

process is so complex as mentioned above.

Recently, the idea of surface oxide complex that governs gasification reaction is generally accepted. The surface oxide complex may be formed on the defect of carbon structure or metal oxide such as CaO in coal. Therefore, the chemical components in ash of each sample were measured by ICP. Figure 3 shows the relationship between measured reaction rate constants and the atomic ratio of calcium and carbon (Ca/C) of the char samples. Even though there is some scattering of data at low reactivity samples, the reaction rate constants correlate well with Ca/C. It could be concluded that the reaction differences of coal samples from de-ash process may be related to the catalytic effect of minerals or amount of active sites.

The one way of utilization of entrained char from flash hydropyrolysis gasifier is partial oxidation gasification to generate hydrogen. Therefore, the reactivities of these chars were studied. The

pressurized drop tube reactor shown in figure 4 was designed and assembled for the preparation of flash hydropyrolysis char. The apparatus consists of three parts that are coal feeder and furnace for pyrolysis and char collector. The raw coal particles were introduced into reactor by screw feeder with vibration as much as 10~80 g/hr. The reactor tube is 20mm i.d. and 850mm long

that is made of Inconel. The maximum operation conditions are 10MPa in pressure and 900 °C in temperature. The following operating conditions were achieved in this year.

Pressure: 0.3 ~ 3MPa, Temperature: 750 ~ 850

°C, Gas feeding rate: 0.7 ~ 1.11 l/min,

Gas: Hydrogen, Nitrogen and Argon

The rate of pyrolysis is defined as follows.

$$X_p = 1 - (A/A_0)$$

where A_0 is ash contents of moisture free raw coal and A is ash contents of moisture free char. The

effect of pressure was shown in figure 5. The fact that the higher pressure suppresses the pyrolysis is

well known. The same trend was observed even though the high hydrogen partial pressure that expects to promote the pyrolysis.

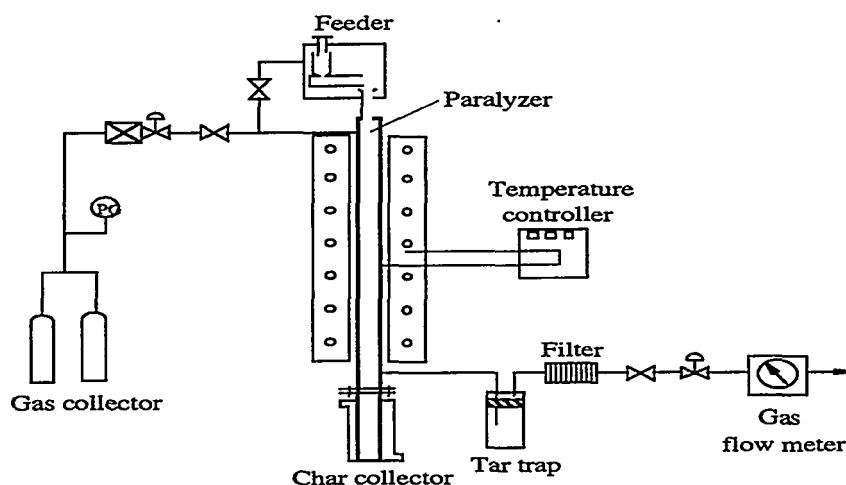


Figure 4 The pressurized drop tube reactor

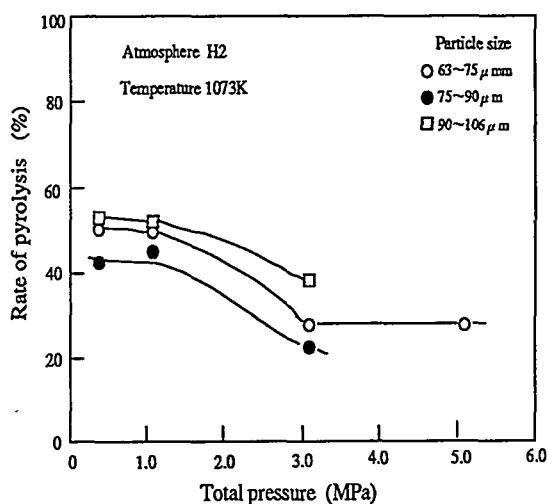


Figure 5 The effect of pressure on pyrolysis

Figure 6 shows the effect of temperature on char surface area for 63~75 μ m sample. The surface area is one of indicator that show the reactivity of char. The Surface area increase with temperature in the case of hydrogen atmosphere. However the effect of the other gas didn't appear clearly.

The hemispherical temperature (melting point) is the one of most important proprieties of ash for gasification process. We have pointed out that the important role of minerals in the mechanism of ash fusion. However the measurement of mineral contents in ash is rather difficult. The chemical element analysis, X ray diffraction method, microscopic observation, DTA analysis and TG

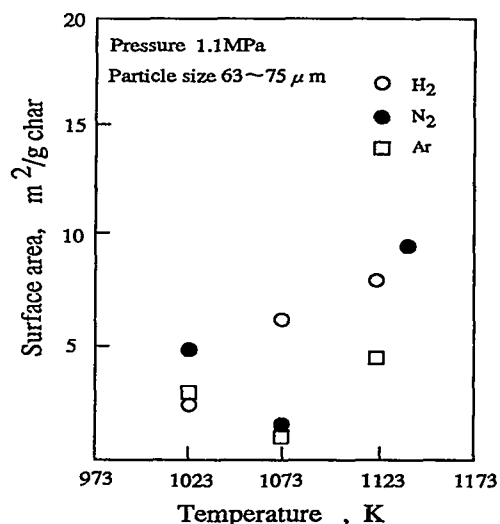


Figure 6 The effect of temperature on the surface area of char

analysis are normally required for this purpose. Therefor the approximate relationship between coal rank and chemical and mineral components was investigated from the practical point of view. The samples that used in this study have 62.9 ~ 93.5wt% carbon contents (C^{daf}). On the basis of the measured carbon content (C^{daf}), which ranges from 62.9 to 93.5 wt%, the samples can be divided into three major groups, namely <75, 75-85 and >85 wt% (Table 1). The groups correspond to the approximate carbon contents for lignite-subbituminous, subbituminous-bituminous and bituminous-anthracite coals respectively. Minerals in coal are both detrital and authigenic in nature. Detrital minerals such as quartz, kaolinite, illite, acid plagioclases, muscovite, rutile, apatite and Fe

Table 1 Average chemical compositions (wt%) for groups in order increasing carbon content

Ash group	Proximate analysis (wt%)									Ultimate analysis				
	(as received)				(db)			(daf)		(wt% daf)				
	W	VM	FC	A	VM	FC	A	VM	FC	C	H	N	O	S
Low	10.1	33.7	29.7	26.5	37.8	33.2	29.0	53.2	46.8	68.9	5.6	1.3	21.3	2.9
Medium	3.2	32.9	47.2	16.7	34.0	48.8	17.2	41.4	58.6	81.1	5.4	1.2	11.5	0.8
High	2.6	16.5	65.9	15.0	17.0	67.7	15.3	20.4	79.6	88.7	4.1	1.2	4.7	1.6
r	-0.67	-0.52	0.87	-0.44	-0.60	0.83	-0.49	-0.86	0.86		-0.56	0.06	-0.95	-0.51

Ash group	High-temperature ash analysis (wt%)										Ratio			
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	K ₂ O	Na ₂ O	TiO ₂	SO ₃	n	SiO ₂ /Al ₂ O ₃	(MgO+CaO)/((K ₂ O+Na ₂ O))	CaO/MgO	K ₂ O/Na ₂ O
Low	49.85	20.89	7.33	2.27	10.21	1.48	0.65	0.95	6.37	12	2.4	4.5	4.5	2.3
Medium	57.42	24.74	5.78	1.36	4.94	1.30	0.95	1.19	2.41	24	2.3	2.8	3.6	1.4
High	54.81	25.28	7.97	1.63	3.87	2.24	0.81	1.29	2.08	7	2.2	1.8	2.4	2.8
r	0.36	0.49	-0.24	-0.42	-0.46	0.12	0.08	0.53	-0.59	43				

Low: 62.9~74.3 Medium:76.4~85.0 High:85.5~83.5 r:Correlation coefficient with C^{daf} n: number of samples

Table 2 Average mineral proportions (vol%) in the crystalline matter of coal for groups in order increasing of carbon

Mineral	Rank group		
	Low C ^{df} =62.9-74.3%	Medium C ^{df} =76.4-85.0%	High C ^{df} =85.5-86.6%
Silicates			
Quartz	27-28	40	31-32
Kaolinite	8	10	9
Illite	4	4	4-5
Montmorillonite	2	1-2	1-2
Biotite + muscovite + chlorite	3-4	3	4-5
Plagioclase + K-feldspar	5	4	3-4
Zeolite + amphibole	2-3	2-3	2
Oxides and hydroxides			
Haematite + goethite + lepidococite	5	5-6	4-5
Spinel	<1	<1	1-2
Corundum + diaspore	3-4	2-3	3
Rutile	1-2	1-2	1-2
Portlandite	<1	<1	0
Brucite	1-2	1-2	1-2
Carbonates			
Calcite + aragonite	9-10	6	7-8
Dolomite + ankerite	2	3	3
Siderite	1-2	2	2-3
Magnesite	<1	<1	<1
Witherite	1	1	<1
Sulfides			
Pyrite + marcasite + pyrrhouthite	5	3	4-5
Sulfates			
Gypsum + anhydrite	5	3	2
Jarosite + rozenite + melanterite + coquimbite	4	3	3
Alunite	1-2	<1	1
Hexahydrate	1-2	<1	2
Barite	1-2	<1	1
Phosphates			
Apatite + vivianite + goyazite	3-4	2	4
Ash(wt%)			
as received	25.6	16.8	18.2
dry basis	28.2	17.9	18.6
Number of samples	11	19	4

and Al oxyhydroxides are commonly stable minerals during weathering and coalification. Authigenic minerals in coal are mainly sulfides, carbonates and sulfates of Fe, Mg and Ca. The authigenic minerals demonstrate more complex origin and transformations during the coal-rank series. The original elemental composition of a coal seam is modified because the circulating solutions can both introduce and leach various elements. Lower-rank coals are enriched in water (Table 1). The diagenetic compaction accompanied by dehydration of these coals causes some alterations in clay minerals, opal, hydroxides, and water-bearing sulfates to more stable dehydrated mineral species. The liberated water migrates and causes substantial leaching and redistribution of various soluble components in coal during filtration and diffusion of aqueous solutions. Most elements are more readily leached from low-rank coals than from high-rank coals. The lower-rank coals are enriched in water-soluble sulfates, carbonates, sulfides. In generally, the total amount of detrital minerals normally increases, while the amount of authigenic minerals commonly decreases, as coal rank

increases.

The hemispherical temperature is commonly estimated based on JIS method. However the atmosphere in gasifier is not same as the condition that uses in JIS method. Consequently, pressurized ash fusion test has performed using the same procedure as JIS method. The obtained results for seven samples are summarized in Table 3. The measured values under CO₂ or argon atmosphere show the lower melting points than that of observations in air. The pressure does not show the apparent effect on hemispherical temperature.

(2) The improvement of gasification process for the protection of the environment.

The desulfurization reaction has been studying using normal pressure tubular flow reactor as well as pressurized air-steam fluidized bed reactor. So far, the decomposition of CaCO₃ is successfully performed even under the existence

of prohibits such as CO₂. It could achieve high conversion under the range of operation conditions that were estimated from equilibrium. The desulfurization reaction itself was confirmed in the gasifier that has high concentration of steam. However, the conversions of sorbent remain at low level. The results of X ray diffraction and EPMA show the evidence that the reaction of H₂S and CaO takes place on only surface of particle. This suggests us that the maintenance of pore structure of sorbent is necessary to promote the desulfurization reaction. The tubular flow reactor was adopted to take the reaction kinetic data. The size of sorbent particle has been changed the range of 420-590 μ m \sim 53—105 μ . The sorbent that has size of 105-210 μ showed the best performance.

6. Future task.

The ash contents modification by density separation and oil agglomeration change the reactivity of coal samples. The behaviors of sample are not so simple. Namely, high ash contents coal shows the higher reactivities than the parent coal while some coal sample showed the same rage of reactivities with parent coal. This phenomenon was may explained by the change of atomic ratio of Ca to C in coal. This behavior probably relates with the amount of active sites. The easy way of estimation of ash melting behavior was established. In this way, the mineral composition was correlated with coal rank. The most suitable pre-treatment of raw coal for certain gasification reactor will be studied based on the combination of data of reactivity and ash melting characteristics.

For the better performance of in-situ desulfurization of gasifier, the sorbent that can keep the pore during the gasification will be investigated. The suppression of alkali metal in product gas will be the research subject for high temperature gasifier.

Table 3 The results of ash fusion test under different atmosphere.

		JIS methode		This Work		
		Oxida- tion	Reduc- tion	Oxida- tion	CO ₂	Ar
Newlands	SP	1400	1315	1220	1190	1205
	MP	1490	1370	1450	1420	1440
	FP	>1500	1495	1470	1430	1450
Ebeneza	SP	>1500	1410		1220	1240
	MP	>1500	>1500		>1500	>1500
	FP	>1500	>1500		>1500	>1500
Blair Athol	SP	>1500	>1500		>1500	1240
	MP	>1500	>1500		>1500	>1500
	FP	>1500	>1500		>1500	>1500
Datong	SP	1310	1120	1225	1100	1160
	MP	1380	1260	1360	1320	1330
	FP	1415	>1500	1380	1345	1350
Taiheiyō	SP	1270	1230	1120	1090	1120
	MP	1320	1300	1315	1290	1290
	FP	1470	1470	1350	1320	1310
Tigerhead	SP	1275	1230	1210	1160	1190
	MP	1380	1305	1380	1390	1360
	FP	1480	>1500	1400	1450	1410
Lithgo	SP	>1500	>1500		1300	1300
	MP	>1500	>1500		>1500	>1500
	FP	>1500	>1500		>1500	>1500

3. DEVELOPMENT OF BITUMINOUS COAL LIQUEFACTION TECHNOLOGIES

(1) Engineering, Construction and Operation of a 150t/d Bituminous Coal Liquefaction Pilot Plant

(2) Supporting Research for the Pilot Plant

① Research on 1t/d Process Supporting Unit (PSU)

② Study on the Synthetic Iron Sulfide Catalyst

③ Coal Selection Studies for Chinese Coal Liquefaction

ENGINEERING, CONSTRUCTION AND OPERATION OF
A 150 t/d BITUMINOUS COAL LIQUEFACTION PILOT PLANT

H. YOSHIDA

Director of Clean Coal Technology Center
New Energy and Industrial Technology Development Organization (NEDO)

Contractor: T. KANO, Nippon Coal Oil Co., Ltd.

Objectives

The objective of this study is to demonstrate the performance of the NEDOL process through the design, construction, and operation of a pilot plant, and to establish the requisite operational technology. In addition, the study is intended to collect and store a wide-range of technical data and know-how for use in commercial plants in the future.

Work Program (1996)

- (1) Study on the research program
 - Making the detailed plans for the initial startup and the first run
 - Making the plans for obtaining the operation data for assembly of the technical package
 - Reflecting the results of research and development conducted on coal liquefaction, including the operation of the PSU, in the pilot plant operation plan
- (2) Construction of the pilot plant
 - Procurement of the equipment and materials, and construction of the pilot plant
 - Inspections for the completion of the pilot plant
 - Preparation work for the initial startup
- (3) Operation of the pilot plant
 - Initial startup of the pilot plant
 - First run
- (4) Maintenance of the pilot plant
- (5) Studies and technical survey
 - Development of the liquefaction reaction simulator
 - Studies on the pulverizing system for the liquefaction catalyst
 - Environmental assessment
 - Study of the neutron attenuation tracer (NAT) method

Summary (1984-1996)

1. Up to FY 1995

A conceptual design of a 250 t/d pilot plant was completed in FY 1984. The basic design of the pilot plant was completed, and the detailed design was begun in FY 1985. The detailed design of the pilot plant was completed in FY1986. In FY 1987, the construction plan for the civil work was made. But, the pilot plant capacity has been modified from 250 t/d to 150 t/d in the end of 1987.

In FY 1988, the basic design of a 150 t/d pilot plant was completed, and the detailed design was begun and completed in FY 1991. Survey and soil tests of the pilot plant site were conducted in parallel with the detailed design. In addition, the

site preparation was made, and the civil work was begun. In FY1992, procurement of the equipment and materials was begun. In FY 1993, the most of the civil work was completed, and the construction work of the facilities on the site was begun. The utility facilities were completed and the operation of the facilities were begun in the end of FY 1995.

2. For FY 1996

(1) Study on the research program

- (a) The plans for obtaining the operation data to develop the technical package were made.
- (b) The detailed plans for obtaining the operation data in the course of the initial startup were made.
- (c) The research programs on the letdown valve, the slurry heat exchanger, and the solvent hydrogenation catalyst were reviewed.
- (d) The installation and test plans for the slurry flowmeter and the high-temperature and high-pressure ball valve were made.
- (e) The plans for producing and delivering the coal liquids to be used for the upgrading operation were made.
- (f) The detailed study plan on the environmental assessment was made.

(2) Construction of the pilot plant

- (a) The remaining equipment and materials were procured, and the construction work on the following facilities was conducted:
 - A liquefaction catalyst pulverizing system, a residue yard, a slurry heat exchanger, and an emergency power system
 - Sampling systems of the liquefaction reactors, a flue gas filter of the process waste water treatment system, a sand filtration unit of the industrial water system, a kerosene tank, and a slurry tank
 - Pavement in the pilot plant area and buildings for the maintenance work
 - Installation of the operation data logging system, and plant supervision televisions
- (b) Inspections for the completion of the pilot plant were conducted as prescribed in the High-Pressure Gas Control Laws and the Fire Service Laws.
- (c) The preparation work for the initial startup was conducted, including flushing of the piping, the initial filling of the catalyst and chemicals, a leakage test for the entire system, mechanical running tests of the rotating machinery, and adjustment work on electrical equipment and instruments.

(3) Operation of the pilot plant

- (a) Continuous operation of the boilers and the utility facilities was begun.
- (b) The solvent hydrogenation reactor was filled with Ni/Mo catalyst, and materials required for the operation were procured, including coal, Tanitoharum seam, Indonesia, and solvent for the initial charging.
- (c) Initial startup of the main units

The main part of the NEDOL process consists of a coal slurry preparation section, a liquefaction section, a distillation section, a solvent hydrogenation section, and a hydrogen production section, as shown in Figure 3. The initial startup of the main units was performed by the following procedure, and problems

occurring during the startup were solved:

- The operations conducted through short circulation lines used water or cold oil. Then, the circulating operations within each section and for the connecting system for the sections were conducted using cold oil.
- Coal conveying, coal pulverizing/drying, and slurry mixing operations were conducted in the coal slurry preparation section.
- Hydrogen production was begun, and the leakage tests for the liquefaction section and the solvent hydrogenation section were conducted using high-pressure hydrogen.
- The initial startup of the pulverizing system for pyrite, which is the liquefaction catalyst, was conducted.
- The solvent hydrogenation section was operated using hot oil, and the initially charged solvent was hydrogenated.
- The hot-oil operations were conducted in the entire system connecting the coal slurry preparation section, the liquefaction section, and the distillation section together.
- The initial liquefaction operation was begun. An amount of coal representing 60% of the design capacity of 150 t/d was processed for 68 hours. The liquefaction residue from the vacuum distillation tower was solidified, and the effects of changes in the process variable on the softening point of the liquefaction residue were investigated.
- After scheduled maintenance was conducted, the pilot plant was started up again, and an amount of coal representing 80% of the design capacity was processed for 39 hours.

(d) First run

Before the first run was begun, the pilot plant was operated to recover the recycle solvent from slurry that was stored in a tank during the shutdown process of the previous operation, and then the hydrogen leakage test, cold-oil operation, and hot-oil operation were conducted.

In the first run, an amount of Tanitoharum coal representing 60% of the design capacity was processed for 243 hours, and then an amount representing 70% was processed for 50 hours. After operation data, including the material balance, were obtained, the pilot plant was shut down to enable preparation for the scheduled inspection, as prescribed in the High-Pressure Gas Control Laws.

(e) Operation results of the first run

- Tanitoharum coal was processed under the standard operating conditions of the NEDOL process specified in Figure 3, and operation data, including the operation characteristics of the pilot plant and the performance of each piece of equipment was obtained. The operation was stable, and the fa (fraction of aromaticity) of the recycle solvent decreased to 0.56, as shown in Figure 1. The softening point of the liquefaction residue increased to 132 °C during operation.
- Operation characteristics of the pilot plant: Stability and responses to changes in the operation condition were investigated for the entire system and each piece of equipment. The operation manual was confirmed to be correct for the pilot plant, and knowledge of operation procedures was obtained.
- Coal slurry preparation section: An amount of coal representing 100% of the

design capacity was pulverized and dried, and the performance of the pulverizing/drying system was evaluated. The pulverizing system for pyrite was operated continuously for 72 hours, and performance data was obtained.

Erosion data on the pyrite pulperizer parts was obtained, and it was estimated based on the data that the pyrite pulverizing system would be able to operate uninterrupted for 40 days.

- Liquefaction section: With regard to the slurry preheating furnace and the liquefaction reactors, data were obtained on the pressure differences between the inlet and the outlet, as well as on heat loss. The gas holdup of the liquefaction reactors was estimated based on the data obtained, and the heat loss of the liquefaction section was calculated. Operations for drawing samples of the internal fluid out of the liquefaction reactors, as well as operations to withdraw the solid rich substances accumulated at the bottom of the liquefaction reactors into the high-temperature separator, were successfully conducted. Time-dependent data on the relation between the valve opening and the flow rate of the letdown valve was obtained, and the data revealed that a significant amount of erosion did not occur in the letdown valve.

- Distillation section: To rise the softening point of the liquefaction residue, various adjustments of the operating conditions were made, such as increasing the recycling flow from the bottom of the vacuum distillation tower, decreasing the amount of flushing oil in the residue handling pump, increasing the amount of stripping steam, and rising the inlet temperature of the vacuum distillation tower. The obtained data was placed in the database for use in the proper planning of the facilities and the proper operation of the pilot plant. Sampling and analysis of the liquefied products were conducted.

- Solvent hydrogenation section: Data on the solvent hydrogenation reaction was obtained. The activity of the hydrogenation catalyst was evaluated based on the reaction rate, and it was confirmed that the hydrogenation reaction of the benzene nucleus mainly proceeded. With respect to the hydrogenated solvent, the correlation between the fa and the hydrogen donating property (PDQI), which is shown in Figure 2, as well as the correlation between the fa and the specific gravity, were obtained. The pressure differences between the inlet and the outlet of the guard filter and the catalyst section of the solvent hydrogenation reactor were measured, and the data revealed that no significant increase in the pressure differences occurred.

- Material balance: Data on the material balance was obtained during the steady operation period, while the state of the recycle solvent remained nearly constant. The material balance of the products was calculated as shown in Table 1.

- Chemical and physical properties: The chemical and physical properties of the samples of the coal, the catalysts, the liquefied products, and the residue were analyzed and placed in the database.

Table 1

Material Balance of the Products

<u>Item</u>	<u>wt% daf Coal</u>
Gas	18
Water	12
Coal Liquids	54
Residue	22
H ₂ Consumption	— 5.9

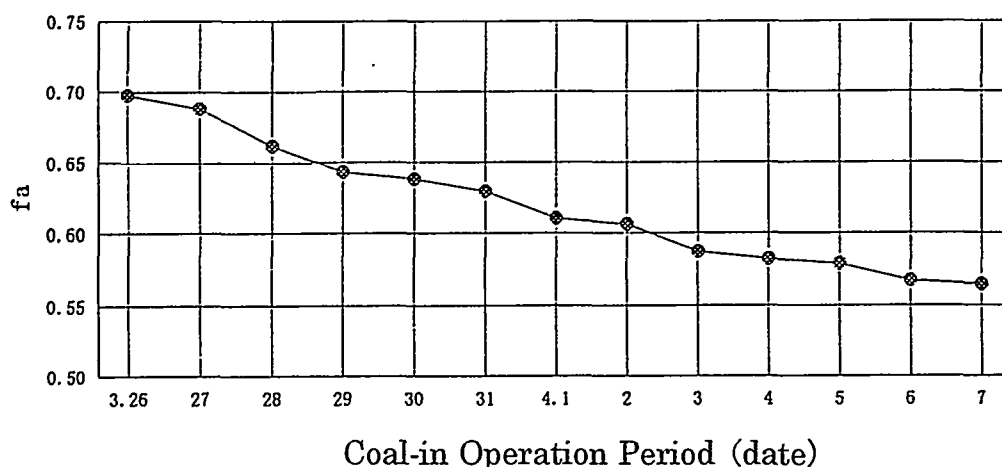


Figure 1 Change of fa of the Recycle Solvent

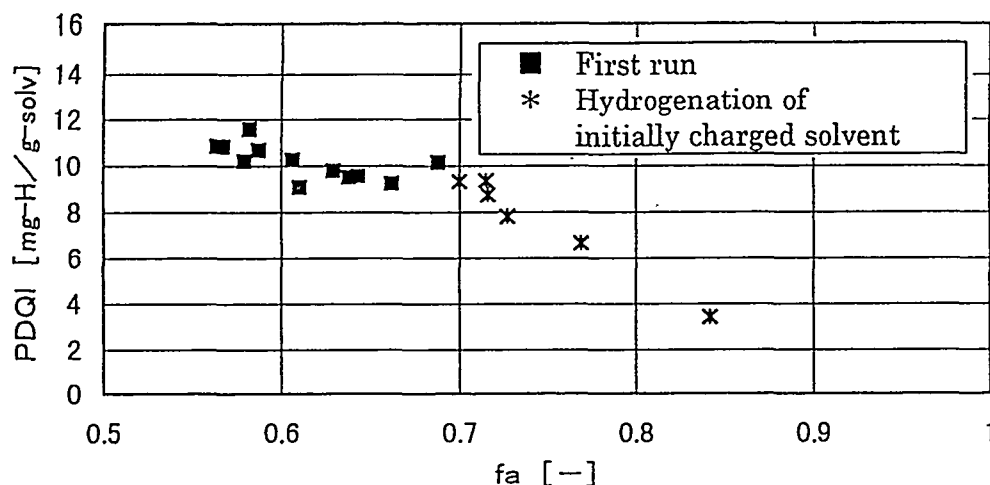


Figure 2 Relationship between fa and Hydrogen Donating Property (PDQI)

(4) Maintenance of the pilot plant

The organization and staff for the maintenance work were determined, and the facilities for the maintenance work were prepared. The preparation of the maintenance manuals was completed. The spare parts required for the operation were obtained.

The plans were made for the periodic inspections prescribed by the High-Pressure Gas Control Laws and the Industrial Safety & Health Laws, as well as the plans for the other scheduled inspections, and the inspections were conducted. The plans for the inspections to be conducted during the operation were made, and the inspection points on each piece of equipment and the piping were determined. The inspections were performed according to the plans, and the inspection data was obtained. In addition, daily and shutdown maintenance work and repairs of the pilot plant were conducted.

(5) Studies and technical survey

(a) Development of the liquefaction reaction simulator

A computer program for estimating the physical properties of Tanitoharum coal

was created through the use of the data obtained by the PSU, and the program was coupled with the liquefaction reaction simulator.

Simulations of the liquefaction reaction of Tanitoharum coal were conducted to predict the composition of the liquefied products at the outlet of each liquefaction reactor of the pilot plant under the standard operating conditions of the NEDOL process. It was predicted that the liquefaction reaction would be complete at the outlet of the second liquefaction reactor, and the conversion of the coal liquids into lighter products would proceed in the third reactor.

(b) Studies on the pulverizing system for the liquefaction catalyst

Copulverized catalyst were made by finely pulverizing the mixture of pyrite and coal, and the optimum ratio of the pyrite and the coal was investigated. A pyrite : coal ratio of 2 : 1 in weight was found to be optimum. In addition, the copulverized catalyst of the increased coal ratio improved the yields of light and medium coal liquids, while the catalyst activity decreased slightly compared to the catalyst of the optimum ratio.

The copulverized catalyst to be used in the operation of the PSU was produced by a continuous pulverizing system, and the sample of the copulverized catalyst was tested using an autoclave to investigate the liquefaction performance. The test results revealed that the copulverized catalyst produced by the continuous pulverizing system had virtually the same liquefaction performance as those produced by a batch pulverizing system.

The copulverized catalyst of coal and iron ore, rather than pyrite, which was cheaper and was expected to be pulverized more easily, was produced, and the properties of the catalyst were examined. It was found that both the required power for the pulverization and the liquefaction performance of the iron-ore copulverized catalyst were at the same level as those of the pyrite copulverized catalyst.

(c) Environmental assessment

The object of this study is to assess the safety of the liquefied products in respect to the environment and the influences of the coal liquefaction plant on the environment of the circumference. Composition analyses and AMES tests of the liquefied products were conducted in order to assess their safety, and notifications of the unregistered chemical substances, as prescribed in the Industrial Safety & Health Laws, were made. Test substances other than the light coal liquid B.P. below 220 °C were judged to be mutagenic, and chromosome tests of the mutagenic substances were required.

Environmental measurements, including air pollution and water and soil quality, were taken during the operation at the liquefaction section area and at the boundary of the pilot plant. The data obtained was placed in the database.

(d) Study of the neutron attenuation tracer (NAT) method

The NAT method is for use in the study of liquefaction reactor hydrodynamics. The performance of the neutron howitzer and detector/analyzer system, which were designed and fabricated based on the test results obtained last year, was investigated under the technical guidance of the Japan Atomic Energy Research Institute. It was confirmed through the test that Gadolinium nitrate, the neutron absorber, which was to be the tracer of the NAT method, had the

expected neutron attenuation rate under static conditions, and that the required performance was satisfied by the system. The intensity of the neutron source and the injection quantity of the tracer required for actual NAT method operation were determined.

Future Tasks

- (1) To demonstrate the performance of the NEDOL process, including confirmation of the maximum liquefied oil yield, the continuous long-run operability, and the applicability to various grade of coal
- (2) To verify the performance of materials and equipment required to be developed, and to finalize operation techniques
- (3) To acquire engineering data for assembly of the coal liquefaction technical package for large plants in the future

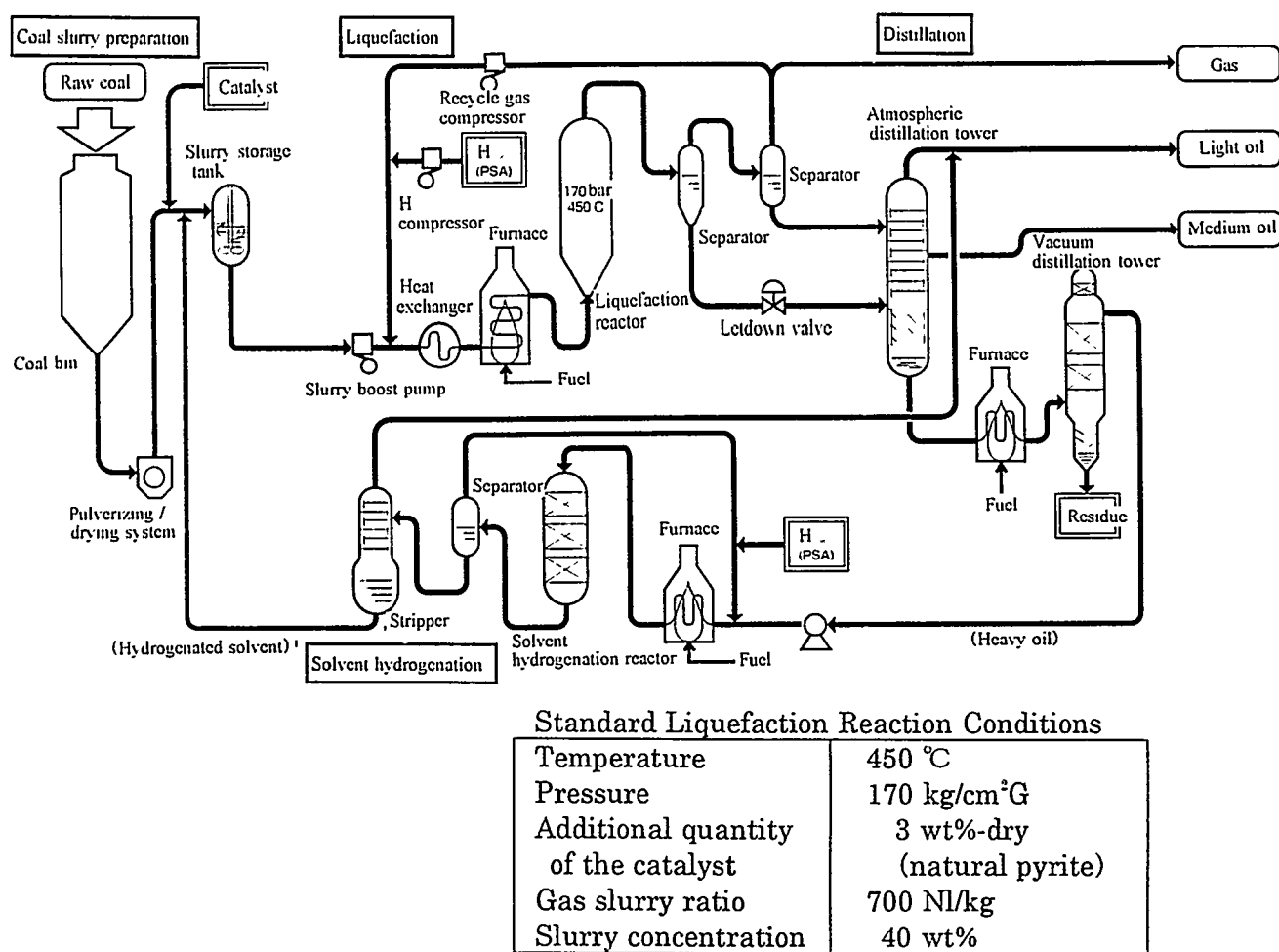


Figure 3 Schematic Flow of the NEDOL Process

Research on 1t/d Process Supporting Unit (PSU)

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M.Kobayashi, Nippon Coal Oil Co.,Ltd

Objectives

In order to support the coal liquefaction research for the pilot plant(PP), the NEDOL Process 1t/d PSU shall be operated to confirm its stability and overall operability. Technical data for future large-scale coal liquefaction plants shall be collected by acquiring knowledge on the correlation between PSU and PP, and enlarging the application range of raw coal.

Work Program

(1) Modification and Maintenance

The following programs shall be conducted.

- (a) Detailed design and procure of the facilities to improve the quality of liquefied oil
- (b) Exchange of the cone at the 3rd coal liquefaction reactor
- (c) Exchange of apparatus for Neutron Attenuating Tracer (NAT) technique
- (d) Overhaul for governmental security inspections, periodic self inspections and repair of equipment after each operation

(2) Planning of Research Program

The following programs shall be formulated and provided.

- (a) Annual and long-term research programs for the operation
- (b) Preparation of various kinds of operation manuals
- (c) Test program to research fluid dynamics in the coal liquefaction reactors
- (d) Test program to improve of the quality of liquefied oil
- (e) Operating plan to provide sample to other institute
- (f) Research program to establish the support for PP

(3) Research Work

In order to confirm the overall operability of the NEDOL process and optimization of the process, the following operations shall be conducted.

- (a) Slurry operation : 62 days/Run and 23 days/Run (totally 85 days)
 - Coal : Tanito Harum coal
 - Catalyst : For liquefaction—Natural Pyrite(NP)

: For hydrotreatment—CH-0401(improved catalyst)

- (b) Oil operation for obtaining engineering data
- (c) Study of fluid dynamics and reaction proceeding
- (d) Analysis and arrangement of operation data

(4) Environmental Impact Study

The following studies shall be conducted.

- (a) The environmental impact during plant operation
- (b) Analysis and study of treatment procedure for waste water

(5) Governmental Procedures

Applications for several inspections shall be submitted at the time of completion of the work.

(6) Technical Surveys

- (a) Surveys for relating of coal liquefaction process shall be conducted.
- (b) Technical surveys on the procedures for engineering and process data acquisition shall be conducted.
- (c) Surveys for establishment of the technology package and the construction of data analysis system shall be conducted.

Summary (1985 — 1996)

1. Up to FY 1995

The PSU was operated with Wandoan coal, which was the design reference coal for the PSU, for 200 days (50 days/Run × 4Runs), with Illinois No.6 coal for 121 days (53 days/Run × 1Run, 46 days/Run × 1Run and 22 days/Run × 1Run), with Wyoming coal for 252 days (49 days/Run × 1Run, 47 days/Run × 1Run, 53 days/Run × 2Runs and 50 days/Run × 1Run), and with Tanito Harum coal for 237 days (50 days/Run × 3Runs, 62 days/Run × 1Run and 25 days/Run × 1Run). Product yields and liquefaction properties under several liquefaction reaction conditions were studied. And various kinds of problems which occurred while the operations were solved.

2. For FY 1996

(1) Modifications and Maintenance

Modifications and maintenance were conducted on the following subjects.

- (a) In order to reduce the heteroatomic compounds in the coal liquid on NEDOL process, the facilities to improve of the quality of liquefied oil were designed in detail and procured part of apparatus.
- (b) The cone at 3rd coal liquefaction reactor was exchanged and investigated
- (c) Apparatus for Neutron Attenuating Tracer (NAT) technique were exchanged

- (d) Overhaul for governmental security inspections, periodic self inspections and repair of equipment after each operation were implemented.
- (2) Planning of Research Program
 - (a) Long-term program for operation research and equipment modifications were reviewed.
 - (b) Detailed research program for the operations (Run0801, Run0802 and oil operation) in FY 1996 was made, including the study of fluid dynamics and reaction proceeding.
 - (c) Manuals for operating procedure were reviewed and prepared.
- (3) Research Work

The PSU was operated for a total of 85 days that is consisted of 63days/Run and 23days/Run (Run0801 and Run0802) with Tanito Harum coal. The effect of coal liquefaction catalyst, catalyst addition, hydrogen concentration of gas feed and slurry feed rate on the yields and properties of products were researched. Further, in condition of reduction of Hydrogen sulfide (H_2S) gas concentration out of solvent hydrogenation reactor, hydrotreatment catalyst properties were researched. Reaction conditions are shown in Table 1.

- (a) Effect of variation of liquefaction catalyst and amount of catalyst addition on the yields and properties of products

Variation of liquefaction catalyst (SIS, NP and NP/C) and amount of catalyst addition on the yields and properties of products were researched in Run0801. And the effects of fluid dynamics and reaction kinetics on product yield and plant operability were examined.

- ① The effect of variation of liquefaction catalyst and amount of catalyst addition on product yields are shown in Figure 1 and 2. The oil yield at 2wt%(amount of catalyst addition) was about 55.0wt%(daf coal basis) by SIS, 54.4wt%(daf coal basis) by NP/C and 53.5wt%(daf coal basis) by NP, the difference of oil yields was small. The oil yield increased with increasing amount of catalyst addition. The residue yield decreased with increasing amount of catalyst addition.
- ② It was recognized that plant operability was good at 2wt%(amount of catalyst addition).
- ③ Coal conversion was presumed to analyze properties of coal liquid in coal liquefaction reactor. As shown in Figure 3, compared with NP, by using SIS yields of IOM, preasphaltene and asphaltene in the 1st and the 3rd coal liquefaction reactor were lower. It was indicated that SIS is superior to NP in liquefaction reaction kinetics. NP and NP/C, which were consisted of Natural Pyrite, were similar in the liquefaction reaction kinetics.

Mean residence time in the 1st and overall coal liquefaction reactors

measured by NAT technique was also similar time.

(b) Effect of hydrogen concentration of feed gas on the yields and properties of products

Effect of hydrogen concentration of feed gas on the yields and properties of products were researched in Run0801. And the effects of fluid dynamics and reaction kinetics on product yield and plant operability were examined.

① At condition of H_2 85vol%, the oil yield at 45wt%(coal conc.) was lower than that at 40wt%(coal conc.). It was because the feed ratio of H_2 gas and hydrogenated solvent to coal was decreased. However, in condition of 45wt%(coal conc.), the oil yield was 56.6wt%(daf coal basis) at 90vol%(H_2 conc.), the oil yield at 90vol%(H_2 conc.) was about 5wt%(daf coal basis) higher than that at 85vol%(H_2 conc.). And the residue yield was 14.4wt%(daf coal basis) at 90vol%(H_2 conc.) , that at 90vol% (H_2 conc.) was about 4wt%(daf coal basis) higher than 85vol%(H_2 conc.). It was considered that liquefaction reaction in the reactor was accelerated by increasing hydrogen concentration in feed gas.

② The pressure drop of slurry preheater at 90vol% (H_2 conc.) was range of 1.2 to 1.3kg/cm², it was not increased compared with that at 85vol% (H_2 conc.). Slurry including deposited solid was drawn out easily from coal liquefaction reactors.

③ Coal conversion was presumed to analyze properties of coal liquid in coal liquefaction reactors. Compared with yields of residue compositions at 85vol%(H_2 conc.), those at 90vol%(H_2 conc.) were slightly higher. However residue yield of material balance at 90vol%(H_2 conc.) was a few lower, coal liquefaction reaction was promoted by increasing H_2 concentration in feed gas at the 2nd and the 3rd liquefaction reactors where H_2 concentration was a little hydrogen.

It was no difference of mean residence time between 90vol% and 85vol% (H_2 conc.) in 1st coal liquefaction reactor measured by NAT technique, but mean residence time in overall coal liquefaction at 90vol% was longer than that at 85vol%. it is considered that liquefaction reaction was promoted at the 2nd and the 3rd liquefaction reactor.

(c) Effect of slurry feed on the yields and properties of products

Effect of Reduction of slurry feed on the yields and properties of products were researched in Run0802. And the effects of fluid dynamics and reaction kinetics on product yield and plant operability were examined.

① The oil yields at 2.0t/d (slurry feed of 80% for standard) was 54.9wt%(daf coal basis), it was almost the same as the yield at 2.5t/d(standard), 55.5wt%(daf coal basis). The middle distillate(220 ~

260 °C) yield was decreased with decreasing slurry feed. And yields of preasphaltene and asphaltene in residue were decreased with decreasing slurry feed, however, particularly $C_1 \sim C_3$ constituents were increased.

- ② The blockade occurred in the circulation laying pipes of slurry feed at liquefaction reaction parts. And the blockade occurred in the residue drawing pipes by adhered deposit on inner walls of vacuum distillation tower, and circulation pipes were also blocked.
 - ③ Coal conversion was presumed to analyze properties of coal liquid in coal liquefaction reactor. The residue yield at 2.0t/d was considerable decreased, compared with the others. Further, mean residence time in 1st reactor and overall reactor measured by NAT technique were elongated with decreasing slurry feed rate. These suggested that decomposition reaction of coal, following asphaltene and preasphaltene was promoted for increasing residence time in liquefaction reactor.
- (d) Effect of hydrogen sulfide(H_2S) gas concentration out of solvent hydrogenation reactor on reduction

It was recognized that kinetic constant of hydrogenation at 0.5vol% (H_2S gas conc.) was approximately the same as that of hydrogenation at 1.0vol% (H_2S gas conc.). Further, the life of hydrotreatment catalyst at 0.5vol% (H_2S gas conc.) was the same as that at 1.0vol% (H_2S gas conc.). Reactor operation at 0.5vol% (H_2S gas conc.) was carried out without trouble.

- (e) Operation for obtaining engineering and process data Effect of slurry temperature out of the preheater, G/L and the kind of solvent on coal liquefaction in initial stage was investigated while coal-slurry passed through the slurry preheater. Furthermore, in order to research properties of hydrogenation reaction under reducing DMDS addition condition out of solvent hydrogenation reactor, preliminary test was carried out.

- ① In the case of increasing temperature at preheater from 370 °C to 450 °C, the yield of IOM was decreased from about 85 wt%(daf coal basis) to 35wt%, it was shown that coal liquefaction was accelerated. Increase of G/L had slight effect, and increase of fa and PDQI of solvent had rare influence on acceleration to coal liquefaction. Residence time in preheater was in the range of 2 to 3 minutes by sample measurement.
- ② Kinetic constant of solvent hydrogenation under 0.4 vol% slightly decreased as compared with 1.0 vol% of Hydrogen sulfide (H_2S) gas concentration out of solvent hydrogenation reactor. As a result, the condition of examination at Run0801 was set up under 0.5 vol% of H_2S

gas concentration and using recycle solvent.

- ③ Effect of slurry preheater condition on coal texture was studied in part of liquefaction reaction in initial stage.

(4) Environmental Impact Study

Analysis of waste water and an acclimation test for activated sludge were conducted, and it was confirmed that the same treatment procedure for waste water as had been previously used was available. Measurements of air, odor and tar mist were conducted during the operation. All were much lower than the control limit. Then it was found that there were no environmental problems.

(5) Governmental Procedure

Application for permits were submitted to respective authorities.

(6) Technical Surveys

The following surveys were conducted for plant operation.

- (a) The study of upgrading of coal liquefied oil
- (b) The study of coal liquefaction reaction in initial stage

Future tasks

- 1 . Effective promotion of support work for PP
- 2 . Research for establishment of NEDOL process technical package

Table-1 Reaction conditions for FY 1996

Run No.	0601	0801			0802	
Operating condition	reference	variation of catalyst			high load operation	
		SIS 2wt%	NP/Coal 2wt%	NP 2wt%	H ₂ 90vol%	slurry feed 2.0t/d
Coal	Tanito Harum coal					
Liquefaction cat. ¹⁾		SIS	NP/Coal	NP		
Temperature (°C)	465	465	465	465	465	465
Pressure (kg/cm ² G)	170	170	170	170	170	170
G/L (Nl/kg)	700	700	700	700	700	700
Cat. addition (wt%) ²⁾	3	2	2	2	3	3
Coal conc. (wt%)	40	40	40	40	45	40
Slurry feed (t/d)	2.5	2.5	2.5	2.5	2.5	2.0
Hydrotreatment cat.	Improved Hydrotreatment Catalyst (CH-0401)					
H ₂ S conc. (vol%)	1.0	0.5			1.0, 0.5	

1) NP: Natural Pyrite, SIS: Synthetic Iron Sulfide,

NP/Coal: co-pulverized Natural pyrite/Coal

2) dry coal basis

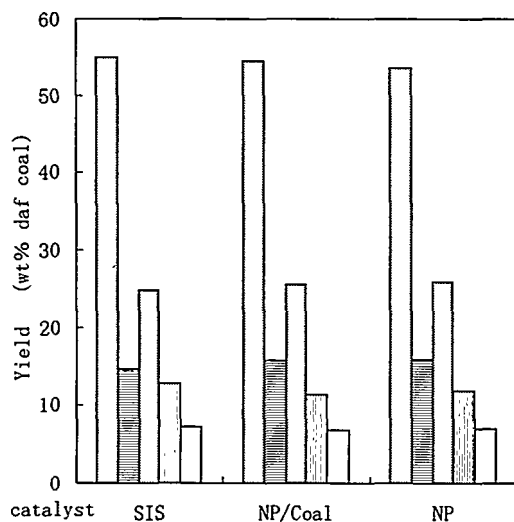


Fig-1 Effect of variation of catalyst on product yields

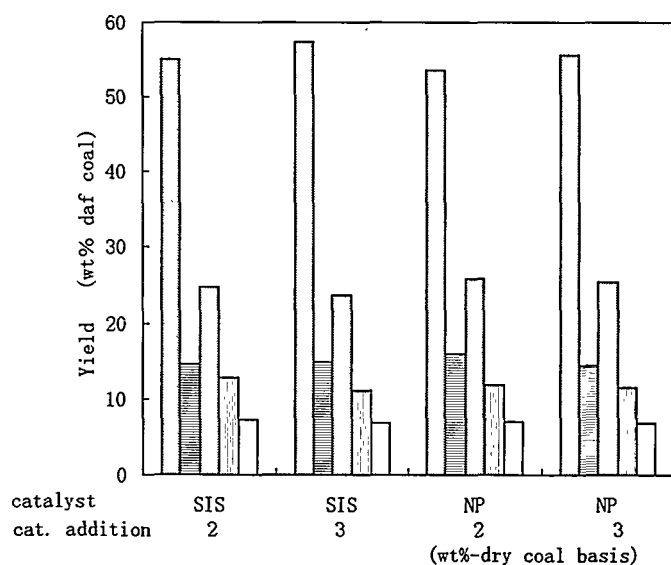


Fig-2 Effect of catalysts on product yields

□ Oil (include C4) Coal Tanito Harum Coal
 ■ Residue Reaction temp. 465°C
 □ Gas Reaction pressure 170kg/cm²G
 □ Water Amount of catalyst 2wt%
 □ Consumed H₂ addition (dry coal basis)
 fa of recycle solvent 0.50~0.55

□ Oil (include C4) Coal Tanito Harum Coal
 ■ Residue Reaction temp. 465°C
 □ Gas Reaction pressure 170kg/cm²G
 □ Water fa of recycle solvent 0.50~0.55
 □ Consumed H₂

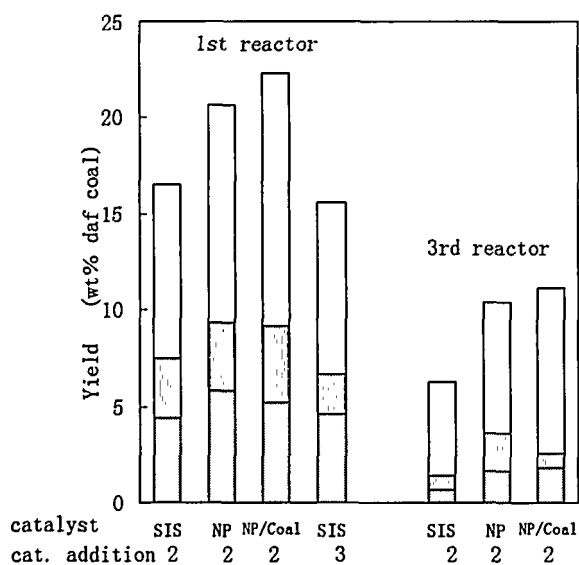


Fig-3 Effect of catalysts and catalyst addition of solvent extracts in solid sample from liquefaction reactor

□ Asphaltene (HI-TS)
 □ Preasphltene (TI-THFS)
 □ IOM (THFI)

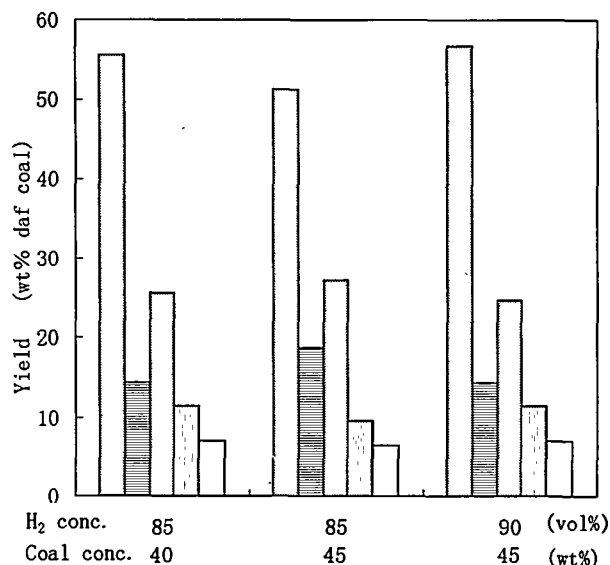


Fig-4 Effect of hydrogen concentration on product yields

□ Oil (include C4) Coal Tanito Harum Coal
 □ Residue Catalyst Natural Pyrite
 □ Gas Reaction temp. 465°C
 □ Water Reaction pressure 170kg/cm²G
 □ Consumed H₂ Amount of catalyst 2wt% addition (dry coal basis)
 fa of recycle solvent 0.50~0.55

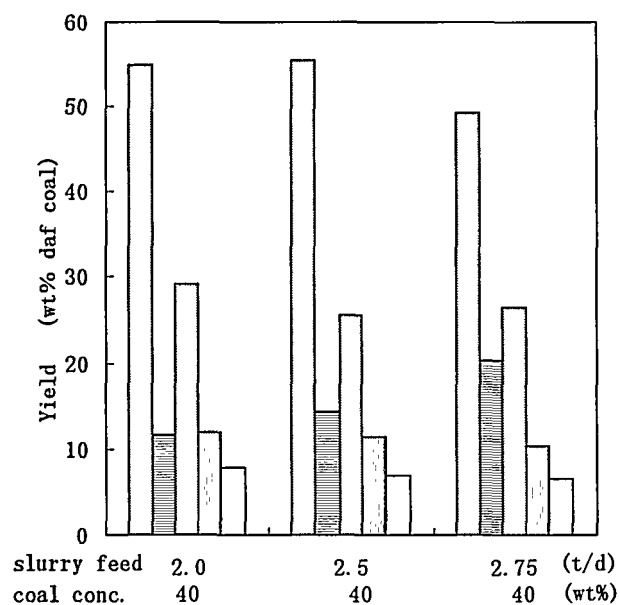


Fig-5 Effect of slurry feed on product yields

□ Oil (include C4) Coal Tanito Harum Coal
 □ Residue Catalyst Natural Pyrite
 □ Gas Reaction temp. 465°C
 □ Water Reaction pressure 170kg/cm²G
 □ Consumed H₂ Amount of catalyst 2wt% addition (dry coal basis)
 fa of recycle solvent 0.50~0.55

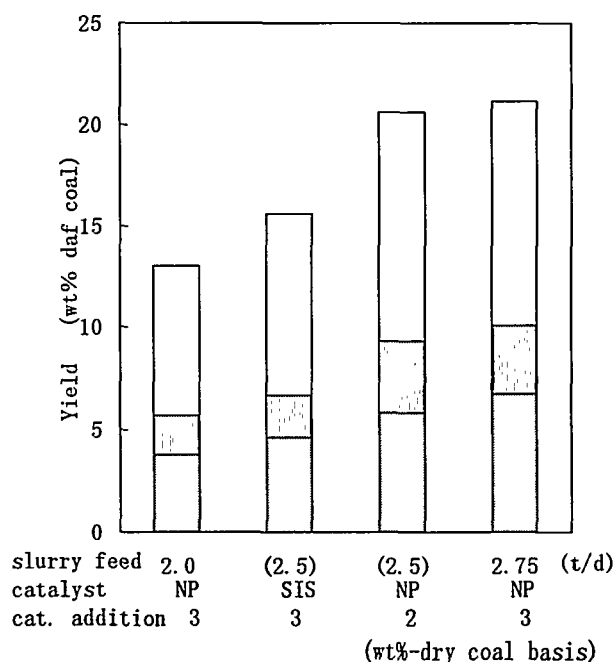


Fig-6 Effect of slurry feed on the proportion of solvent extracts in solid sample from the 1st liquefaction reactor ():reference

□ Asphaltene (HI-TS)
 □ Preasphltene (TI-THFS)
 □ IOM (THFI)

STUDY ON THE SYNTHETIC IRON SULFIDE CATALYST

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Objectives

1. To develop a production method of the synthetic iron sulfide catalyst to be used in the NEDOL bituminous coal liquefaction process.
2. To assist the research work in the NEDOL Pilot Plant by developing a catalyst production technology based on the dry process.
3. To supply the synthetic iron sulfide catalyst to 1 t/d PSU produced by the dry process.
4. To evaluate the performance of the produced catalyst and the production method.
5. To study for a conceptual design of a large scale production unit.

Work Program

1. Catalyst Supply

To supply the synthetic iron sulfide catalyst to PSU after grinding in oil.

2. Maintenance

To inspect and repair the apparatus.

3. Characteristics Study

To evaluate coal liquefaction activity of the catalyst to be supplied to PSU and to study characteristics of the catalyst and its materials.

4. Technical Evaluation

To study several items in laboratory, such as the preparation method of raw

material iron sulfate, the operating conditions of fluidized bed reactor, catalyst characteristics after hydrogenation reaction, grinding catalyst with coal, and dispersing agent, for technical evaluation of the catalyst production method based on the dry process, and to study a conceptual design of a large scale production unit.

5. Detailed Work Program for FY 1996

Summary (1991-1996)

1. Up to FY 1995

The installation of the small scale apparatus has been decided in FY 1991. The basic and detailed design work of the apparatus and the procurement of a part of the equipment were made in FY 1991. In FY 1992, the process and equipment design for the waste gas treatment section which would be installed in the area of PSU and the procurement of the equipment, electricals and instruments and the modifications of the existing facility of PSU were made.

A part of civil work for the sulfiding section was made.

In FY 1993, the construction of the apparatus was completed and commissioning and three test operations were made. Operating conditions to obtain the desirable product quality were studied. The obtained product catalyst was verified to have better coal liquefaction activity than wet method synthetic iron sulfide catalyst by the test using 1000 ml autoclave. In FY 1994, an in-line sulfur incinerator of unreacted sulfur in the waste gas was installed before the waste gas cooler in order to keep longer continuous operation.

In FY 1995, 1,952 kg of catalyst was produced in 8 days operation at the production rate of 11 kg/hr and supplied to PSU. A part of the technical evaluation of the catalyst production method using dry process was conducted based on engineering data obtained by the small scale apparatus operation. (Study for operability, study for development work)

2. For FY 1996

(1) Catalyst Supply

In order to prevent catalyst particle sedimentation in PSU, catalyst grinding in oil by a high shear rate dispersing machine was conducted before supplying the catalyst to PSU. Average particle size of catalyst ground in 30 minutes was 2.0 microns which was smaller than 4 microns of the target. In addition, a catalyst sample, made by the same process, was supplied to China.

(2) Modification and Maintenance

In order to make more stable operations, some modifications to the feed system and the piping after the reactor of the small scale apparatus were made. There were not serious general corrosion with 0.1~0.2 mm depth but some pitting corrosion was observed.

(3) Characteristics Study

A coal liquefaction test of the catalyst to be supplied to PSU was made using autoclave. The effect of catalyst on product yields are shown in Fig-1. Oil yield using dry method synthetic iron sulfide catalyst (D-SIS) to be supplied to PSU was higher than those of pulverized natural pyrite catalyst (NP) or wet method synthetic iron sulfide catalyst (W-SIS).

As studies on characteristics of the catalyst, chemical composition, surface potential, net density, bulk density, repose angle, flash point and ignition point were measured. In addition, chemical composition of raw material iron sulfate and coordination state of Fe in catalyst after hydrogenation reaction were measured.

(4) Technical Evaluation

Technical evaluation of the catalyst production method based on the dry process were conducted:

(a) Study of the preparation method of raw material iron sulfate

Studies on drying process of iron sulfate from heptahydrate to monohydrate using small scale dryers in dryer manufacturer's were conducted, and a comparison of characteristics of particles such as diameter of iron sulfate particle was made. Direct-heated rotary dryer showed the preferred product characteristics.

(b) Study of catalyst characteristics after hydrogenation reaction

Chemical composition and particle size of several kinds of iron sulfide catalyst after hydrogenation reaction in autoclave under the same condition as coal liquefaction test without coal were analyzed.

The observation of catalyst by a scanning electron microscopy made clear that primary particle of pyrrhotite were agglomerated to several microns particles.

(c) Evaluation of ground catalyst with coal

Coal liquefaction tests of the catalyst ground with coal using several grinding machine were made using autoclave. The same oil yield was obtained by only a small amount of the ground catalyst, but the large

grinding power and the capital investment would not justify the catalyst grinding.

(d) Study of dispersing agent

A coal liquefaction test by addition of dispersing agent at high temperature was made using autoclave. Oil yield was higher than no additive case. This suggests the effect of dispersing agent to prevent from agglomeration of catalyst during the temperature rising stage.

(e) Study for a conceptual design of a large production unit

A process development study of the catalyst production for a large scale production unit was conducted for a feeding process of gaseous sulfur to the reactor and its material and heat balances. The cross sectional area of the reactor could be reduced to a half, calculated by a simple scale-up method based on the small apparatus, and the capital investment of the large production unit could be reduced.

As a comparative study of the production method of iron sulfate monohydrate, which is the raw material of catalyst, was made for a direct crystallizing of monohydrate from heptahydrate. It was found that this process was more economical than the dehydration process. Some studies will be made the effect for the liquefaction activity of catalyst made from this process.

A part of investigation on the process of sulfur recovery and sulfuric acid production from literatures and vendor's informations was made.

A block flow diagram of the catalyst production method for a large scale production unit is shown in Fig-2.

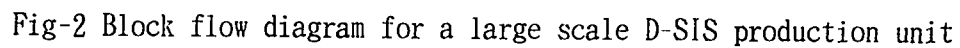
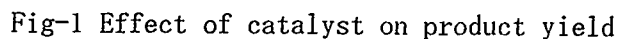
(5) Work Program

Detailed work program for the FY 1996 was made.

Future Tasks

The technical evaluation work will be made succeedingly concerning following items.

- Study of the preparation method of raw material iron sulfate.
- Evaluation of the catalyst production method based on the dry process.
(Study for development work, study for a conceptual design of a large scale production unit)
- Economic evaluation based on a conceptual design of a large scale production unit.



COAL SELECTION STUDIES FOR CHINESE COAL LIQUEFACTION

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Objectives

To clarify the properties and liquefaction characteristics of Chinese coal by the Japan/China joint studies, and compile fundamental data for coal type selection and technical development.

Work Program

Liquefaction test of Chinese coals using natural mineral catalyst is carried out by a small-sized continuous bench scale unit(BSU), installed at Central Coal Mining Research Institute (CCMRI) of China, and basic studies such as autoclave test and analytical test are promoted jointly with China.

Summary(1980-1996)

1. Up To FY1995

Coal analysis and coal liquefaction test by autoclave were carried out for three Chinese coals (Shengli coal, Huolin coal, Huangxian coal) in Japan in FY1980.

NEDO and CCMRI signed an agreement to develop Chinese coal liquefaction technology jointly in FY1981.

NEDO constructed a small size continuous bench scale unit(BSU) at CCMRI in Beijing, China in FY1982, according to the agreement.

Four runs of operation were carried out in order to get liquefaction characteristics of Chinese coals and to make Chinese engineers master their operation technique in FY1983.

Gas recycle system and solvent recycle system were installed to the BSU in FY1984 and in FY1985, respectively.

Six kinds of Chinese coals including two types of lignite were tested to obtain liquefaction characteristics in FY1986 and FY1987. Xianbeng coal, Meihekou coal, etc. were processed under two operation modes, once through mode and solvent recycle mode. Shengli coal was processed under once through operation mode.

Data logging system was installed to the BSU in FY1986 to 1987. Autoclave tests were carried out for two Chinese coals (Tienju coal and Shenmu Simengou coal) in Japan in FY1987.

In FY1988, Chenpei coal, Tienju coal and Shenmu Simengou coal were tested by the BSU. The Coal oils were brought back to Japan and analyzed.

Autoclave tests of eight Chinese coals were conducted in Japan.

In FY1989, Fuxin Qinghemmen coal and Chifeng Yuanbaoshan coal were processed in the BSU, and the coal oil samples from these operations were brought back to Japan and were analyzed closely. Besides, in order to match the base lines of data between China and Japan, an autoclave, a distillation apparatus and a GC distillation apparatus were installed in Beijing.

In FY1990, once-through operation of Fushun coal, and once-through and solvent circulation operations of Hailaerh coal were executed. In the once-through operation of Fushun coal, as a comparative study, in addition to the liquefaction test of the hitherto used iron oxide, liquefaction test using fly ash was conducted. As a result, the fly ash was found to have a catalytic performance equivalent to that of iron oxide. Primary oils derived from Hailaerh coal were closely analyzed and examined in Japan.

In FY1991, two mode of solvent circulation operations of Fushun coal were executed. The catalyst (Fe_2O_3 :reagent) addition rate was 3wt% to daf coal. Primary oils were closely analyzed and examined in Japan. The results for such analyses showed high yield of production oil. The liquefaction properties of Fushun coal were recognized to be similar to those of Tienju coal tested in FY1988.

In FY1992, two mode of solvent circulation operations of Shengli lignite, and six cases of once-through operation and ten cases of similar NEDOL mode operation for Tienju coal were executed. Hydrogenated solvent and 3 wt% of FeS_2 catalyst to daf coal were used in similar NEDOL mode operation.

The test results of Shengli lignite cases showed the superior conversion rate and yield of production oil. Hydrogen consumption and asphalt yield were recognized to be small.

Also, the results of Tienju coal cases with hydrogenated solvent showed lower consumption of hydrogen and higher yield of production oil in comparison with DAO solvent case.

In FY1993, Five cases of similar NEDOL mode operation, five cases of once-through operation and one case of solvent circulation operation for Long kou coal were executed. and also, another each five cases of similar NEDOL mode operation for Fuxin Haizhou coal, Yin zhou Xing ron

zhuang coal and Shenmu Guojiawan coal were executed. Test results for Long kou coal showed the superior conversion rate and yield of production oil. Fuxin Haizhou coal showed fairly good result for liquefaction characteristics. But the results for Yin zhou Xing ron zhuang coal and Shenmu Guojiawan coal were not relatively good for liquefaction.

In FY1994, Four cases of similar NEDOL mode operation, three cases of once-through operation and one case of solvent circulation operation for Helong Jing Yilan coal were executed. and also, another each two cases of similar NEDOL mode operation for Shan Dong Yin Zhou Tangcun coal, Liao Ning Fuhun Laohutai coal, and Shenyang Puhe coal. Further, one case of Fuxin Haizhou coal were executed.

Test results for Yilan coal showed very superior conversion rate and yield of production oil. Yilan coal have rich deposits and superior characteristics for liquefaction. Liquefaction characteristics for other four coals are fairly good.

As for the conversion rate, Puhe coal showed the best result over the Yilan data. Fushun Laohutai and Fuxin Haizhou coals showed equal good performance and Yin Zhou Tangcun coal was a little worse than the others. As for the production yield, the four coals are approximately equal each other and have less yield than that of Yilan coal.

In FY1995, three cases of similar NEDOL mode operation using 3 wt% FeS₂ catalyst and three cases of once-through operation and one case of solvent circulation operation using (3 wt% Fe₂O₃ + 0.8 wt% S) catalyst for Shuangyashan coal were executed. and also, another similar NEDOL mode operation for two cases of Pingzhuannggushan coal and each three cases of Meihekou and Yunnan-xianfeng coal using 3 wt% catalyst, further, one case of Yunnan-xianfeng coal using 2 wt% catalyst were executed.

The test results of Shuangyashan coal showed high conversion rate but a little high asphalt yield. So, it would be better to apply more severe reaction condition to take high yield of production oil. Pingzhuannggushan and Meihekou coal showed high conversion rate and high yield of production oil on standard reaction condition. While, Yunnan-xianfeng coal showed similar superior result on more mild condition. Catalyst(FeS₂) rate was enough at 2 wt% for this coal.

2. For FY 1996

(1) BSU Liquefaction Test

To examine the liquefaction characteristics on Chinese coals and catalytic properties of natural mineral existing in China, BSU liquefaction tests for three kinds of Chinese coals with natural mineral catalyst were carried out under the NEDOL mode once-through operation. For base data, the liquefaction test using synthetic iron sulfide catalyst was also done.

As the test catalyst, two particle sizes of natural mineral and mineral added molybdenum ash were applied.

Coal used

- Helong Jing Yilan coal
- Shenmu Ningtiaota coal (2nd seam)
- Shenmu Ningtiaota coal (3rd seam)

Natural Mineral used for catalyst

- Iron pyrite mined from Liaoningsheng Dashiqiao
- Iron ore mined from Neimengguzizhiqu Baotou
- Molybdenum ash mined from Shanxisheng Jinduicheng

Catalyst used addition quantity(per dry coal)

For Helong Jing Yilan coal

- (A) Iron pyrite (particle size: ave. 17.5 μm) 3wt%
- (B) Iron pyrite (particle size: ave. 1.34 μm) 3wt%
- (C) Iron pyrite (size: ave. 1.34 μm) 2wt% + Mo ash 0.5wt%
- (D) Synthetic iron sulfide catalyst 3wt%

For Shenmu Ningtiaota coal (2nd & 3rd seam)

- (E) Iron ore (particle size: ave. 36.6 μm) 3wt%
- (F) Iron ore (particle size: ave. 3.0 μm) 3wt%
- (G) Iron ore (size: ave. 3.0 μm) 2wt% + Mo ash 0.5wt%
- (H) Synthetic iron sulfide catalyst 3wt%

For catalyst No. (E) to (G), sulfur was added.

Test results are summarized in Table 1.

Particle size of iron pyrite effected remarkably on oil yield of Helong Jing Yilan coal, and the addition effect of Mo ash was recognized so that the oil yield was slight lower than one of synthetic iron sulfide catalyst.

As for Shenmu Ningtiaota coal (2nd & 3rd seam), oil yield from both seam coals was almost same, although inert material in 2nd seam coal was 8% higher than one in 3rd seam coal.

The effect by the difference of particle size and the addition of Mo ash were not recognized on oil yield.

(2) Autoclave Test

The autoclave tests of Helong Jing Yilan coal using molybdenum ore mined from Shanxisheng Jinduicheng(China) and iron ore including V and Ti mined from Sichuansheng Panzhihua(China) as catalyst were carried out to examine catalytic properties of natural mineral such as activity, particle size effect, addition quantity in coal, etc.

As the results, molybdenum ore showed superior oil yield (max. 73.2%). On the other hand, iron ore with V, Ti did not show good oil yield (max. 57.4%).

- (3) A small size mill was installed in CCMRI to crush natural mineral catalyst, and NEDO's measurement equipments such as a X-ray diffractometer, a CHN ultimate analyzer and a particle size analyzer were moved to CCMRI and utilized for the analysis and measurement of many kinds of natural minerals to obtain basic data.

Future tasks

To conduct NEDOL mode once-through liquefaction tests for Chinese coal and naturally existing mineral catalyst using BSU in order to support the feasibility study by China and Japan jointly for a model coal liquefaction plant in China.

To search for naturally existing mineral catalyst suited for the above and to carry out its analysis and performance test by an autoclave. To investigate the separation method of ash and inert materials in coal.

TABLE 1. BSU LIQUEFACTION TEST RESULTS
(FY1996)

COAL	CATALYST			TEST RESULT Oil Yield (%)
	CATALYST TYPE	AVERAGE SIZE (μm)	ADDITION RATE (wt% per dry coal)	
Helong Jing Yilan	(A) Iron Pyrite	17.5	3	49.32
	(B) Iron Pyrite	1.34	3	67.79
	(C) Iron Pyrite + Mo	1.34 + <74(Mo)	2 + 0.5(Mo)	70.18
	(D) Synthetic Catalyst	(FeS ₂)	3	74.64
Shenmu Ningtiatoa (2nd seam)	(E) Iron Ore	36.6	3	58.68
	(F) Iron Ore	3	3	58.16
	(G) Iron Ore + Mo	3 + <74(Mo)	2 + 0.5(Mo)	57.91
	(H) Synthetic Catalyst	(FeS ₂)	3	64.11
Shenmu Ningtiatoa (3rd seam)	(E) Iron Ore	36.6	3	56.03
	(F) Iron Ore	3	3	61.29
	(G) Iron Ore + Mo	3 + <74(Mo)	2 + 0.5(Mo)	61.47

Note: For catalyst (E) to (G), sulfur was added. (E), (F): 1.85wt%/dry coal (G): 1.2wt%/dry coal

4. BASIC RESEARCH FOR COAL LIQUEFACTION PROCESS DEVELOPMENT

(1) Upgrading Technology

① PDU Research for Coal Oil Upgrading

② Bench Scale Research for Coal Oil Refining and Upgrading

(a) Bench Scale Research for Coal Oil Refining and Upgrading

(b) Development of A New Type of Catalysts

(c) The Development of Technology for the Separation and the Utilization of Heteroatomic Compounds from Coal-derived Liquids

③ Environmental Safety Assessment Tests

(2) R&D for Environmentally Acceptable Coal Liquefaction Technology

① Research on Improvement of Coal Liquefaction Process

② Research on Novel Concepts for Coal Liquefaction Technology Development

(a) Advanced Technology for Coal Liquefaction

(b) The Development of Highly-dispersed Iron Catalyst for Coal Liquefaction

(c) Coal Liquefaction under Advanced Conditions

▪ Coal Liquefaction under Advanced Conditions

▪ Research on City-Mode Coal-Waste Co-Liquefaction Process

③ Survey and Information Exchange with Overseas Organization

(a) Applicability Study of Coal Liquefaction Technology

(b) Preliminary Survey on the Mongolian Coal

PDU Research for Coal Oil Upgrading

H.YOSHIDA

Director of Clean Coal Thechnology Center

New Energy and Industrial Technology Development Organization (NEDO)

Contractor : K.NIWA, Petroleum Energy Center

Objectives

Crude Coal liquid causes decoloration, the emission of a pungent odor, the accumulation of sludge, and so on, during storage; due to the fact that it contains many heteroatoms such as nitrogen and oxygen, aromatic compounds, and gummy matter.

It is therefore indispensable to upgrade the coal liquid itself in order to introduce it into existing petroleum-product distribution systems, and to satisfy the qualification criteria for petroleum products.

Thanks to the basic and fundamental research that was made over the past years, refining technologies through hydrogenation refining, and reforming have been researched.

Research is now at the stage of confirmation of its performance through the use of commercial plant tests, and research for upgrading the scale Process Development Units (PDU) in order to prepare samples for engine test evaluation and obtain engineering data has become necessary.

The purpose of the present PDU research is as follows:

① Confirmation of coal-liquid refining and reforming technologies

- Preparation of samples for practical performance evaluation
- Acquisition of engineering data
- Establishment of refining/reforming-process technologies
- Confirmation of continuous stable operation

② Quality confirmation of coal-liquid products

- Quality examination through engine tests, etc.
- Recognition by users and the automobile industry
- Confirmation of product storage stability

Work Program

Research plans include the long-term storage stability evaluation of the coal liquid, as well as evaluation of the design, construction, operation of the plants shown below and the products produced in those plants.

(1) Liquid source

The liquids used in PDU are the coal liquids produced in the 150-t/d bituminous-coal (Tanitoharum coal) liquefaction plant and the 50-t/d brown-coal (Yallourn coal) liquefaction plant.

(2) PDU operation mode

The following operations are carried out to upgrade coal liquid to gasoline and gas oil:

① First-step hydrogenation refining mode

The whole liquid (naphtha and kerosene + gas-oil fractions) is refined by hydrogenation in order to denitrate, deoxygenate and desulfurize.

(Quantity target: Nitrogen 1,000 ppm or less)

② Atmospheric-pressure distillation

Coal liquid, refined through first-step hydrogenation, is fractionated using an atmospheric-pressure distillation apparatus into light component gases, naphtha, kerosene, gas oil, and heavy oil. Fractions other than naphtha and gas oil are not refined, as they are not objects of study in the PDU research.

③ Second-step hydrogenation refining (naphtha and gas oil)

Second-step hydrogenation refining is carried out only on the naphtha fraction in order to denitrate, and desulfurize, it to a level at which reforming-catalyst poisoning is avoidable, as the naphtha fraction goes through, catalytic reformation process to improve its octane value (Naphtha quality target: Nitrogen 1 ppm or less, sulfur 1 ppm or less)

In addition, second-step hydrogenation refining is carried out on the gas oil fraction to improve its cetane index (Gas-oil quality target: Nitrogen 10 ppm or less; sulfur 500 ppm or less)

④ Catalytic reformation

The heavy naphtha fraction, which went through second-step hydrogenation refining, is reformed to improve its octane value.

(Quality target: Octane value of 95 RON or higher)

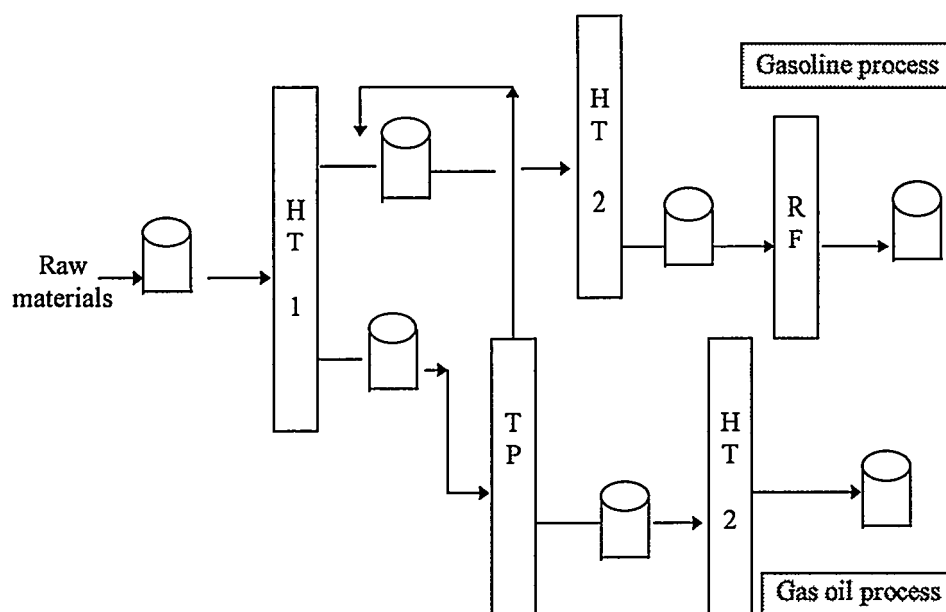
⑤ Hydrogen generation plant

Hydrogen, required for hydrogenation refining and reformation, is generated. Odorless butane and steam are used as raw materials. The generated hydrogen is purified by PSA.

⑥ Other facilities

In addition to on-site facilities, ①~⑤, off-site facilities such as tanks and drum-filling equipment, as well as common facilities such as utility suppliers, cooling towers, exhaust-gas treatment equipment (ground flares), and wastewater treatment facilities (wastewater incinerators and denitrators), are furnished.

The process flow is shown in the figure on the following page.



(Legend)

First-step hydrogenation refining:	HT1
Second-step hydrogenation refining:	HT2
Atmospheric-pressure distillation:	TP
Catalytic reforming:	RF

Summary

1. Up to FY 1996 (1983-1996)

We have been carrying out basic and fundamental research on coal-liquid upgrading technology since 1983, and have found technologies for its upgrading through hydrogenation refining, etc.

Based on the results of this basic and fundamental research, research on the quality evaluation of coal-liquid products and on experimental plants for demonstrating the technology for refining them were launched.

Since 1991, crude coal liquid has been stored in an acceptance tank to assess its preservability.

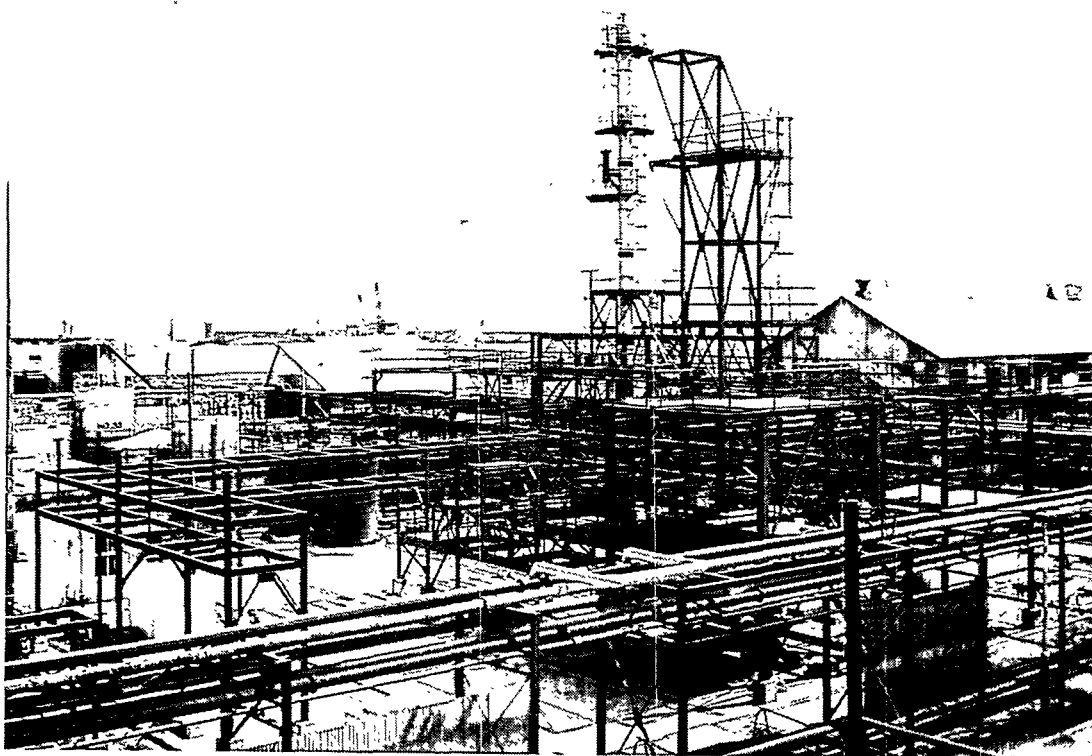
Construction of the experimental plant began in 1995, so 1996 is the second year of construction.

2. For FY 1996

(1) Construction

In 1996, the foundation and structure of common facilities and the low-pressure equipments were constructed and installed.

The photograph below shows the site upon completion of construction for end of 1996.



(2) Process design

(a) Study on process flow alteration

Laboratory-scale test results indicated that some gummy matter in the fraction may deposit during refining of the naphtha fraction alone, resulting in clogging. It therefore became apparent that in the original flow scheme of fractionating naphtha and gas oil refining them separately by hydrogenation, the hydrogenation refining of naphtha may become impossible in a long-term operation.

Accordingly, in order to prevent clogging due to the deposition of gummy matter, the PDU flow was altered to remove gummy matter and its precursors through first-step hydrogenation refining prior to the fractionating of naphtha and gas oil, to fractionate naphtha and gas oil by atmospheric distillation, and to carry out second-step hydrogenation refining of the fractions separately in order to obtain the required refined naphtha and gas oil.

For first-step hydrogenation refining, the flushing condition of the reactor effluent was studied to determine the temperature of separation and the amount of wash water necessary to ensure the prevention of chloride and sulfide deposits. In addition the flushing temperature of the naphtha and gas-oil fractions of Tanitoharum coal, as well as the flow pattern, wall temperature, and pressure decrease inside the heating-furnace tubing were studied in attempt to lessen clogging caused by the deposition of gummy matter.

(a) Analytical results

The total acid number declined slightly, but other items showed little change. The total acid number is an index of oxidative degradation that increases during oxidation, but the test results show the opposite tendency, indicating that a mild reduction occurred during storage in a nitrogen atmosphere. This is believed to show that nitrogen gas sealing has been properly maintained. (The storage tank is kept pressurized at 150 mmAq using nitrogen.)

Thus, the coal liquid is judged to have been kept in good condition.

Summary of the condition of coal-liquid storage

Item of analysis	Viscosity	Bromine Number	Total acid Number	Sludge	SS
Behavior on degradation	Increase	Increase	Increase	Increase	Increase
Storage test result	Flat	Flat	Slight Decrease	Flat	Flat
Storage condition	Good	Good	Good	Good	Good

(b) Amount of and changes in coal-liquid stock

The total decrease over five years is 4.9 (2.2%). In 1996, a decrease of 1.5 occurred in one year. The primary cause of the decrease is considered to be the evaporation of light fractions into the air and sampling (16 for once x two/year). A greater decrease in the tank storing coal liquid from Wandoan coal than that in other tanks was observed, indicating that the decrease was caused by evaporation.

Future Tasks

Crude coal liquid from Tanitoharum coal produced in the 150-t/day bituminous-coal liquefaction plant is planned to finally be received in 1997. Hereafter, facing the final stage of construction, we will carry out the check of the final design package, prepare for operation and education, and study the storage of crude oils, specifically liquefaction oils from Tanitoharum coal and Yallourn coal. We will make absolutely sure that construction is completed and that the necessary preparations for operation have been made, and we will be careful not to leave anything out in preparing for future operational studies.

(b) Study of the on-site facility configuration

Although the switch to first-step hydrogenation refining of the whole liquid caused changes in some equipment in hydrogenation and reforming plants, an increase in the number of tanks required, and a change in the interconnecting lines, the number of facility components itself has remained the same as designed in 1994.

(c) On-site basic plan conditions

Taking into account the need to gather data for commercial plant design and the production of sample oil for necessary tests, the capacity of the main plants, the "hydrogenation/reforming plant", and the "atmospheric distillation plant" was determined to be 40 BPSD, and the accompanying plants, the "hydrogen generator", the "wastewater treatment plant", the "cooling-water system", and the "waste-oil treatment plant", were designed accordingly.

(d) Off-site basic facility plan

① Tank plan

Existing tanks at the Funakawa Refinery of the Japan Energy Corporation are being studied in an effort to ensure that their capacities can meet the storage requirements, and are to be used as storage facilities for feedstock, secondary feedstock, intermediate products, and end products. Nitrogen gas sealing equipment, heating coils, and deodorizing equipment are to be installed according to the properties of the contents. Deodorizing pots are also to be equipped on tanks that require the absorption-removal of pungent-smelling hydrocarbon vapor.

② Receiving/shipping facility plan

Taking into account the number and capacities of existing tanks available, as well as the type and capacity of receiving facilities at the destination, receiving by means of rollies and shipment in drums are planned.

(3) Study and setting of the operation schedule

(a) Preparation for operation

Among the study items to be carried out during the operation preparation period beginning in 1997, manuals are to be prepared and an operator education plan is to be made.

(b) Manual items preparation

Manual items were prepared. Here, the manual items are materials for the education and operation standards, and each is used as follows:

- Materials for education: Acquisition of basic knowledge to help operators master operation
- Operation standards: Rules for unit operations

(c) Study on the operational study plan (subject of the study)

A draft of the Funakawa research plan on the PDU study subject was prepared. Detailed study will be carried out hereafter in the discussion on the technological package headed by NEDO.

(d) Personnel study plan

Two different requirements for the number of operators per shift, as shown below, are possible for the scale of the PDU plant.

- Case ① Four /shift + full-time operator 0
- Case ② Three/shift + full-time operator 4

One of the two cases will be adopted, taking safety and operability into account.

With the support of the organization of the Funakawa Refinery of Japan Energy Corporation in supplying necessary staff members, other than operators, for operation management, analysis, analytical study, and maintenance, a few full-time staff members and some staff members who also work for the refinery will effectively run the plant.

(e) Study on practical performance evaluation tests

① Necessity of performance evaluation

As coal liquid contains more heteroatom and aromatic compounds than petroleum fuels for transportation, sufficient refining and reformation will be carried out to ensure high quality, but unknown factors involving the new product cannot be neglected.

Moreover, as the performance of engines and other automobile equipment is improving, and environmental regulation are becoming more severe, recognition of the product by the automobile industry and users has become more important than ever.

It is planned to have third-party organizations carry out practical performance evaluation of the gasoline and gas oil from refined coal liquid, in order to compare them with petroleum fuels and confirm their qualities.

② Evaluation test items

Because flammability, clearness, serviceability, and exhaust characteristics are the required practical qualities of automobile fuels, test items such as physical-property tests on fuels, engine and actual car running tests (exhaust gas test, acceleration test, and durability test), and immersion tests are considered practical performance tests on the refined coal-liquid gasoline and gas oil.

③ Amount of product required

Because flammability, clearness, serviceability, and exhaust characteristics are the required practical qualities of automobile fuels, exhaust gas tests, acceleration tests, durability tests, and immersion tests are planned as practical performance tests on the refined coal-liquid gasoline and gas oil, and the amount of product required for these tests were estimated. This will be discussed in detail with the organizations that will carry out the tests.

(4) Coal-liquid storage

In the course of the coal-liquid upgrading study, coal liquids (coal liquids from Yallourn coal and Wandoan coal) were received from the coal liquefaction pilot plant in December 1991, and stored in a tank for over five years as a long-item storage test.

The purpose of this test is to determine the degradation tendency of coal liquid, and to demonstrate that coal liquid can be stored in an existing storage facility of a liquid refinery without problems involving quality or handling.

Bench Scale Research for Coal Oil Refining and Upgrading

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Director of Clean Coal Thechnology Center

New Energy and Industrial Technology Development Organization (NEDO)

Contractor : K.NIWA, Petroleum Energy Center

Objectives

Development of coal-derived liquids refining technology which is most adaptable to the liquid fuel refining technology of Japan and the utilization system thereof, and refined products utilization technology.

Work Program

(1) Study on hydrotreatment of coal-derived naphtha and middle distillate

(a) Study on upgrading technology

The experiments about two stage neat-hydrotreatment of Tanitoharum coal-derived middle distillate with micro-reactor were carried out.

(b) Development of utilization technology

The cause and the restraint of coloring or sediment formation about coal-derived middle distillate were investigated.

(2) Study on hydrotreatment of kerosene and gas oil fraction derived from coal

(a) Study on upgrading technology

The experiments of two stage hydrotreatment applied to Tanitoharum coal-derived liquid have been carried out at a micro-reactor.

(b) Development of utilization technology

Accelerated storage stability tests have been performed for coal-derived liquids.

Summary (1983-1996)

1. Up to FY 1995

(1) Study on hydrotreatment of coal-derived naphtha and middle distillate

From FY 1983 to 1993, the study of hydrotreatment has been carried out for whole fractions or each fraction derived from coals; Wandoan, Illinois, Wyoming, Battleriver and Yallourn. And also their hydrotreated liquids have been evaluated as fuel products.

From FY 1994, the study on neat-hydrotreatment of Tanitoharum coal-derived liquids has been started. As for naphtha fraction, the hydrotreating conditions to be reforming feed were determined. Though middle distillate was hydrotreated to fuel for diesel, there was a limit to improve cetane index by the one stage hydrotreatment, especially with high temperature and high pressure conditions. So the two stage hydrotreatment has been studied to increase cetane index by ring-opening of naphthenic compounds.

(2) Study on hydrotreatment of kerosene and gas oil fraction derived from coal

One stage hydrotreatment was studied for kerosene and gas oil fraction, both of which were derived by the liquefaction of Wandoan, Illinois, Wyoming and Battleriver coal, and Yallourn brown coal, and it was also done for the raffinate oil of these fractions, which were extracted with either methanol/water or alkali.

The refining conditions were fixed, and the products were studied by several kinds of fuel evaluation tests such as color, Cetane number, low temperature fluidity, thermal stability and combustibility test by both gas turbine and diesel engine.

Two stage hydrotreatment (i.e. for the first stage, the fraction of kerosene plus gas oil from Tanitoharum coal was charged and for the second stage, the mixture of petroleum feed and the product from the first stage were fed.) was also studied.

For the first stage, the operation conditions and the relation-ships between the degree of hydrodesulfurization reaction and the sludge formation were examined, and some catalysts including the one developed by NEDO were evaluated by means of catalyst life test.

For the second stage, the catalyst and the refining conditions were selected, and the maximum allowable blend ratio of the first stage product to petroleum feed as the feedstock of the second stage was decided by the second stage product stability test.

2. For FY 1996

(1) Study on hydrotreatment of coal-derived naphtha and middle distillate

(a) Study on upgrading technology

(i) Optimization of first stage hydrotreatment

The first stage hydrodenitrogenation with high-pressure condition induces diaromatic compounds to be naphthenic completely at the same time. And it causes over-cracking in the second stage, ring-opening of naphthenic compounds. Therefore it prefers to be hydrotreated with low-pressure condition in the first stage, the possibility of incomplete naphthenization and complete hydrodenitrogenation at 5MPa was studied. As a result, complete naphthenization was restrained to 60 or 50vol%, but hydrodenitrogenation was short of the target (<10ppm) in addition to the deactivation of catalyst. So it turned out to be a limit of once-through hydrotreatment in the first stage.

(ii) Control of naphtha or diesel yields and properties

Using two kinds of catalyst on the market, one was a noble metal contented and the other zeolite-based, the second stage hydrotreatment of the first stage hydrotreated middle distillate (N<10ppm, saturated hydrocarbon contents>96vol%) by alumina-based catalyst was evaluated. As a result, the diesel fraction of hydrotreated oil by noble metal catalyst had highest cetane index and was upper 45 as JIS diesel fuel. But its yield extremely decreased as shown Fig.1, because of over-cracking to gas or naphtha fractions. Though cetane index was also improved by zeolite-based catalyst, diesel fraction yield decreased as shown Fig.2.

(iii) Simulation of efficiently two stage hydrotreatment system

Methyltetralin was selected as the model compound from among naphthalenes and tetralins that were the main ingredients of middle distillate, and the fundamental performances of above-mentioned two catalysts were evaluated by the model reactions. As a result, it turned out that both catalysts had ability on hydrocracking but hardly selectivity on ring-opening of naphthenic compounds to long-chained alkyl structures without over-cracking. For the selective ring-opening, it was important to take account of hydrocarbon structure just before the reaction. Especially, it was more effective to open the naphthenic ring from partially hydrotreated diaromatic compounds like tetralins. In this case, it was expected that the hydrodenitrogenation and partially hydrodearomatization were efficiently accomplished by recycling system at a low pressure in the first stage.

(b) Development of utilization technology

The storage stability of typical nitrogen compounds contained in middle distillate was tested under the condition of ASTM D 4625-86 at 43 degrees for three weeks. As a result, it found to be three types as follows; almost nothing to change (anilines, quinolines, indole, carbazoles), colored (partially hydroindole), sediment formation (alkylindole, partially hydrocarbazole), and alkylindoles were extremely unstable. As the restraint of coloring or sediment formation, mildly hydrotreatment at the beginning also seemed to be effective other than getting out of contact with air, because it was just easy to be denitrogenate by hydrotreatment.

(2) Study on hydrotreatment of kerosene and gas oil fraction derived from coal

(a) Study on upgrading technology

(i) Catalyst evaluation for the second stage hydrotreatment

H01 catalyst(Ni-Mo type), which had showed the highest performance on Cetane number, gas oil yield ,hydrodenitrification (HDN) and hydrodesulfurization (HDS) , was evaluated its catalyst life.

The test conditions were as follows;

Feed stock: maximum blend ratio of coal-derived product from the first stage to petroleum feed

reaction temperature: 360 °C

hydrogen pressure: 70kg/cm³

LHSV: 1 Hr⁻¹

and H₂/Oil: 1,000NI/l

Consequently after 2,000 hr run, the Cetane index of the product (as whole oil : naphtha plus gas oil fraction) showed 44 - 47 which satisfied with JIS of No.2 gas oil(more than 45) , and the Cetane number of the gas oil fraction (distilled) showed the higher value of 54-56 which fulfilled JIS of No.1 gas oil (above 50) .(Fig.3)

The HDN reaction completed more than 99.6% and the HDS reaction reached to above 98.95% .

These values have been kept almost at constant level during 2,000 hr run .H01 catalyst , therefore , was demonstrated to have very high activity and long life both on HDN and HDS .

(ii) Study on countermeasures to prevent plugging at PDU

Severe plugging was observed at the micro-reactor test by Idemitsu Kosan Co.,Ltd. when coal-derived oil was hydrotreated.

Plugging, therefore, was examined by the micro reactor test to check whether it might occur at PDU or not and to study on some countermeasures to prevent it.

The feedstock was whole oil (naphtha plus gas oil fraction) derived from either Tanitoharum coal or Yallourn brown coal.

As the results, plugging was observed in case of Tanitoharum coal-derived whole oil when the naphtha ratio was above 75wt% and it was not observed below 50wt% at all. In case of Yallourn brown coal-derived whole oil, plugging was not found out around 50wt% of the naphtha ratio.

At PDU, therefore, the naphtha ratio in the feedstock should be presumably set around 50wt%. HT-1 process scheme at PDU was also designed so as not to occur severe plugging; heat exchangers were rearranged and the reactor distributor was selected and so on. (Fig.4)

(b) Development of utilization technology

The accelerated storage stability test (ASTM 4625-86) of the product from the two stage hydrotreatment showed no problem in storage; the amounts of sludge formation was lower than 2mg/100cc which was permitted by ASTM.

Future Tasks

(1)Study on hydrotreatment of coal-derived naphtha and middle distillate

The conditions of recycling system in the first stage will be preliminary studied for the efficient hydrodenitrogenation and partially hydrodearomatization.

(2) Study on hydrotreatment of kerosene and gas oil fraction derived from coal

On the study of two stage hydrotreatment the catalyst selection and its catalyst life evaluation,the reaction condition and the maximum blend ratio of coal-derived oil to petroleum feed were decided.

Other technological studies such as on plugging problem at PDU and on one stage hydrotreatment which were also completed.

The theme, therefore, is to finish in this year.

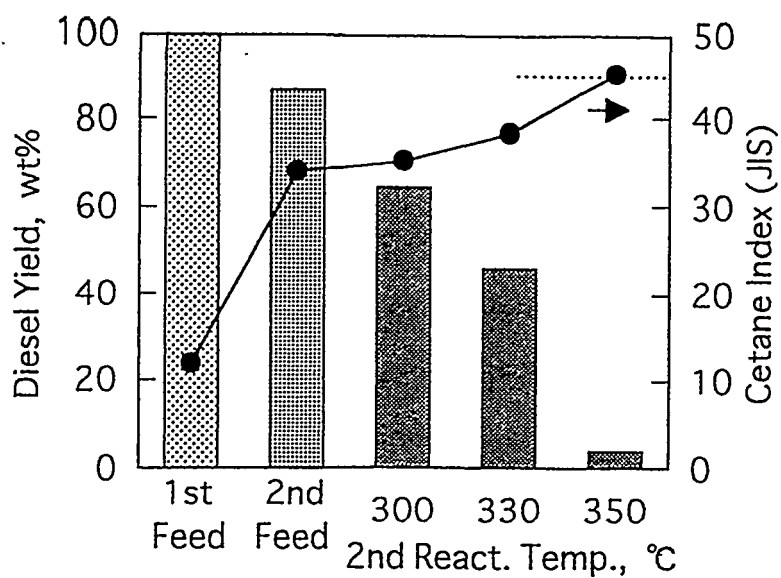


Fig. 1 Result of hydrotreatment of middle distillate by alumina (first stage) - noble metal (second stage) catalyst (5MPa, LHSV 1hr⁻¹, H₂/Oil 700Nm³/kl)

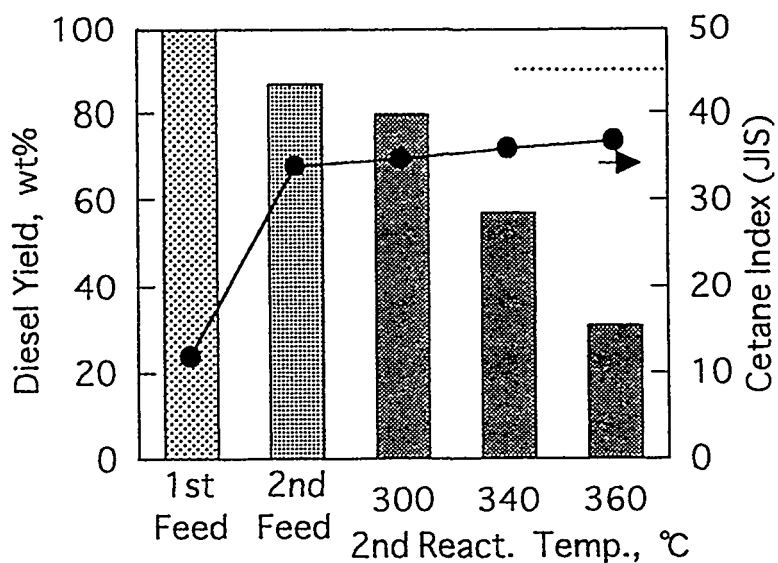


Fig. 2 Result of hydrotreatment of middle distillate by alumina (first stage) - zeolite (second stage) catalyst (5MPa, LHSV 1hr⁻¹, H₂/Oil 700Nm³/kl)

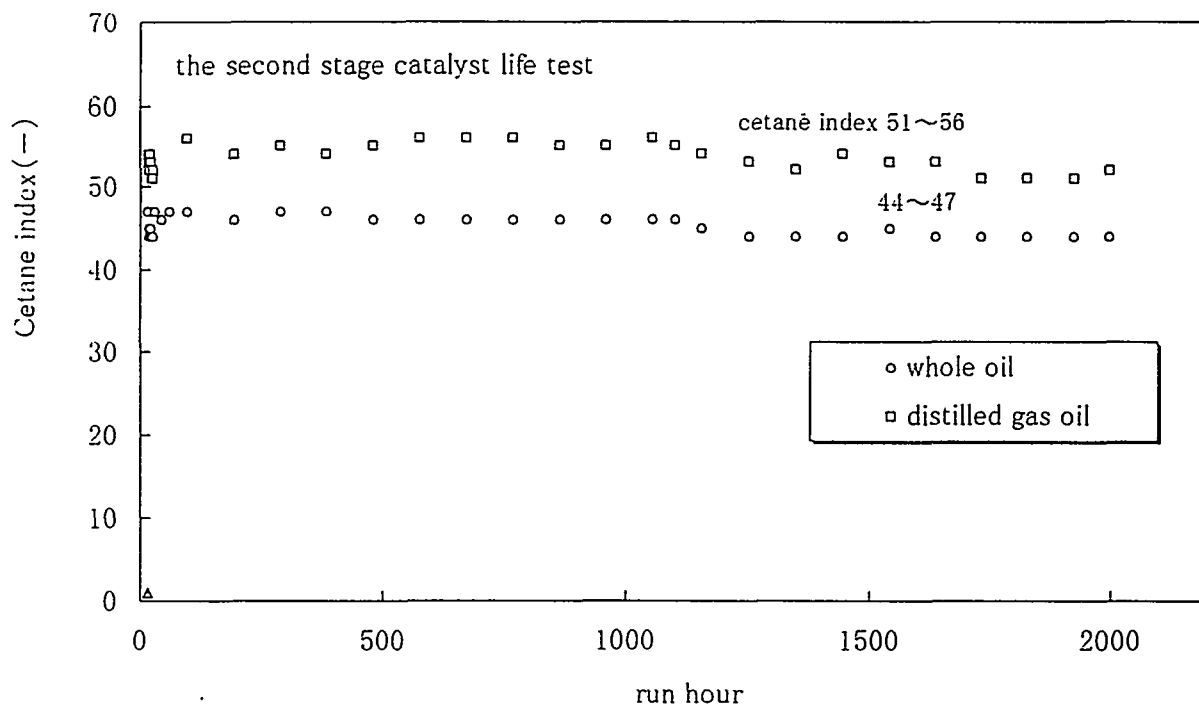


Fig.3 Time chart of Cetane index

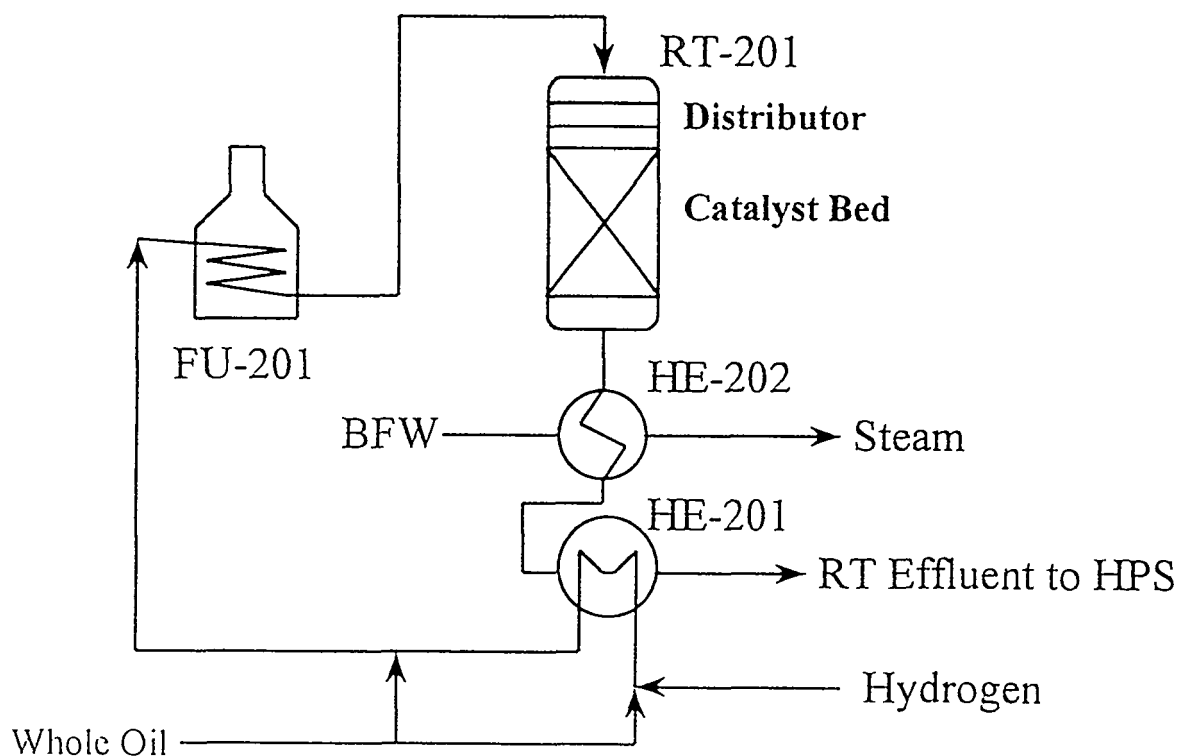


Fig.4 PDU HT-1 Flow Scheme

SOME UPGRADING TECHNOLOGY
(DEVELOPMENT OF A NEW TYPE OF CATALYSTS)

H.YOSHIDA

Director on Clean Coal Technology Center
New Energy and Industrial Technology Development Organization (NEDO)

Contractor: J. FUTIGAMI, Catalyst and Chemicals Industries Co. Ltd.

Objectives

To improve the quality of coal-derived liquids, we developed (1) hydrogenation (hydrodenitrogenation and hydrodearomatics) catalysts and (2) hydrocracking (opening aromatic ring) catalysts fitted for the refining reaction of coal-derived liquids (each fraction of naphtha, kerosene and light gas oil) produced in the coal liquefaction process to developing in Japan.

Work Program

Catalyst design for purification of coal-derived liquids is carried out on the basis of catalyst functions to fulfill the needs of upgrading of coal-derived liquids. These functions are studied by model test reactions and upgrading reaction of coal-derived liquids. We prepare these catalysts and study the relation between the physical properties and the reaction characteristics. To develop the practical catalyst, the life of catalyst is determined by higher order analysis of the physical properties by means of X-ray photoelectron spectroscopy (XPS) and X-ray microanalyzer (XMA) etc.. Screening of prepared catalysts and analysis of produced oil are realized efficiently reactors. After the fiscal year 1994, improvement of catalysts and preparation method of large amount of development catalysts are investigated in order to adapt the technical elements of the process development unit (PDU) to the service-condition compatibility. Moreover, the dynamical characteristics of catalysts are investigated by bench tests.

Summary (1988-1995)

1. Up to FY 1995

· FY 1988

- (1) Catalyst design, preparation of small amount of catalysts, batch reaction test of model compounds were carried out.
- (2) Catalyst screening devices (3 units) were manufactured and trial operation was put into practice.

· FY 1989

- (1) With duplication of screening device, many kinds of hydrogenation catalyst

were prepared and batch reaction test and continuous reaction test were executed.

(2) Moreover, the short time life tests of high active hydrogenation catalysts were carried out.

· FY 1990

(1) Each kind of hydrocracking catalyst was prepared and batch reaction test, continuous reaction test, and short time life test of high active hydrocracking catalysts were performed.

· FY 1991

(1) The improvement of hydrocracking catalysts were carried out by adding oxygen-proof and nitrogen-proof to them.

(2) We offered hydrocracking catalysts to RAPAD.

· FY 1992

(1) Catalyst was improved to be suited for mixing treatment with petroleum fuel.

(2) The hydrocracking catalysts were offered to RAPAD.

· FY 1993

(1) Hydrogenation catalysts were improved to have long life.

(2) Hydrocracking catalysts were improved to have long life.

· FY 1994

(1) Improved hydrogenation catalysts were presented to RAPAD.

(2) By improving, long life hydrocracking catalyst was obtained.

(3) Large amount of hydrogenation catalyst (1000ℓ) were prepared for PDU test.

(4) To study dynamic characteristics of catalyst by bench test, catalyst function combination analyzer was manufactured and commissioning was put into practice.

· FY 1995

(1) Long life hydrogenation catalyst was obtained by improving.

(2) Long life hydrocracking catalyst was prepared by improvement.

(3) Large amount of hydrocracking catalyst (1000ℓ) were prepared for PDU test.

(4) Reaction dynamic characteristics of catalysts were investigated by bench test.

2. For FY 1996

(1) Large quantity of preparation test of hydrocracking catalysts, (2) investigation of reaction dynamic characteristics of hydrocracking catalysts and (3) total evaluation of development hydrogenation and hydrocracking catalysts were enforced in the fiscal year 1996.

(1) Large quantity of preparation test of hydrocracking catalysts

About 200ℓ of development catalyst was in need for PDU pilot test. So that, a preparation method of large quantity of catalyst should be established. Large amount of preparation test from laboratory scale level (100cc) to pilot plant scale level (1000ℓ) were carried out in the plant in Wakamatsu. The physical properties and hydrodenitrogenation (HDN) activity of prepared catalysts were evaluated and compared with that of catalysts developed. The test feedstock used was hydrotreating oil of the middle distillate obtained from Brown coal. This distillate was upgraded using a continuous flow reactor. The reaction conditions selected for upgrading coal-derived liquids were as follows; catalyst volume, 15mℓ; LHSV, 2.0hr⁻¹; H₂ pressure, 6.9MPa;

reaction temperature, 370°C; H₂/oil, 1000Nℓ/ℓ; reaction time, 500hr. The characteristics of the catalysts development and large amount prepared catalysts were shown in Table 1. Fig.1 shows the results from short-term catalyst performance test for the upgrading of the coal-derived liquids.

Table 1 Properties of hydrocracking catalysts

	Development catalyst	Large amount prepared catalyst
Surface area (m ² /g)	3 5 0	3 4 8
Pore volume (cm ³ /g)	0 . 3 6	0 . 3 5
W O ₃ (wt%)	2 3 . 8	2 4 . 4
N i O (wt%)	3 . 4	3 . 7

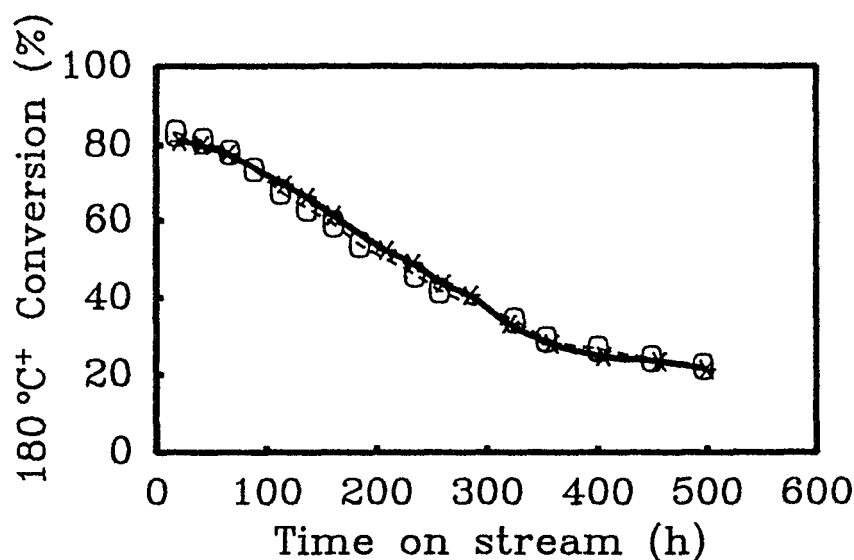


Fig.1 Hydrocracking activities of the catalysts a short-term performance test
*: Development catalyst, O: Large amount prepared catalyst

The obtained results proved that the physical properties and the activities of catalysts of the preparation tests of pilot plant scale level were able to reproduce the catalytic functions of laboratory scale level.

(2) Discussion of reaction dynamic characteristics of the hydrocracking catalysts

To protect any trouble in PDU pilot test, the effects of change of reaction conditions, such as pressure and LHSV, on catalytic functions in operating were investigated by the catalytic function multiple analyzer. Change test of temperature, pressure and LHSV and feed stop test of coal-derived liquids (stop for 10min) were studied (Fig.2).

When the reaction conditions were changed, the catalytic activity decreased about 2% and 10% with changing LHSV and pressure, respectively. So that the effect of pressure on the activity was larger than that of LHSV. The decrease of activity was thought to be caused by accumulation of carbonaceous material and adsorption of basic nitrogen compounds on the surface of catalyst. About 2% of activity was decreased by stopping feed of coal-derived liquids.

The above obtained results made clear the catalytic activity of hydrocracking catalyst was changed much larger than that of hydrogenation catalyst by variation of reaction conditions. Main factor of activity change was thought the solid acid property of hydrocracking catalyst. Accordingly, the handling of hydrocracking catalyst requires circumspection.

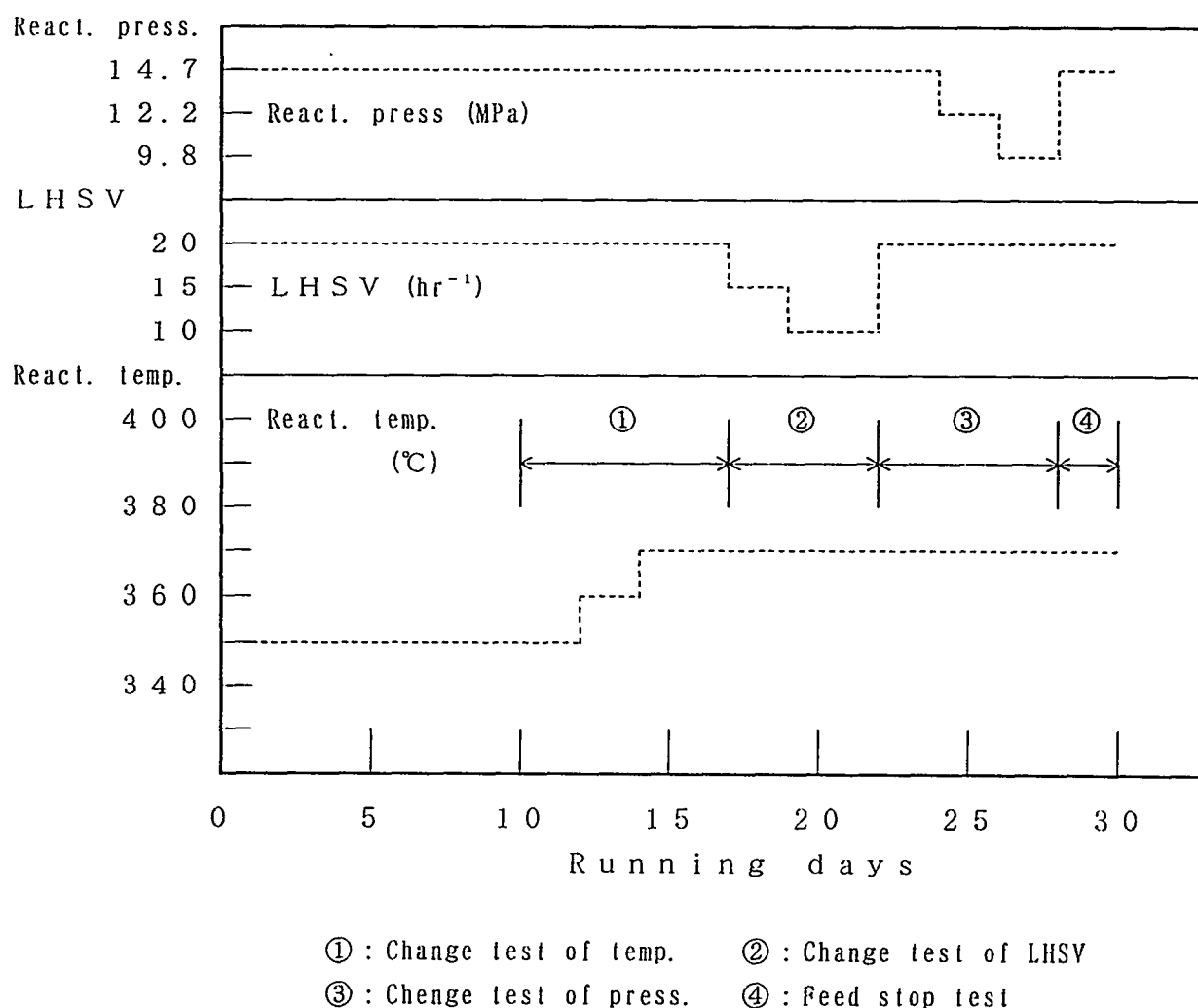


Fig.2 Running method of reaction dynamic characteristics of the hydrocracking catalyst

(3) Evaluation of development catalysts

(a) Hydrogenation catalyst

The final confirmation of the catalytic functions of the reference catalyst (catalyst with the highest activity in the commercial one) and the development catalysts was carried out. Table 2 shows the characteristics of the reference catalyst and development catalysts. The test feedstock used was gas oil fraction obtained from Tanitoharum coal used in PDU. This distillate was upgraded using a continuous flow reactor. The reaction conditions were as follows; catalyst volume, 15ml; LHSV, 2.0hr⁻¹; H₂ pressure, 6.9MPa; reaction temperature, 370°C; H₂/oil, 1000Nℓ/ℓ; reaction time, 500hr. The results of HDN activity were shown in Fig.3.

Table 2 Properties of hydrogenation catalyst

		Referece catalyst	Development catalyst
Surface area	(m ² /g)	1 9 5	1 6 7
Pore volume	(cm ³ /g)	0 . 3 9	0 . 5 0
Pore diameter	(Å)	7 5 .	1 0 4
<hr/>			
W O ₃	(wt%)	—	2 9 . 2
M o O ₃	(wt%)	1 8 . 8	—
N i O	(wt%)	3 . 8	4 . 2

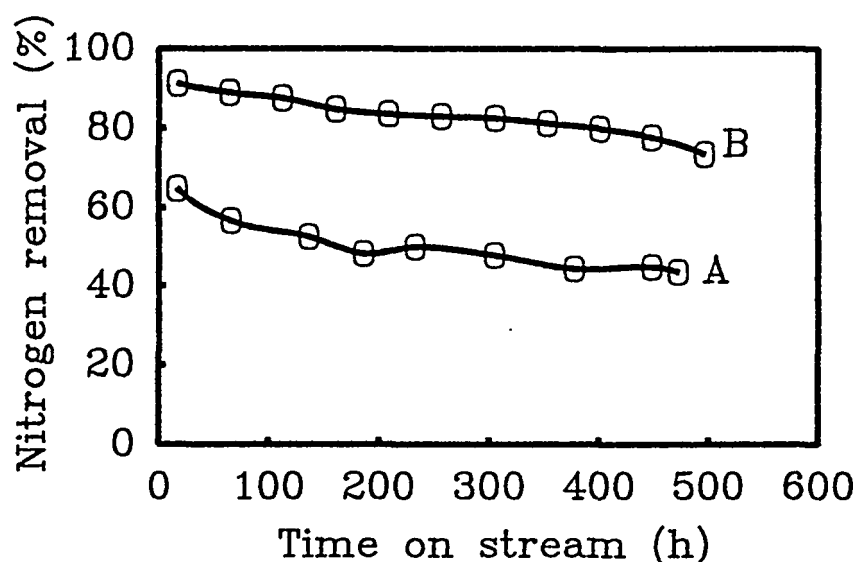


Fig.2 HDN activities of the catalysts a short-term performance test
A: Reference catalyst, B: Development catalyst

The results showed the activity and life of development catalyst were higher and larger than that of the reference catalyst. The same tendency of higher activity of development catalyst was proved in the case of coal-derived liquids of other kinds of coal.

(b) Hydrocracking catalyst

The final confirmation of catalytic function of the reference catalyst (commercial one) and development catalysts was identified by the continuous reaction test (500hr) of hydrotreating oil of middle distillate obtained from Brown coal. Table 3 shows the characteristics of the reference catalyst and development catalysts. The reaction conditions were as follows; catalyst volume, 15ml; LHSV, 2.0hr⁻¹; H₂ pressure, 6.9MPa; reaction temperature, 370°C; H₂/oil, 1000Nℓ/ℓ; reaction time, 500hr. The measurement results of hydrocracking activity were shown in Fig.4.

Table 3 Properties of hydrocracking catalyst

	Referece catalyst	Development catalyst
Surface area (m ² /g)	3 7 5	3 5 0
Pore volume (cm ³ /g)	0 . 4 4	0 . 3 6
W O ₃ (wt%)	1 6 . 5	2 3 . 8
N i O (wt%)	4 . 6	3 . 4

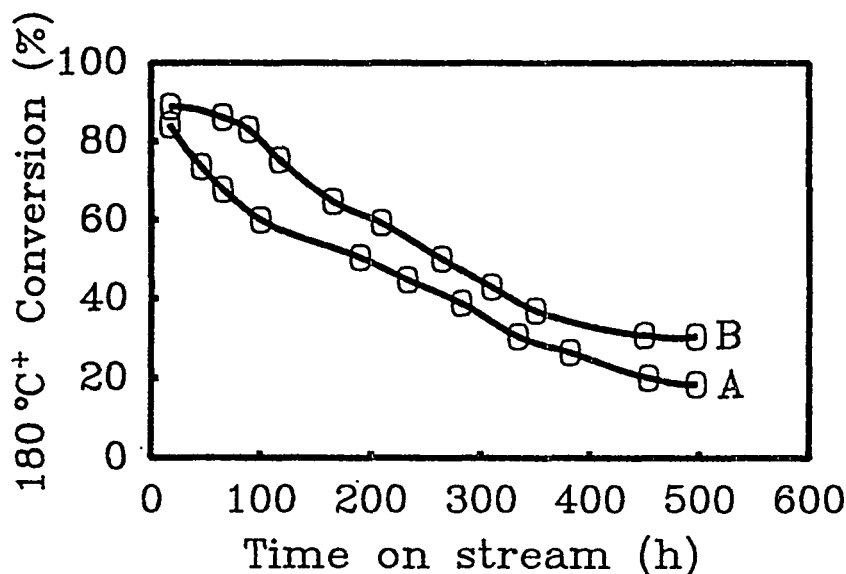


Fig.4 Hydrocracking activities of the catalyst a short-term performance test
A: Reference catalyst, B: Development catalyst

The hydrocracking activities of development catalysts were higher than that of the reference catalyst. On the life test for 500hr, short time, the development catalysts kept higher activity than the reference catalyst.

These above results proved that the development catalyst had higher activity and longer life than that of the reference catalyst.

Future Tasks

We'll establish a preparation techniques of hydrogenation catalyst in the plant scale (3000kg of catalyst). Examination items are described as follows:

- (1) Physical properties and catalytic functions of preparation catalysts in plant scale should be identified to reproduce that of development catalyst.
- (2) The activity levels of catalysts prepared in plant scale level should be confirmed by measuring the initial activity of the reference, development and preparation catalyst in plant scale level by means of continuous flow reactor.

The Development of Technology for the Separation and the
Utilization of Heteroatomic Compounds from Coal-derived Liquids

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Contractor: N. NAGANO , NIPPON STEEL CHEMICAL Co., Ltd.

Objectives

The objectives of this research are to develop an efficient process for separating heteroatomic compounds from coal-derived liquids and to investigate their usages.

This research contributes to the coal liquefaction process in the following ways;

- (1) Decreases the cost of upgrading treatment of coal-derived liquids
- (2) Improves the cost performance of the coal liquefaction process by utilizing heteroatomic compounds as chemical sources.

Work program

The work program of this research is as follows;

- (1) Detailed investigation of the possibility and problems when applying following industrial separation processes to the coal-derived liquids.
 - (a) Acid/base extraction
 - (b) Hot water extraction
 - (c) Organic solvent extraction (water-methanol system)
 - (d) Supercritical gas extraction
 - (e) Surfactant aided extraction
- (2) Experimentally confirm the applicability of those separation processes cited above to the coal-derived liquids (naphtha and middle distillate) by using existing apparatus. Also try to construct new process.
- (3) Select the best process among those based on the experiments and confirm detailed performance and carry out cost estimations of it by using bench-scaled testing apparatus manufactured for this program.
- (4) Investigate their utilizations of the heteroatomic compounds separated from coal derived liquids.

Summary (1987-1997)

1. Up to FY 1996

(1) Following the scheme, we compared validity of mutual processes.

They are acid/base extraction, Hot water extraction, supercritical gas extraction, organic solvent extraction, surfactant aided extraction.

Base extraction and organic solvent (water-methanol) extraction were appreciated to be superior from the points of operation ease and process feasibility.

(2) Base extraction process; this process already exists in coal-tar chemical industries. We found this process can be applied without further modification.

There are 3 disadvantages.

They are a) Condensation of sodium salt of organic acids. This causes process corrosion and lowers effect of NaOH (catalyst). b) Decomposition rate of phenolates is fairly low. c) The amount of by-products and disposals is as much or even more than that of product itself.

(3) Organic solvent (water-methanol) extraction; We carried out simulation study of phase separation phenomena of each heteroatom containing compound.

This proved that using following coefficient as valuables, degree of extraction and selectivity of phenols are predictable.

{ distribution coefficient of phenols in oil/water, water concentration (water / (water + methanol)) }

(4) Feasibility study; Feasibility of the process was evaluated in case of 50,000 BPD scale coal-derived naphtha extraction plant. Cost of investment and utilities were evaluated for both base and organic solvent (water-methanol) extraction.

Base extraction process has higher cost of investment and lower cost of process utilities.

This process is more sophisticated and product fuel oil has higher purity.

After these reasons above, we concluded that base extraction process to be best.

On the other hand, organic solvent (water-methanol) extraction process instead has lower cost of investment and both acid and base can be extracted at one time, we decided to continue the research of this process on as a "back up".

(5) Importance of separation of heteroatom containing compounds;

a) Effect on hydrogen refining: hydrogen consumed on hydrogen refining decreases to $1/2 \sim 1/3$. Also reaction rates of both desulfurization and denitrogen are accelerated. As hydrogen is very expensive, these effects are beneficial.

b) Effect on environment: Phenol contained in crude coal-oil turns to benzene which

is known to be highly poisonous after hydrogenrefing. By Separating phenol before hydrogenrefing, benzene content in product oil becomes very low.

(6) Research on new utilizations of by-products:

In case of phenols, applications for resin or for fuel sdditives are now under re-search. But they are not yet put to practical use. Other deriveratives are rarely researched.

So, utilization of separated phenols is left as a big problem.

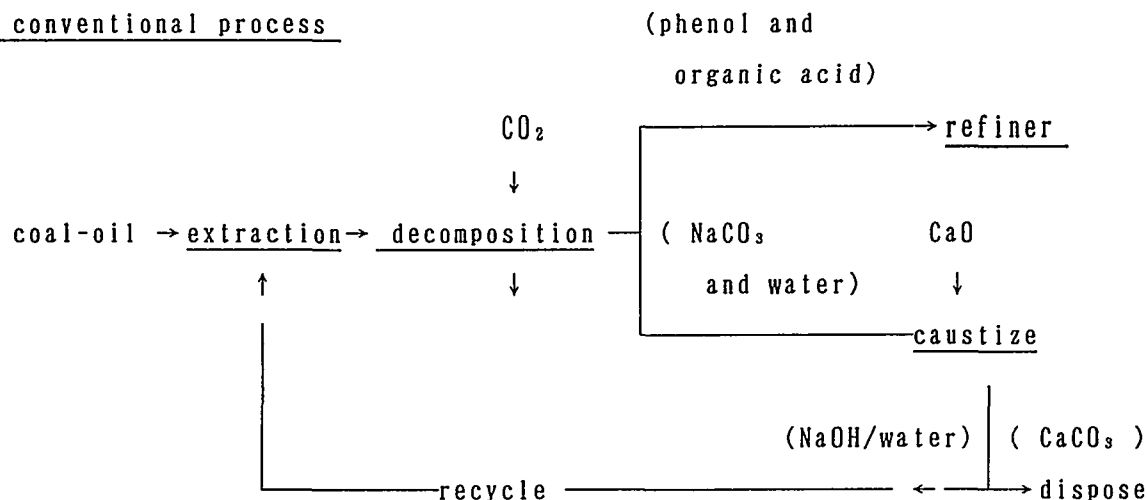
As for present counterplan, most probable is to sale them to existing market which is fairly large.

(7) Study on "future" base extraction process: conventional base extraction process requires large amount of CO_2 and CaO . Disposal of large amount of CaCO_3 is also a problem. These requirments restrict freedom of location.

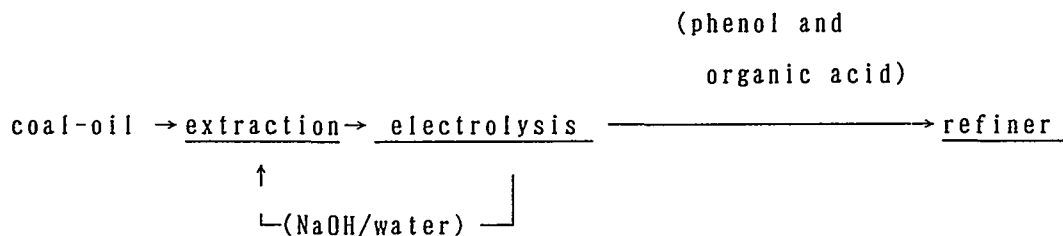
Hence, alternative technology is prospected.

In FY 1995, we discovered electrolysis. Abstract of this process is as follows. First, whole coal-oil is base extrcted. Recoverd mixtures of phenolates and salts of organic acids are directly reduced to original phenols and organic acids by electrolysis. NaOH , charged at base extrction, is also recovered completely. The characterics is this process is free from disposals.

conventional process



electrolysis



2. For FY 1996

2-1 application study on separation and purification of heteroatom containing chemicals

(1) Elimination of organic acids:

Acidic compounds in coal-derived oil are recovered as salts when treated with base extraction. Most of salts except phenols stay in water (not in oil) and don't decompose by CO_2 treatment. This water is reused after treated with lime, then NaOH . As salts in water stays unchanged by these treatment, so concentration of them gradually increases. These salts are known to cause corrosion.

For elimination of these salts, we studied NaCO_3 treatment.

Treating with NaCO_3 before base extraction, most of salts were eliminated, but high molecular weight aliphatic acids couldn't be eliminated.

Incomplete elimination causes corrosion someday, we couldn't adopt NaCO_3 treatment in this study.

(2) Electrolysis:

We've got a patent on this process as the possibility of it was confirmed through the basic research.

This process uses bi-polar membrane film on electrolysis. Durability of the film were examined by batch-wise at laboratory scale.

It proved that durability is over 200 hrs. But at that time the film showed slight degradation both physically and appearance. Damage of the film showed this process needs modifications either construction of the electrolysis cell or film itself.

During the test, consumption of electric power was 2.5 kW/kg- NaOH .

If we take cost of electricity 10 yen/kwh, total cost of utilities are about even. (complete estimation will be carried out in FY 1998)

2-2 basic research:

(1) Environmental effect of deheterogenation: light oil of liquified coal has a defect that poor emission characteristics when used as diesel fuel. This comes from its high aromaticity.

We assumed that some specific aromatic compounds may influence emission characteristics and examined the relationship between them.

We discovered that emission of smoke and amount of particulates has good relation with concentration of aromatic tert-carbons in first order.

Emission of smoke and amount of particulates is least when pure paraffinic hydrocarbons are used and increased as concentration of aromatic tert-carbons gain

-ed.

Through this research, aromaticity of fuel should increase emission of particulates and also NOx.

(2) Analysis organic solvent extraction (water-methanol system):

In this process, add methanol first to coal-oil, then add water. Through this procedure, phenols are fast extracted.

a) Measurement of K (distribution coefficient of phenols between oil and water)

Using pure compounds, K-values were measured for each compound at equilibrium.

K-values showed same action for all compounds examined (⇒ see fig. 1, 2).

It means that this process can extract many heteroatom containing compounds, such as single ringed phenol derivatives or nitrogen containing compounds.

This confirmed that this process fits well to separate heteroatoms from coal-oil.

b) Application to tanitohalm coal derived oil:

This oil was produced at PSD (1 ton/day process support unit) and has boiling point ranging 50 to 180°C. Elemental analysis shows oxygen content 2.6 wt%, nitrogen content 0.5 wt%. Extraction was carried out at standard condition.

Extract (water-methanol) contained 4% of neutral oil.

This value is too high according to the result given above. So, the reason of this discrepancy is now under research.

c) Survey on new process: surfactant sided extraction

This method has lower acid recovery and higher neutral oil carriage.

This year, we tried steam-stripping to separate neutral oil from extracted mixture. Selective separation of neutral oil was impossible, then we ceased to study this process further.

(3) Construction of separation and purification scheme:

Crude phenols separated by base extraction itself is a mixture of vast kind of phenol derivatives.

The aim of this study is to give more additional values to separated phenols by constructing a scheme to purify phenols which can be used as chemical resources.

First, hydro de-alkylate crude phenols to reduce number of derivatives into 2 (phenol and cresol), then distillate and divide them into pure phenol and cresol.

This year, we estimated reaction rates of dealkylation and dehydroxylation for several phenol derivatives and simulated the hydro de-alkylation of coal-oil.

This calculation showed that when reaction temperature is held over 700°C, all phenol derivatives could be reduced to phenol and B.T.X.

Future tasks

(1) Application study

- a) Prepare for demonstration of base extraction process (process design)
- b) Complete electrolysis process (basic research)
- c) Demonstrate possibilities of recycle use of NaOH

(2) Basic research

- a) Complete water-methanol extraction process
- b) Complete refining process for water-methanol extracted phenols
- c) Demonstrate separation and purification scheme by hydro de-alkylating separated phenols

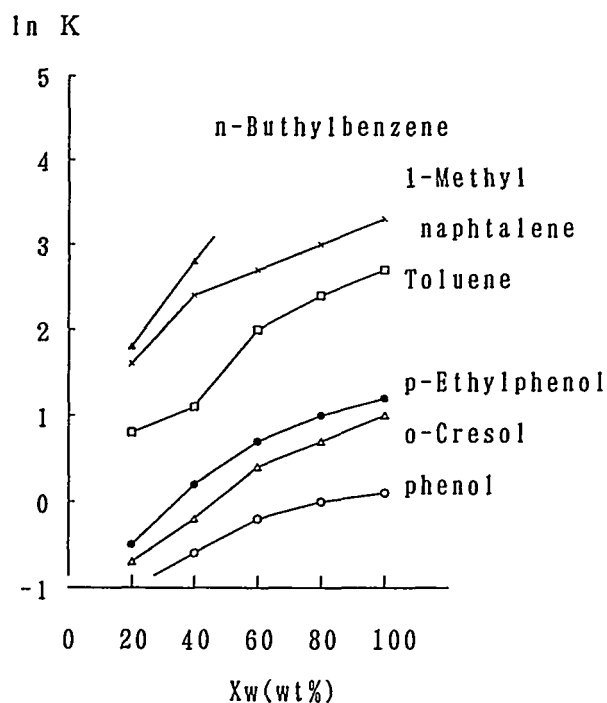


Fig-1 K-values of hydrocarbons and phenols

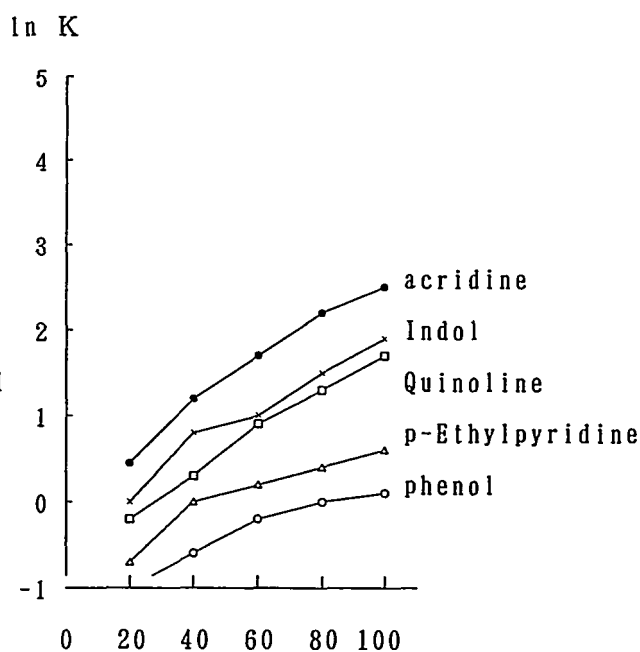


Fig-2 K-values of Nitrogen containing compounds

Study of Upgrading Technology
(Environmental Safety Assessment Tests)

Takakazu Suzuki
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New Energy and Industrial Technology Development Organization (NEDO)

Contractor : Hideto Akaki Chemicals Inspection & Testing Institute (CITI)
 Hisao Ono Mitsubishi Chemical Safety Institute Ltd.

Objectives

NEDO has conducted toxicological studies on several kinds of coal-derived liquids which were newly developed in Japan. They aimed to obtain basic data concerning the health of workers in coal liquefaction plants and environmental conservation, and also to assure public acceptance of the distribution and transportation of such liquids. Test items were selected from the Industrial Safety and Hygiene Law, the Law Concerning the Examination and Regulation of Manufacture, etc. of Chemical Substances* of Japan and "MPD" (Minimum Pre-marketing Set of Data) of the OECD. Analytical studies and surveys of information from abroad were also conducted in order to confirm the evaluation.

* Hereinafter abbreviated as the "Chemical Substances Control Law".

Work Program

During this fiscal year, studies were conducted on the light and medium oils derived from the integrated operations in the brown coal liquefaction pilot plant; the naphtha fraction, mixture of kerosene and light-oil fractions and mixture of heavy oil and residues of crude oil derived from the bituminous coal-liquefied oil; and the naphtha fraction and mixture of kerosene and light-oil fractions of refined oil derived from the bituminous coal-liquefied oil, and the data obtained were compiled.

Summary (1983-1995)

1. Up to FY 1995

To study the safety of brown coal-derived oils, some preliminary data were obtained in

1987 from the liquefied oils of the first hydrogenation process during the early stage of operation at an Australian pilot plant. In 1988 a variety of tests were conducted using the mixture of all the liquid fractions derived from the integrated test operations at the brown coal liquefaction pilot plant in order to determine the overall safety of the liquefied oils. The mixture was used because it shows the comprehensive character of derived oils. Since 1989, a series of data covering the items of the Industrial Safety and Hygiene Law, the Chemical Substances Control Law, and MPD of the OECD have been compiled for the mixture of all the fractions as well as for each fraction of the oils derived from the integrated operations at the brown coal liquefaction pilot plant. As a result, detail data concerning the safety of the liquefied oils derived from the brown coal liquefaction pilot plant were obtained. Further, a variety of tests to determine the safety of bituminous coal-derived oils have been started.

2. For FY 1996

(1) Physical-chemical properties

"Tests of Physical-Chemical Properties" of OECD/MPD were conducted in accordance with the required guidelines, using the mixture of kerosene and light-oil fractions of crude oil derived from the bituminous coal-liquefied oil. The coal-derived liquid has a complex composition with a large number of compounds and does not always produce fixed values for physical-chemical properties. Therefore, the results from these tests should be used with prudence.

Bituminous light oil

• Boiling point	(No fixed value)
• Density	0.9509 g/cm ³ (20°C)
• UV absorption spectra	(Changes by acidic and basic conditions)
• Water solubility	(No fixed value)
• Vapor pressure	490 Pa (20°C)
• Hydrolysis	(Little possibility)
• Dissociation constant	(No dissociation)
• Adsorption/ desorption (log K'oc)	3.18

(2) Acute Oral Toxicity

"Acute Oral Toxicity Tests" of OECD/MPD were performed using male and female rats of Crj:CD (SD) strain in accordance with the required guidelines, using the mixture of kerosene and light-oil fractions of the refined oil derived from bituminous coal liquefied oil. As a result, the single oral dose toxicity was extremely low, and the 50% lethal dose (LD₅₀) is estimated to be more than 2,000 mg/kg for both male and female rats.

Bituminous light oil: LD₅₀>2,000 mg/kg

(3) Eye irritation

"Acute Eye Irritation/Corrosion Tests" of OECD/MPD were conducted with male rabbits of the Japanese white species (SPF) in accordance with the required guidelines, using the naphtha fraction of crude oil derived from the bituminous coal-liquefied oil and the mixture of kerosene and light-oil fractions derived from bituminous coal. As a result, the degree of the eye irritation was classified according to the AFNOR method as follows:

Bituminous naphtha: maximum mean total score 22.3 →

"Moderately irritating"

Bituminous light oil: maximum mean total score 29.2 →

"Severely irritating"

Therefore, the naphtha fraction gave a reversible, moderate irritation, and the mixture of kerosene and light-oil fractions, a reversible, severe irritation.

(4) Repeated oral doses

"Repeated Dose Toxicity Tests in Mammalian Species" of the Chemical Substances Control Law were performed using male and female rats of Crj:CD(SD) strain (SPF) in accordance with the required guidelines, using the mixture of kerosene and light-oil fractions of refined oil derived from the bituminous coal-liquefied oil. As a result, the absolute effective level of this mixture was judged to be 20 mg/kg/day or so based on the clinical signs, body weight changes, food consumption, hematology, clinical biochemistry, urinalysis, and organ weights of the animals. However, the non-observed-effect level

(NOEL) of this mixture will be judged from results of autopsy and histopathological examinations to be performed in the next fiscal year.

(5) Mutagenicity (Bacteria)

"Reverse Mutation Tests in Bacteria" of the Chemical Substances Control Law (The "Mutagenicity Tests in Microorganism" in the Industrial Safety and Hygiene Law) were performed for both presence and absence of metabolic activation system of five strains in accordance with the required guidelines, using the light and medium oils derived from the integrated operations in the brown coal liquefaction pilot plant and the naphtha fraction and mixture of kerosene and light-oil fractions of refined oil derived from the bituminous coal-liquefied oil. As a result, the following results were obtained:

Light oil	: negative (-)
Medium oil	: negative (-)
Bituminous UG naphtha	: negative (-)
Bituminous UG light oil	: negative (-)

(6) Mutagenicity (Chromosomes)

"Chromosomal Aberration Tests in Cultured Mammalian Cells" of the Chemical Substances Control Law and the Industrial Safety and Hygiene Law were conducted for both presence and absence of metabolic activation system of CHL/IU cells in accordance with the required guidelines, using the light and medium oils derived from the integrated operations in the brown coal liquefaction pilot plant, and the mixture of kerosene and light-oil fractions and mixture of heavy oil and residues of crude oil derived from the bituminous coal-liquefied oil. As a result, the following results were obtained:

Light oil	: positive (+)
Medium oil	: positive (+)
Bituminous UG light oil	: negative (-)
Bituminous UG heavy oil	: negative (-)

(7) Biodegradability

"Ready Biodegradability Tests" of the Chemical Substances Control Law were performed by BOD measurement with the standard active sludge in accordance with the required guidelines, using the mixture of kerosene and light-oil fractions of crude oil derived from the bituminous coal-liquefied oil. As a result, the following result was obtained:

Bituminous light oil: 13% by BOD

(8) Fish toxicity

"Acute Toxicity Tests" of OECD/MPD were performed using killifish and carp in accordance with the required guidelines, using the water-soluble fractions (WSF) of the naphtha fraction and mixture of kerosene and light-oil fractions of crude oil derived from the bituminous coal-liquefied oil. As a result, the 50% lethal concentration (LC₅₀) for 24 to 96 hours was as follows:

	LC ₅₀ (96 hr.)	
	Killifish	Carp
Bituminous naphtha fraction	: 0.581 ml/l	0.304 ml/l
Bituminous light oil	: 0.0164 ml/l	0.0155 ml/l

(9) Analytical examinations

The mixture of kerosene and light-oil fractions of crude oil derived from the bituminous coal-liquefied oil were extracted and fractionated into acidic, neutral, and basic components. Benzo(a)pyrene, etc. and phenols were quantitatively determined as toxic indicator compounds, and pyridine and aniline, as basic substances. As a result, the following results were obtained:

	Benzo(a)pyrene		Benzo(a)anthracene		
Bituminous					
naphtha	<1.36		4.73		mg/kg
	Total phenols (each phenol)		Pyridine	Aniline	
Bituminous					
naphtha	13878	(25 to 7210)	<6.82	22.3	mg/kg

3. Future Tasks

Since the last fiscal year, we have conducted a series of environmental safety evaluation studies on the individual fractions of the liquids derived from bituminous coal and selected proper test items from the Chemical Substances Control Law, the Industrial Safety and Hygiene Law, and "MPD" of the OECD to compile their data. Further, we will make a comprehensive judgement of the coal-derived liquids after having performed the environmental safety assessment tests in the same way.

On the other hand, we detected a difference by RUN between the light and medium oils derived from the integrated operations in the brown coal liquefaction pilot plant, but confirmed that there was no difference in the results.

Research on Improvement of Coal Liquefaction Process

T. Suzuki

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Contractor: Y. Kageyama, Nippon Brown Coal Liquefaction Co., Ltd.

Objectives

Research and development is made for the purpose of substantial improvement of reliability, economics and environmental compatibility of coal liquefaction process;

- (1) to solve common technical problems of coal liquefaction process by using a continuous liquefaction test facility of bench scale unit (BSU) and related equipment.
- (1) to contribute to the progress of the coal liquefaction technology as a whole and the coal liquefaction technical package of year 2000.

Work Program

(1) Improvement of coal properties

Prior to liquefaction, coal is thermally treated in solvent to suppress scale formation caused by alkaline earth metals in the reaction process and to obtain higher slurry concentration for high process efficiency. In this thermal pretreatment, high concentration of CO₂ can be recovered, which enables further industrial processing of CO₂ to improve environmental compatibility of the coal liquefaction process.

Furthermore, research is made to optimize solvent properties and catalyst activity at this pretreatment to improve coal reactivity at the liquefaction stage. Based on this research, the effect and limitation of the pretreatment are cleared and the basic idea and the possibility of the pretreatment process are examined.

(2) Optimization of the liquefaction reaction condition

Research is made on the improvement of solvent properties, catalyst activity and the optimization of reaction conditions, such as coal liquid bottom (CLB) and gas recycling to maximize yield of high quality liquefied oil and to suppress the formation of scale. Based on the overall evaluation of these research results, the process concept has been constructed and the possibility for the practical use is examined.

(3) Improvement of the quality of liquefied crude oil

The effect of the heavy solvent and/or hydro-treated solvent on yield pattern of the

liquefied oil is examined to make clear the possibility of lightening and improvement of the quality of liquefied crude oil. Also the effect of using this improved solvent as recycling solvent is examined.

Summary (1981~1996)

1. Up to FY 1995

The Brown Coal Liquefaction project, which was started in 1981, carried out the design, construction and operation of 50 T/D pilot plant in Australia. All these works were completed successfully in 1990. Since then, the conceptual design of a demonstration plant and follow-up study were carried out. Finally, all the results were compiled as the project report, which consists of 10 volumes, totally 10,000 pages, and all programs related to the pilot plant operation were completed in 1993.

In 1991, a special advisory board committee was set up under "Industrial Technology Council" to evaluate the result of the pilot plant operation. The Council proposed that fundamental research should be continued for 3 years to improve the reliability, economics and efficiency of the coal liquefaction process. On the other hand, the energy resources problems of fossil fuels, including coal, are entering into a new phase, as it impacted upon the matter of safeguarding the global environment. Consequently, imbalance between energy resources and environmental problems is expected to become more serious in 21st century.

Considering such circumstances, environmentally compatible coal conversion complex was advocated with the Promotion Headquarters of the "New Sunshine" Program, Agency of Industrial Science and Technology, Ministry International Trade and Industry.

The project started in 1994 succeeding the results of the preliminary study in 1993 to improve the reliability, economics and environmental compatibility of the coal liquefaction technology.

2. For FY 1996

(1) Improvement of coal properties

(a) Effect of solvent properties in coal pretreatment under nitrogen atmosphere on coal liquefaction

The effect of solvent hydro-treated by Ni-Mo-P/Al₂O₃ catalyst using small fixed bed reactor on the coal liquefaction reaction was examined. By the pretreatment at 380°C for 30min. using hydro-treated solvent, the heavy materials were hydrogenated. And at the next coal liquefaction step, the formation of hydrocarbon gasses were suppressed and the oil yield was improved compared with the case of using non hydro-treated solvent.

However, the liquefaction reactivity was decreased compared with the case of no pretreatment. In the case of the nitrogen atmosphere, it is desirable to pre-treat the coal in solvent under 350°C.

(b) Effect of hydrogen gas and catalyst in the process of coal pretreatment

Under the condition of pressurized hydrogen gas with γ -FeOOH catalyst pulverized in solvent, coal was pretreated with 3L autoclave and the effect of this condition on the coal liquefaction reactivity was examined. As a result, the pretreatment (380 ~ 400°C for 30min.) suppressed the formation of hydrocarbon gases and improved the yield of HS (Hexane soluble) in the coal liquefaction reaction. Moreover, yield of HS for unit amount of the hydrogen consumption was improved. Based on these results, the possibility of the improvement of hydrogen usage efficiency and the decrease of reaction time at the high temperature was suggested by the multi step temperature profile reaction which the low temperature reaction of 380-400°C was combined with the high temperature reaction of 450°C. In addition, it was confirmed that the yield of liquefied oil was improved to 63% compared with 50% in the case of single step temperature profile reaction under the multi step temperature profile reaction using in-line hydro-treated solvent and added CLB.

(c) Effect of "Dual Peaks Solvent System" in the process of coal pretreatment

It is expected that the concentration of coal in the reactor can be increased by removing the light fraction in the "dual peaks solvent system" at the pretreatment unit. The coal and dual peaks solvent system, which consists of heavy solvent (b. p. 300-420°C) and light solvent (b. p. 180-300°C), were thermally treated at 320°C for 30 minutes under pressurized nitrogen atmosphere using 3L autoclave. After removing the light solvent by distillation, the coal liquefaction test was done in the same facility. As a result, it has been cleared that oil yield was increased in proportion to the ratio of light solvent and concentration effect of coal slurry. Moreover, it was found that there was a correlation between the viscosity of coal slurry and solid (THFI, THF insoluble) concentration after the thermal pretreatment. From these results, it was found that the oil yield could be improved with increasing coal concentration in the slurry by thermal pretreatment using dual peaks solvent system.

(d) Effect of thermal pretreatment on coal liquefaction and scale formation mechanism

The decomposition behavior of the oxygen functional group of coal during the thermal pretreatment was examined using 1-methylnaphthalene and tetralin as model solvent with

chemical analysis and ^{13}C -NMR method. It was found that the formation of dibenzofuran type ether linkage was generated easily above 400°C by the dehydration of the hydroxyl group of the brown coal under the poor hydrogen donor ability solvent used. It was suggested that thermal pretreatment at high temperature causes the decrease of coal liquefaction reactivity.

On the other hand, the test piece was installed in autoclave in order to investigate the mechanism of carbonate scale formation and the adhesion behavior. As a result, it was clarified that the amount of the adhesion of carbonate to the surface of test piece was proportional to a concentration of ion exchangeable metal in liquid phase. Also, it was found that the carbonate contained in the mineral of recycled CLB hardly adhered as a scale. By the observation of SEM, the structure of scale on the test piece was found that firstly the pyrrhotite from iron catalyst adhered on the surface of the test piece, then the calcium carbonate, dolomite and sodium chloride etc. piled on it. And the amount of scale was proportional to the concentration of catalyst in the liquid phase in the autoclave. These results suggested that the adhesion of pyrrhotite is concerned with the initial stage of the formation of scale.

The condition to control the scale formation was examined using BSU based on these results. Two cases were examined. One case was that the amount of natural iron ore (pyrite) as a catalyst was less than 1% on mafc (as Fe) and CLB was recycled. Another case was that the amount of natural iron ore (limonite) or $\gamma\text{-FeOOH}$ as a catalyst was less 1% on mafc (as Fe) and heavy solvent was used. Both cases showed that the rate of scale formation was decreased to one fifth compared to the case of 50t/d PP using NBCL-K catalyst while the oil yield were maintained as high as 60% on mafc. From these results, it will be possible to operate the plant for one year without scale trouble by the optimization of catalyst and reaction condition. This estimated continuous operation time "one year" corresponds to five times of proven continuous operation time 1700 hours of 50t/d PP in Australia.

(2) Optimization of liquefaction conditions

(a) Effect of solvent properties on liquefaction reaction

BSU tests were carried out under the condition of small amount of catalyst loading and usage of heavy solvent (b. p. $300\text{--}420^{\circ}\text{C}$) as a circulation solvent. Catalysts used were the natural pyrite, limonite and $\gamma\text{-FeOOH}$. As a result, it was found that the activity of recycled catalyst can be maintained and the amount of new catalyst loading can be reduced by keeping the concentration of hydrogen sulfide in a reactor to be 0.5–1vol%. Furthermore the prolonged residence time in a reactor could reduce the amount

of γ -FeOOH catalyst to 0.3% on mafc (as Fe). Even the case of using cheaper natural pyrite or limonite, the amount of catalyst can be reduced to 1% on mafc (as Fe) keeping the oil yield to be above 60% on mafc and the high quality.

(b) Effect of catalyst characteristic on liquefaction reaction

The liquefaction activity of various iron catalysts were compared using autoclave. Among these catalysts, iron oxyhydroxide catalyst demonstrated the highest activity, and it was found that the tendency of increasing of the oil yield is proportional to sulfur to iron (S/Fe) atomic ratio in the reactor. Based on these investigation and analysis of catalyst, the dominant factors for the activity of iron catalyst were the ratio of pyrrhotite of iron sulfide, the crystal size of pyrrhotite and keeping the concentration of hydrogen sulfide over 1% in the reactor to prevent the deactivation of recycled catalyst. Moreover, the activity of synthetic hematite (α -Fe₂O₃) were lower than the pyrite catalyst. Since the natural iron ore (limonite) which contains the iron oxyhydroxide has higher activity than pyrite and is easy to be pulverized. From these results, the natural iron ore is considered to promise as a cheap, practicable liquefaction catalyst.

(c) Effects of gas and CLB recycling on liquefaction reaction

In order to clarify the gas recycling mechanism on liquefaction kinetics, the liquefaction tests using a gas flow type 5L autoclave, which can withdraw the light fraction continuously from it, were carried out. As a result, the oil yield was increased while CLB and the hydrocarbon gas yields were decreased in the case of using the full fraction range solvent. However, in the case of using a heavy solvent, this effect was small. These results were same as the tests using BSU. Because the light fraction formed in the reactor is withdrawn from the reactor when the gas flow is increased, it is thought that the decomposition of the light fraction is prevented and therefor the yield of the hydrocarbon gas is decreased. Moreover, it was found that the oil yield increases with increasing of H₂S concentration in the recycling gas. However, the effect of CO is small. Consequently, the role of the gas recycling is to maintain the concentration of H₂S in high to keep activity of the recycled iron catalyst, and also to prevent the decomposition of light fractions to improve the oil yield.

The effect of the different recycling routes of CLB on the liquefaction performance was investigated using BSU. The oil yield increased when CLB was directly recycled to the first reactor compared with the recycling to the coal slurry making section. This suggested that retrogressive reaction of CLB occurred at the pre-heater section when

CLB was heated with the coal slurry and this reaction decreased the oil yield. And the comparison of the cases where CLB is recycled to the first reactor or to the second reactor showed the oil yield was almost the same. Although the real residence time of a reactant of the reactor section was slightly longer when CLB was recycled to the second reactor. On the base of the same real residence time, the high oil yield can be achieved when CLB is recycled to the first reactor directly without passing the pre-heater.

(d) Improvement of quality of liquefied crude oil

It was found that the viscosity of coal slurry using in-line hydro-treated solvent was decreased greatly compared with coal slurry using the non hydro-treated solvent. This reason is that the oxygen compound in the solvent was decreased by in line hydro-treatment. And the possibility to increase the concentration of coal slurry was expected to be up to 50wt%.

Future Tasks

The effect of the dual peaks solvent system in the thermal pretreatment section and the multi step temperature profile reaction shall be further investigated. And, the improvement of quality of coal liquefied oil by in-line hydro-treatment and the effect on the storing stability of coal liquefied oil shall be further investigated. After the research and development using BSU, the facility will be inspected and the result will be used as the reference information on the selection of the plant material.

Advanced Technology for Coal Liquefaction

T. Suzuki

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Objectives

Research and development are carried out for fundamental and innovative concept for the coal liquefaction technology in the next generation with higher environmental compatibility and higher process efficiency. The work will contribute to the progress of the coal liquefaction technology and the technical package of year 2000.

Work Program

(1) Fundamental research for highly dispersed catalysts with high activity

Study is to be carried out on preparation, pulverizing, dispersion and prevention of agglomeration of catalyst, behavior of sulfurization of catalyst, evaluation of catalyst characteristics, catalytic activity for liquefaction and liquefied oil characteristics. In addition, the practical catalyst candidate such as the limonite iron ore is selected.

(2) Fundamental research on possibility of perfect coal liquefaction process

Study is to be carried out on the control of initial stage reaction of liquefaction to evaluate the possibility of perfect coal liquefaction especially by utilization of solvent and catalyst function. Also, study is to be carried out on optimization of oil to gas yield ratio, especially from the effective utilization of hydrogen point of view. The process concept based on these results is constructed and the possibility of practical use is summarized.

Summary (1981~1996)

1. Up to FY 1995

The Brown Coal Liquefaction project, which was started in 1981, carried out the design, construction and operation of 50 T/D pilot plant in Australia. All these works were completed successfully in 1990. Since then, the conceptual design of a demonstration plant and follow-up study was carried out. Finally, all the results were compiled as the project report, which consists of 10 volumes, totally 10,000 pages, and all the

programs were completed in 1993.

In 1991, a special advisory board committee was set up under "Industrial Technology council" to evaluate the result of the pilot plant operation. The council proposed that fundamental research should be continued for three years to improve the reliability, economics and efficiency of the coal liquefaction process. On the other hand, the energy resources problems of fossil fuels, including coal, are entering into a new phase, as it impacted upon the matter of safeguarding the global environment. Consequently, imbalance between energy resources and environmental problems is expected to become more serious in 21st century.

Considering such circumstances, environmentally compatible coal conversion complex was advocated with the Promotion Headquarters of the "New Sunshine" Program, Agency of Industrial Science and Technology, Ministry International Trade and Industry.

The project started in 1994 succeeding the preliminary study in 1993 to improve substantially the reliability and economics and environmental compatibility of the coal liquefaction technology.

2. For FY 1996

(1) Research of highly dispersed catalysts with high activity

(a) Sulfurization behavior of iron catalyst

Sulfurization behavior of the iron catalyst was examined using rapid heating autoclave. It was found that fine pyrrhotite (Fe_{1-x}S) particles are generated via Fe_3S_4 at near 250°C and then the crystal grew with the temperature in the case of the iron oxyhydroxide system. The TEM photograph observation showed that the ruin particle of the iron oxyhydroxide existed at the low temperature but these ruin particles disappeared and big growth of the pyrrhotite crystal was observed at high temperature. On the other hand, the ruin particle is not observed for iron oxide catalyst ($\alpha\text{-Fe}_2\text{O}_3$) and the pyrrhotite phase is generated on the surface of the particle near 300°C and the crystal growth rapidly occurred above 400°C . As for the pulverized pyrite ore, the transition temperature to pyrrhotite was near $300\text{--}400^\circ\text{C}$ and in the course of transition the pyrrhotite particles were melted to make a big crystal. The pulverized limonite ore transited to pyrrhotite at 300°C , then crystal growth was occurred via fine pyrrhotite crystal. So, the crystal size of pyrrhotite from limonite ore was relatively small as well as the synthesized $\alpha\text{-FeOOH}$. It is thought that the catalyst activity depends on the transition temperature of pyrrhotite and the growth rate of the crystal.

(b) Effect of amount of sulfur on iron catalyst

When the amount of sulfur was increased, the crystal growth rate at 450°C was suppressed in the case of γ -FeOOH catalyst, and in the case of limonite catalyst, the crystal size of pyrrhotite was small. It is effective to prevent crystal growth of pyrrhotite at high temperature that the partial pressure of hydrogen sulfide in the reactor should be kept above 1 volume %.

(2) Basic research on the possibility of residue less coal liquefaction

(a) Scouting study on the initial stage condition during coal liquefaction

The relationship between the hydrogen consumption through the stage of preheating to liquefaction and properties of the products was examined using rapid heating autoclave in order to find the optimized condition of hydrogen transfer in coal liquefaction. In the case of γ -FeOOH catalyst, a large consumption of hydrogen at preheating stage was observed and the HS (hexane soluble) yield was improved compared with pyrite catalyst. As γ -FeOOH catalyst can donate hydrogen especially at the initial stage of liquefaction, a decomposable and high H/C ratio pre-asphaltene is made and the formation of hydrocarbon gas is prevented. As a result, this catalyst brought high HS yield. Moreover, it was found that pre-asphaltene can be decreased and HS yield can be improved further by using an in line hydro-treated solvent.

(b) Analysis of structural changes of coal throughout the liquefaction reaction

The oxygen functional group of Indonesia Banko coal, which is promising for a feed stock of coal liquefaction plant, was analyzed by FT-IR and solid ^{13}C -NMR. As a result, it was found that the oxygen functional groups such as the carboxylic group, hydroxyl group etc. were less and more of aliphatic carbons than that of the Australian Yallourn coal

Future tasks

The possibility of the practical use of the limonite iron ore selected as a high performance catalyst shall be investigated, and also the method of maintaining the activity of the recycled catalyst shall be examined. The difference of initial liquefaction stage of the various kind of coal shall be examined, and the flexibility of the liquefaction process will be improved. Moreover, the basic data of the solvent de-ashing for various kind of coal shall be collected.

The Development of Highly- dispersed Iron Catalyst for Coal Liquefaction

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Objectives

The objectives of the study is to improve the performance and economic viability of the NEDOL process. As one approach, attention is paid to the highly dispersed iron catalysts searching the possibility of the reduction of catalyst amount through preparation of iron catalyst loaded on coal and liquefaction tests. Results of the work will make for the technical package 2000.

Work program

Based upon the fundamental research on coal liquefaction catalyst, in order to construct the AWIP preparation and liquefaction system which will be feasible technically and economically among others from a view point of industrial application, the followings were studied;

- Catalyst preparation and liquefaction tests
 - a) effect of sulfur to iron ratio at reaction
 - b) effect of AWIP preparation and liquefaction conditions
 - c) effect of reaction pressure for 50wt% coal slurry
- Application of AWIP to other coals

Summary (1991~1996)

1. Up to FY1995

We have prepared and tested three types of catalyst loaded on coal as dispersed catalyst or catalyst precursor as shown below.

CIS $\text{FeSO}_4 + \text{Na}_2\text{S} \rightarrow \text{FeS}, \text{FeS} + \text{Coal} \rightarrow \text{FeS on Coal}$

AIP $\text{FeSO}_4 + \text{Coal} + \text{Ammonia} \rightarrow \text{iron hydroxide on coal}$

AWIP $\text{FeSO}_4 + \text{Coal} + \text{Process wastewater} \rightarrow \text{Iron hydroxide on coal}$

All the catalysts showed a higher activity than direct introduction of Synthesized Iron Sulfide (SIS) catalyst. Among them, AWIP exhibited the highest activity.

One of the attractive features of the catalyst-loading approach is only to load the catalyst or catalyst precursor on a fraction of the feed coal. This fraction is then mixed with the remainder of the feed coal. At the mix rate of 5~10 wt% and mean catalyst content of 0.6 wt% (as Fe+S), the oil yield was almost the same as the results of standard catalyst (SIS : 3 wt%). From the results of batch tests conducted so far, when the activity of the catalyst used was compared by the oil yield at the same catalyst amount, the ranking was AWIP > AP, CIS > SIS. Among them AWIP is most attractive in view of preparation cost as predicted from the above equation.

The other attractive features of AWIP is that it is effective for the liquefaction of high concentration coal slurry to keep the oil yield as almost the same as in the case of 40wt% coal slurry at the worst.

According to TPS (Temperature Programmed Sulfurization) and TPR-S (Temperature Programmed Reduction of Sulfided materials) analyses for AWIP on carbon black and AWIP on no carrier, mean diameter of pyrrhotite is smaller and sulfur to iron ratio is higher for AWIP on carbon black, and the reduction temperature in TPR-S is in the order of AWIP on carbon black > single AWIP > SIS. The same phenomenon will be expected in AWIP on coal system and this will be one of the reasons this type of catalyst has higher activity.

2. For FY1996

In regard to the AWIP preparation and mix - liquefaction system - using the process wastewater and the inexpensive iron compound, catalyst component (Fe) is precipitated and loaded on a fraction (X) of the feed coal (100). This fraction is then mixed with the remainder of the feed coal and sulfur prior to liquefaction reaction -, some preparation and liquefaction tests were conducted.

(1) Batch preparation of AWIP and liquefaction tests

(a) AWIP preparation conditions and liquefaction conditions

Figure 1 shows the relation between the oil yield and hydrogen initial pressure for the liquefaction test using AWIP on Tanito Harum coal. Hydrogen initial pressure over 70 kg/cm² gave the decreased oil yield at catalyst addition of 0.38wt% (as Fe and S/Fe=1.0). In contrast to this, at the same Fe addition rate but sulfur to iron ratio of 2.0 the reactivity was recovered at hydrogen initial pressure of 80 kg/cm² and over.

In the next place, tests conducted at catalyst addition rate of 0.6wt% (as Fe+S) showed that the catalytic activity at sulfur to iron ratio of 2.0 (Fe:0.28wt%) was higher than that at sulfur to iron ratio of 1.0 (Fe:0.38wt%). Figure 2 shows these relations in the case of Shenmu coal.

In order to rationalize the AWIP preparation system a new preparation procedure (PREP2) a little different from the standard preparation procedure (PREP1) was developed.

Figure 3 summarizes the liquefaction test results over the prepared AWIPs by two modes. Liquefaction test was conducted at sulfur to iron ratio of 1.0 and 2.0. Almost the same level of oil yield was obtained between the two preparation modes when compared at the same catalyst amount and sulfur to iron ratio.

As a result we got to the conclusion that further reduction in catalyst preparation cost would be possible by cutting down the amount of iron through the proper selection of the preparation procedure and liquefaction conditions.

(b) Effect of reaction pressure for 50wt% coal slurry using AWIP catalyst

In order to investigate the possibility of mitigation in liquefaction reaction conditions, we conducted liquefaction experiments at reaction pressures less than 170 kg/cm², standard pressure of this study, for 40wt% coal slurry. Decreasing tendency of oil yield according to lowering the reaction pressure was smaller than expected. We confirmed that the same relations were obtained for 50wt% coal slurry liquefaction. Test results of AWIP/Tanito Harum coal are summarized in Figure 4.

(c) AWIP property and liquefaction performance

AWIP with no carrier (single AWIP) has lower catalytic activity than AWIP on coal as mentioned above. According to Moessbauer analysis a difference in their composition of iron compounds was observed between the two.

Also the Moessbauer analyses and observations of TEM images on AWIPs on coal revealed that the preparation procedures and/or conditions might affect the catalytic activities.

(2) Coals tested

We applied the AWIP to three Chinese coals additionally to the coals so far tested and confirmed that the AWIP could be applicable to various coals with carbon content of 69~81wt% including those coals.

Foresaid Figure 2 is an example of Chinese Shenmu coal with high inertinite content of 32% for #2 seam coal and 24% for #3 seam coal.

(3) Continuous AWIP preparation apparatus

We assembled the small sized continuous preparation apparatus. After completion a mechanical running and preliminary preparation tests were conducted. The apparatus is equipped with feeding pumps, powder feeders and mixing vessels, and we selected the preparation sequence and performed the trial operations in two modes.

Future Tasks

- (1) Investigation into continuous preparation conditions of AWIP on coal
- (2) Investigation into preparation conditions and catalyst property
- (3) Investigation into coal liquefaction conditions and product yield
- (4) Performance test using Bench Scale Unit and Process Supporting Unit

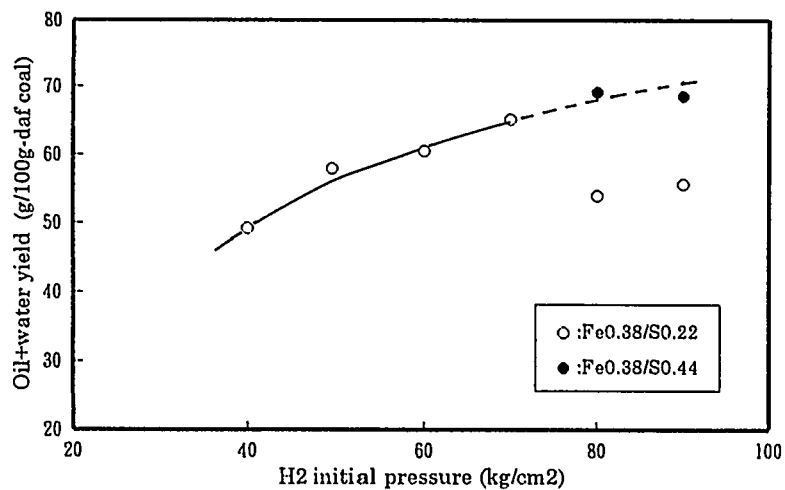


Fig.1 Relation between hydrogen initial pressure and oil yield
(Tanito Harum / 500ml Autoclave)

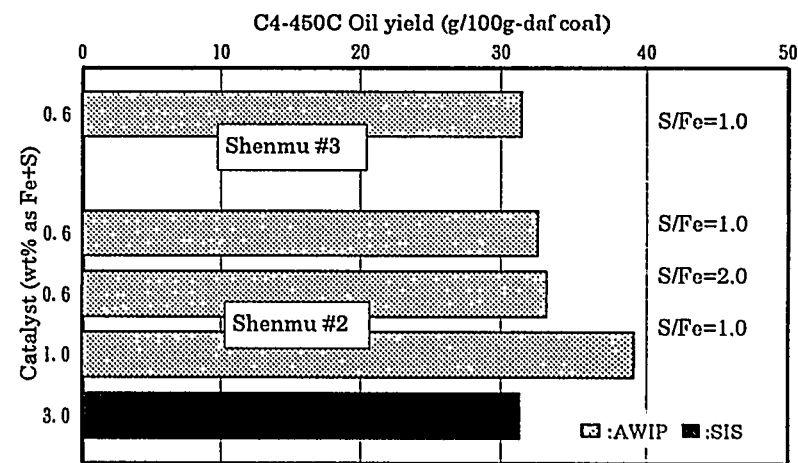


Fig.2 Effect of sulfur to iron ratio on oil yield
(Shenmu #3 & #2 / 0.01t/d continuous unit)

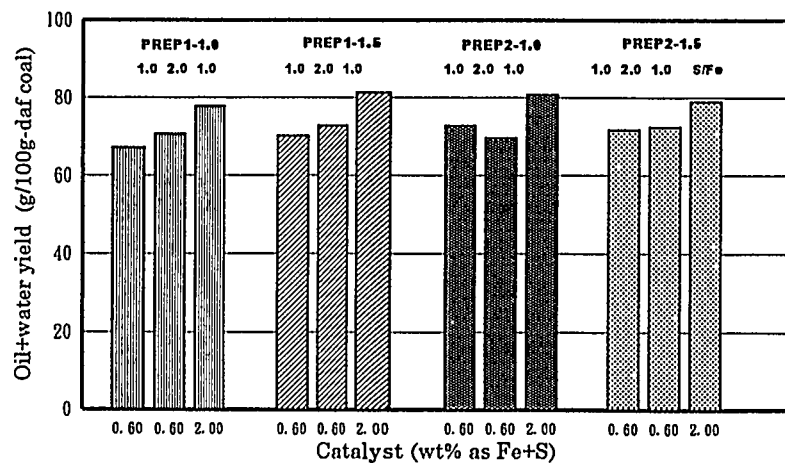


Fig.3 Effect of AWIP preparation and liquefaction conditions on oil yield
(Tanito Harum / 500ml Autoclave)

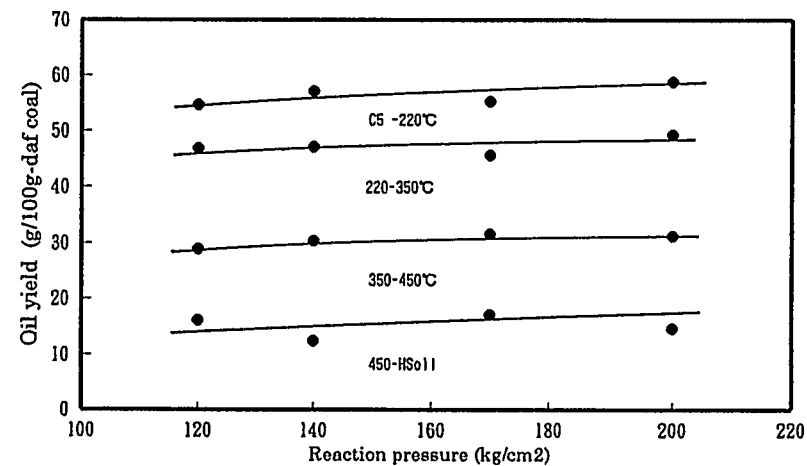


Fig.4 Reaction pressure and oil yield for high concentration coal slurry
(Tanito Harum AWIP0.6wt%/50wt% coal slurry/0.01t/d continuous unit)

Coal Liquefaction under Advanced Conditions

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Objectives

To construct a basis of advanced and environmentally acceptable coal liquefaction technology.

Work Program

(1) Liquefaction and pyrolysis of finely pulverized coal

Improvement of conversion on liquefaction of coal by finely pulverization of coal and catalyst. Investigation of reaction between coal and hydrogen gas.

(2) Basic studies on mild conversion of coal

Elucidation of transfer mechanism of hydrogen from gas phase and/or solvents over carbon-supported metal catalysts in the coal liquefaction system in order to increase oil yield by deep hydrogenation at lower temperatures.

(3) Basic studies on structures and liquefaction reactivities of low rank coals

Investigation of liquefaction processes suitable for low rank coals by better understanding their chemical structures and reactivities

(4) Biotreatment of sulfur containing compounds in coal-derived oil

Advanced biological desulfurization and development of energy saving biological desulfurizing methods.

(5) Characteristics of coal liquefaction residues and their handling

Investigation of relationships between characteristics of coal and its liquefaction residue, and basic studies on combustion characteristics of coal liquefaction residue..

Summary (1993-96)

1. Up to FY 1995

(1) Liquefaction and pyrolysis of finely pulverized coal

Reaction mechanism of finely pulverized coal was investigated. Relatively higher conversion was obtained on liquefaction of finely pulverized coal. Reactivity of swollen coal by solvent was studied.

(2) Basic studies on mild conversion of coal

The structural change of coal by non-equilibrium plasma treatment which was accompanied by dewatering and deoxygenation and its effect on the liquefaction reactivity have been investigated. In addition, we applied hydrogen plasma to the

reduction of ruthenium supported over various kinds of metallic oxides such as manganese oxide-nickel oxide catalyst etc. We found that the plasma treatment did not give higher catalytic activity than the conventional reduction method when the temperature of hydrogen plasma was the same as that in conventional reduction. However, the plasma treatment significantly shortened the reduction time.

(3) Basic studies on structures and liquefaction reactivities of low rank coals

Artificial coals were prepared by hydrous pyrolyses of cellulose, red pine, peat and leaf at 200-400 degree C, and their structures were compared with those of natural coals by using elemental analysis, FT-IR and ¹³C-NMR. The hydrogenated products of artificial and natural coals were characterized by capillary GC and GCMS, and compared one another.

(4) Biotreatment of sulfur containing compounds in coal-derived oil

Various kinds of mercaptans were found to be degraded by methyl mercaptan oxidase purified from sulfur oxidizing bacterium, *Thiobacillus thioparus* TK-m. To use this enzyme for removing mercaptans from coal-derived oil, we revealed the method to get a lot of amount of the cell and the enzyme, the best conditions for the enzyme to degrade mercaptans, and the degradation rate of various mercaptans by the enzyme. Then we revealed that the intact cells of strain TK-m degraded the various mercaptans.

(5) Characteristics of coal liquefaction residues and their handling

The genesis and fate of carbonaceous materials formed during coal hydrogenation and the significance of such materials in the operation of continuous coal hydrogenation reactors were investigated.

2. For FY 1996

(1) Liquefaction and pyrolysis of finely pulverized coal

100 mesh coal (70 μ m) and finely pulverized coal (8 μ m) were decomposed by using thermo-balance under the pressure of 760 Torr and 1 Torr of hydrogen and helium respectively. Under 1 Torr of hydrogen, reaction between coal and hydrogen atom, produced by microwave discharge, was carried out. Conversion was obtained from weight of sample and products were detected by mass spectrometry.

Under helium gas, carbon dioxide, carbon monoxide, and methane were produced. Conversion of coal increased with temperature. Remarkable effect of pressure was not observed on the conversion of coal under helium. On the other hand, methane was produced over 800 degree C under higher pressure of hydrogen. Production of methane was detected from the reaction between coal and hydrogen atom over 600 degree C. Benzene and toluene were not observed in this reaction system. Slightly higher conversions and yield of products were observed on the pyrolysis of finely pulverized

coal than 100 mesh coal. The slight effect of coal diameter implies that interaction between the surface of coal and hydrogen gas was not enough due to small sample holder of thermo balance.

The specific surface area from BET multi point plot was calculated from the nitrogen adsorption isotherm at 77 K for raw and finely pulverized Taiheiyo coal and their char heat treated in argon flow. Raw Taiheiyo coal (particle size of 150-300 μm) showed no adsorption of nitrogen at 77 K. Its char heat treated at 800 degree C showed 20 m^2/g of specific surface area. The development of surface area during heat treatment was not affected by the oxidation on raw coal with nitric acid treatment. On the other hand, finely pulverized coal with average particle size of 4 μm and its char heat treated above 600-800 degree C showed the specific surface area of 10 m^2/g and 175-200 m^2/g , respectively. Therefore, the increase of specific surface area of finely pulverized coal and its char was resulted in the decrease of particle size, but not by the oxidation during the pulverize process.

(2) Basic studies on mild conversion of coal

The elucidation of hydrogen transfer is still essential for the understanding of liquefaction reaction and further for the design of efficient process of which the retrogressive reactions are effectively suppressed. Additionally, the development of highly active and dispersed catalyst has been required to improve the process performance. In this work, the mechanism of hydrogen transfer over metal-supported active carbon catalysts and their catalytic activities were studied. Metal (Fe, Co, Ni and Ru)-supported and unsupported active carbon catalysts were prepared and the transfer of hydrogen from donor solvent and gas phase was quantitatively measured in a fixed bed flow reactor under liquefaction conditions.

The following results were obtained; 1) the metal free active carbon was catalytically active for both dehydrogenation of donor solvent and hydrogenation of aromatic compounds, and hydrogenation rate depended on the amount hydrogen atom dissociated on the carbon, 2) the addition of metals onto the carbon significantly promoted dehydrogenation from donor solvent, but the hydrogenation of aromatic compounds behaved differently among metals used. Ni and Ru greatly improved hydrogenation activity of active carbon, while Co and Fe lowered the hydrogen transfer ability of active carbon throughout temperature range. Based on these results, the mechanism was discussed.

(3) Basic studies on structures and liquefaction reactivities of low rank coals

Ishikari peat and biodegraded leaf were extracted with benzene-ethanol at 100, 150, 200 and 250 degree C. The yields of the extracts were 29-40wt%, and they consisted mainly of asphaltene(hexane-insolubles) and hexane-soluble polar material. There was not a significant difference between the structures of asphaltenes from peat and

biodegraded leaf. It is assumed that asphaltene contains normal alkyl chains, polycondensed cyclic skeletons, lignin-like monoaromatics and sugar which are linked with ester, ether and amide bonds and have oxygen-functional groups such as COOH and OH. Polycyclic skeletons may be derived both from polycyclic constituents in lipids and from the condensation products of carbohydrates with lignin, lipids and/or protein. Asphaltene extracted at 100 degree C was much abundant in normal alkyl chains and polycyclics from lipids. The nonextractable residues were mainly composed from polycyclic skeletons which were formed from the condensation reaction of biopolymers during a peatification or a biodegraded process. The bridge bonds in low rank coals are rich in ester, ether and amide, then the usage of super critical solvent like methanol and alkali catalyst will improve the extract yield. The extraction followed by hydrogenation should be a promising way to convert peats to fuel oils.

(4) Biotreatment of sulfur containing compounds in coal-derived oil

(a) Advanced biological desulfurization

We obtained an organic solvent-sensitive bacterium capable of degrading dibenzothiophene (DBT) under microaerobic (nitrogen exchange) conditions. The bacterium with the highest DBT-degradable activity was mutated and an *n*-heptanol-resistant mutant was selected. Although the parents strain did not grow in 0.1% v/v *n*-heptanol at all, the mutant did grow even in 50% heptanol and could still retain the ability to degrade and assimilate DBT in 5-10% heptanol, nonanol, or decanol under microaerobic conditions. The percentages of odd-chain fatty acids (C15 and C17), unsaturated fatty acids (especially the trans form), and isooctadecanoic acid were significantly greater in the mutant strain than the parent strain.

(b) Development of energy saving biological desulfurizing methods

To develop bioreactors for removing mercaptans from coal-derived oil, the basic research was carried out. As a model of coal-derived oil, *n*-hexane was used. As mercaptans in coal-derived oil, we used ethyl mercaptan, *n*-propyl mercaptan and *n*-butyl mercaptan which are contained in the low boiling point fraction of coal-derived oil. To 10 ml-vials, 3 ml of *n*-hexane containing 0.1 mM of one of these mercaptans, and 3 ml of the cell suspension of the sulfur oxidizing bacterium, *Thiobacillus thioparus* TK-m were added, and then the vials were sealed and shaken. Every mercaptans were degraded. The less number of carbon atom was contained in the molecule of the mercaptan, the faster the mercaptan was degraded. When all the three mercaptans were added to the same vial, the degradation of each mercaptan was performed simultaneously. The degradation rate of each mercaptan was almost same in the both cases. By the experiments using various amount of the cells, we supposed that in these degradation experiments the rate limiting process was not the degradation rate of the cells, but the diffusion rate of the mercaptans from the *n*-hexane layer to the cell suspension. By the

degradation of the mercaptans the production of sulfate was observed. Thus we have revealed that we can remove mercaptans from coal-derived oil by adding cell suspension of strain TK-m to the oil containing mercaptans.

(5) Investigation of coal liquefaction residues

Various coal liquefaction residues were obtained from the operations of 1 t/d PSU. To examine the relationship between properties of coals and their liquefaction residues, coals and their liquefaction residues were analyzed and tested. The liquefaction residues were hydrogenated in an autoclave again. Consequently, it was found that the liquefaction residues still contain rather high quantity of intermediate constituents, such as asphaltene and preasphaltene.

A pressurized thermogravimetric analyzer(TGA) and a high pressure drop-tube reactor(HP-DTR)were used to estimate the combustion characteristics of the coal and the liquefaction residue for the effect of pressure. The ignition temperature of the coal and the liquefaction residue lowered with an increase in pressure. UC%, an index of unburned carbon on combustion, of coal decreased from 8% at atmospheric pressure to 1% at 2.0 MPa. Similarly, UC% of liquefaction residue decreased from 21% to 2%. As a results of SEM, it was found that size of spherical ash in combustion residue was bigger with increasing pressure. Additionally, as a peak intensity of XRD for combustion residue at 2.0 MPa was very weak, it was suggested that ash was more melted and progressed more amorphous state at higher pressure. These results suggest that the increase in pressure is effective to improve the combustion reactivity of coal and liquefaction residue.

Future tasks

To investigate the effective method for separation of coal macerals.

Research on City-Mode Coal · Waste Co-Liquefaction Process

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Clean Coal Technology Center

New Energy and Industrial Technology Development Organization(NEDO)

Contractor: Y. Tsuru The Japan Institute of Energy

1. Objectives

It can be said that it came in the complete grade about the manufacture technology of the liquid fuel from the coal. But, it is the present condition that the manufacture cost is still high toward the price of the present crude oil, and is low as for the competition power.

As for the cause, the first with three is low the efficiency of the capacity of the reactor. The second is high the rate of the cost of hydrogen, and it is necessary the development of the use for the residue by third.

As the way for improvement the capacity efficiency of reactor, Co-liquefaction with the heavy oil (distillate from petroleum or unused natural heavy oil as oil sand bitumen) and coal will reduce the catalyst circulation process.

It thinks about the use of the waste plastics which has the nature which gives it hydrogen as a method which reduces the amount of use of hydrogen. If it can be placed on one of the ways of disposing of a waste plastics, a degree of contribution to the solution of the social problem along with the waste becomes high. Furthermore, this method is thought predominance to be formed in the transport of the product and the point of the consumption if it becomes possible to be built a coal liquefaction equipment in the densely populated district where a waste plastics occurs.

And, hydrogen under the high pressure and high concentration like before is not necessary any more, if the residue produced in the coal liquefaction can be used as a caking additives for the coke manufacture. In other words, it doesn't need to raise the yield ratio of the light fuel oil any more, and the reducing of the pressure of hydrogen will be possible.

From the above thing, the decrease of the cost of equipment, the decrease of the manufacture cost and effect such as improving of the oil product can be expected by doing the treatment which mixed coal, heavy oil and waste plastics.

The investigation research of the possibility that the phenomenon shown in the above happens should be done in the wide range.

2. Work program

- (1) Advance the investigation of the possibility of the technology that it disposes of coal, heavy oil and the waste plastics together.
- (2) Research referring to the coal liquefaction technology until now from FY 1996.

- (3) Examine the compound process which has the following purpose concretely.
- (4) Use low price COG as the hydrogen source which is produced in the ironworks, and hydrate coal and heavy oil (ex. tar sand bitumen) comparatively on the mild condition.
- (5) Furthermore, attempt a cost reduction by taking hydrogen from the waste such as a plastics.
- (6) Produce the formation oil which can change into the product, and a binder for the coke manufacture at the existent oil factory.
- (7) Examine independent subjects described below, and make a final summary in FY 1998.
 - ① Execution of the foundation investigation
 - ② Execution of the macro-feasibility study for the propriety as a commercial plant
 - ③ Examination as a commercial plant

3. Summary

- (1) Plan for the new process

The economical liquefied process which coal, heavy oil and waste plastics were used for has been proposed. (Refer to the figure described below)

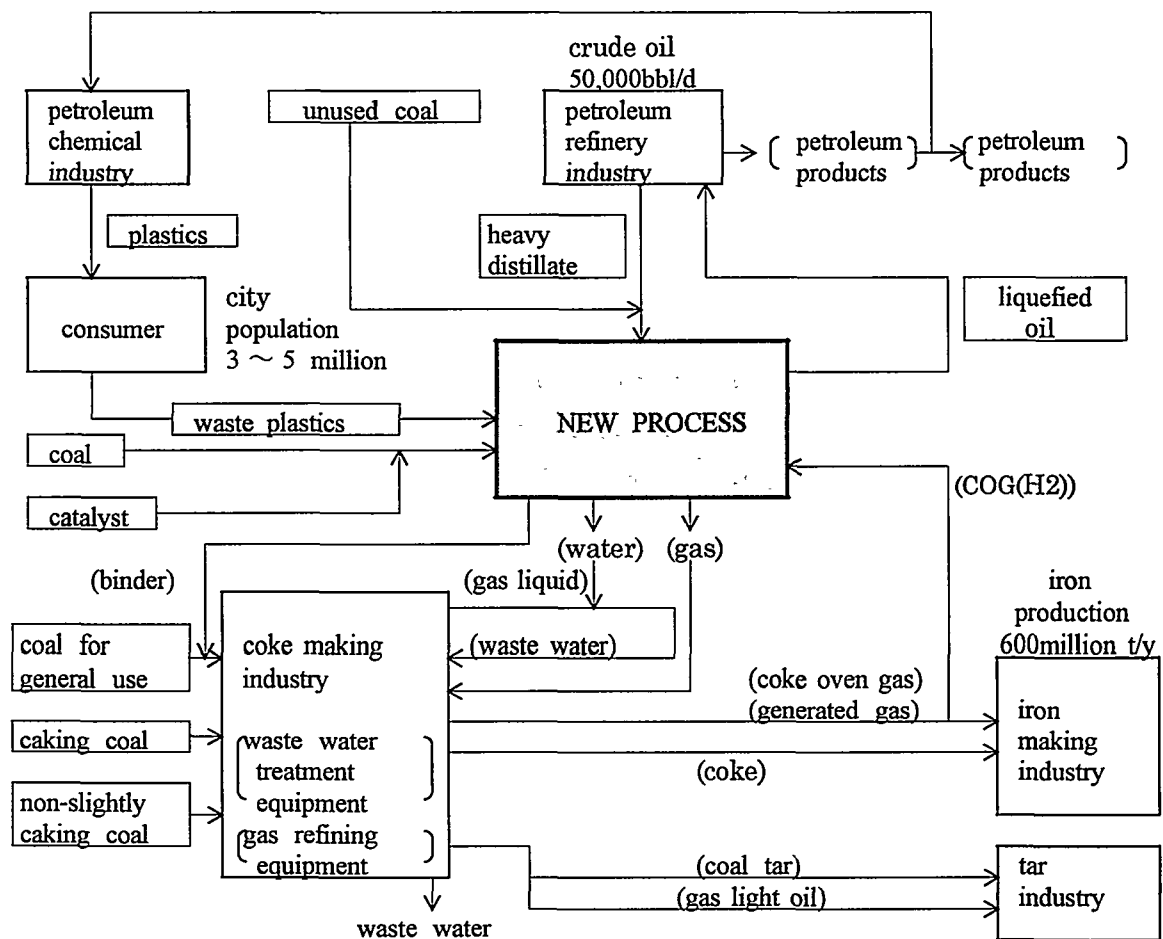


Figure Coal, heavy distillate, waste plastics co-liquefaction process

This process can use the coke oven gas (COG) which contains hydrogen in a large quantity as a source of supply of hydrogen. Therefore, construction of the process into the ironworks with the coke oven is desirable. And, electric power, steam, water for industrial use and other utilities could be offered from the ironworks, too.

The whole big reduction of the equipment is possible including the manufacture of hydrogen, the utilities, the treatment of the drainage, and so on. The residue can be used as a caking additives of the coke manufacture though residues increase when it disposes of coal on the mild condition. This thing will become a big advantage to build this process in the ironworks.

The decomposition temperature of the waste plastics almost corresponds to the liquefaction temperature of it. Therefor, it can be expected that oil can be gain comparatively easily by treating coal with heavy oil.

(2) Subjects of new process

① The present condition and the subjects of the material as a raw

At present, as for the research of the coal liquefaction project, though Tanitohalm coal is being given to the candidate of No.1, an economical examination including other coal is necessary.

The C heavy oil and the asphalt from the petroleum, the tar from coal and the oil sand, and so on are raised as a candidate of the cheap heavy fuel oil which can be supplied in a large quantity.

② The present condition and the subjects of the treatment technology of the material as raw

Coal liquefaction technology, a catalyst and the technology related to the quality improvement of the liquefied oil are studied in the clause of (4)Studies on related subjects.

There are co-liquefaction processes in which a heavy distillate and an oil sand and coal are hydrated and decomposed at the same time. HRI (in America) puts the power in the development of this technology.

Some liquefaction equipment of the waste plastics work even in Japan.

About these technology are studied in the clause of (4)Studies on related subjects..

③ The evaluation the coal as a raw material of coke and a caking additive

Though the quantitative technique that evaluated heavy oil as a caking additives until now wasn't established, it was established how can to estimate MF (reflectance) at Ro (fluidity) easily from the analysis value of the heavy oil.

And, it tried as for the way of evaluating the economy which could be compared with the raw coal by Ro, MF and other characteristic value of caking additives

(3) The results of the element research

The foundation test investigation to confirm the possibility of this process was done in FY 1996 to realize the above plan.

① The examination for certification (collect fundamental Data)

a. Examination for investigating quality of mixed raw materials

We have acquired knowledge on quality of mixed slurry compared with coal (Tanitohalm coal), heavy oil (tar sand bitumen), waste plastics (PP, PE, PS). We have measured viscosity of slurry and examined conditions under which slurry can be transported during co-liquefaction with 0.01t/d continuous test machine. The results shows that the viscosity of mixed slurry was 5,000 cp at 80 ~ 90 °C and the slurry could be transported to the 0.01t/d test machine.

b. Liquefaction test of mixed raw material with gas with high hydrogen content

We have examined co-liquefaction test of coal (Tanitohalm coal), heavy oil (oil sand /coal liquefaction recycle oil mixture), waste plastics (PP, PE, PS) under a high pressure and high temperature. The results showed that liquefaction proceeded smoothly by adding waste plastics.

c. Mixed raw material liquefaction test with COG

To improve the economical efficiency, we have examined liquefaction tests with mixed gas similar to COG(less concentration of hydrogen), using synthetic pyrite as catalyst and under mild conditions. The results show that the conversion of coal to oil was higher than 90% at 450 °C under 60 kg/cm² and the consumption of hydrogen was about 2%. These results suggest that this method is concluded to be economical.

(4) Studies on related subjects

We have investigated six related items and performed feasibility studies.

① The present condition and the problem of the liquefaction technology of the coal

a. The effect of the addition of the coal in the hydrating treatment of the residue oil

b. Effect on addition of metal acceptor in the upgrading reactor of the residue oil /

Investigation of the life of the catalyst by the removal of the harm of the catalyst and the upgrading reactor of the oil product

c. Effect as a solvent of the third element (in such cases as the fragrance group, the polarity solvent) in the hydrating liquefied treatment of the residue oil and the coal

d. The design of the recycling and regenerating systems of the catalyst for upgrading the residue oil

e. The effect of the combination of the extraction and resolution reaction on a super-critical condition in the coal, waste plastics co-treatment

- ② The present condition and the problem of the nature of the liquefied oil and the technology to improve its quality

When a new liquefaction process is developed, however a difficult point is the thing of whether to concentrate a hetero- element in the residue how.

Though a strong idea hasn't been submitted yet, it is probably the first to examine the distribution of nitrogen caused by the progress of the liquefaction.

- ③ The present condition of the treatment of the heavy distillate of the petroleum

The amount of vacuum distillation residue which comes out from the oil refining process is about 20 million tons a year in Japan. As for the economy as well, it is judged that the residue can be substituted by the substitutive fuel such as coal. Therefore, it is the quantity that a hindrance isn't brought about in fuel balance even if all the products which are born newly by this process become raw material such as a binder.

On the other hand, the IPP business which a heavy distillate is used for as the fuel as a recent new tendency appears.

From now on, the above subject is to give careful consideration to the amount of heavy distillate which can be used as a raw material of this process.

- ④ The present condition and the problem of the waste plastics treatment technology

It is to become the biggest point whether it can get enough contact on macro molecular level to cause an interaction as for the coal because it is a solid. The development of the pre-treatment technology will become necessary to improve the contact. If a removal of hetero and ash in the coal and separation on the plastic side can be done at the same time, this process can become the process which is fully of value in the energy and the environment fields.

Therefore, it hopes for the execution of the following research.

- a. Study the change of the liquefied character when various plastics were mixed with the phenol plastic (mimic low grade coal).
- b. The development of the way of pre-treatment of coal and plastics mixture (bojun, water heat treatment, oxidation, super-critical reaction)
- c. Understand the liquefied character of the mixture in the pre-treatment and the development of the catalyst to get high yield and the way of operating.

- ⑤ The present condition of the Co-processing technology

In the co-processing of the coal and the bitumen, the addition the coal or the liquefied oil promotes lightening and repression of the reverse response of the bitumen.

These reactions are based on the chemical structure of coal and bitumen. Therefore, a much more detailed examination from now on is necessary.

⑥ About the catalyst and the form of the reactor in the new process

We have to judge the selection of the form of the reactor synthetically from activity, life, form and strength of the catalyst, and the reaction rate which reaches it, reaction heat, the contribution of the catalyst-less response, and so on.

4. Future Tasks

The above results suggest that the new process will be available as a commercial plant. Consequently, after this fiscal year we will perform further studies.

The subjects to be investigated in the future are as follows;

- 1) Quantitative investigation on effect of heavy oil and waste plastics-addition
(to reduce recycle solvent and hydrogen consumption)
- 2) Optimum mixing ratio of heavy oil and waste plastics
(comparison of respective treatment of heavy oil and waste plastics and treatment of mixture of them using the process proposed here)
- 3) Uses and value of products
(quality and use of light, middle, and heavy oil; quality of residues and its use as binder; quality of gas products and water products; possibility of using coke making facilities for this new process)

We will investigate above mentioned issues by performing tests for confirmation and will carefully study feasibility of commercial process.

Applicability Study of Coal Liquefaction Technology

T. Suzuki

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Objectives

To investigate the applicability of coal liquefaction technology for various foreign coals through the international cooperation in R&D, and to receive and train engineers from foreign countries.

To contribute to the improvement of domestic and foreign liquefaction technology through exchange of information with countries involved in R&D in coal liquefaction.

Work Program

(1) Applicability study

Coals are obtained from Australia, Indonesia, India and Russia for evaluation of liquefaction characteristics and properties. As to Indonesian coals, especially, substantial progress will be made in such manner as liquefaction test by BSU. Site survey is also to be made in Indonesia and Russia. Especially, an applicability study for Indonesian coal liquefaction plant is to be done.

(2) Exchange of personnel and information and survey of liquefaction technology

Collection and exchange of information on coal liquefaction technology is to be made. Expert meetings are to be held with Indonesian counterpart and engineers are also invited from Indonesia.

Summary (1981~1996)

1. Up to FY 1995

(1) Russian Republic

In 1992, we visited Fossil Fuel Institute in Moscow of Russian Republic and the coal liquefaction plant (ST-5) at Tula City for the purpose of survey of Russian technology and exchange of information on coal liquefaction. Possibility of collaboration in R&D was also discussed. In 1993, further visits were made to FFI and International center for Business cooperation in Krasnoyarsk and Borodino coalfield, one of coalfield located in Kansk Achinsk area. During these visits, it was agreed that Russian

counterpart supply three kinds of coal samples for evaluation of liquefaction characteristics of Kansk Achinsk coals. Coal liquefability of these samples was examined and the technical information was exchanged.

(2) Republic of Indonesia

In 1993, a request was proposed to NEDO by Agency for the Assessment and Application of Technology (BPPT) for collaboration of R&D in coal liquefaction technology. Memorandum of Understanding (MOU) was exchanged between the two parties in January 1994. This MOU stipulated various collaborative activities, such as exchange of information through the annual expert meeting, invitation and acceptance of trainees to R&D facilities in Japan, applicability study for Indonesian coals including joint site survey and other necessary actions. In March 1994, first site survey was carried out at several coalfields in Sumatra and three kinds of coal samples were obtained. Data on deposit and distribution of coal seams were also obtained. After basic analysis was made for those samples with regard to chemical composition, slurry viscosity, pyrolysis and liquefaction reactivity, some experiments were done using a continuous liquefaction test facility of bench scale unit (BSU).

2. For FY 1996

(1) Applicability study

(a) Applicability study for Indonesian coal

An applicability study was done for the 30,000 t/d coal liquefaction plant at south Sumatra using Banko coal based on the two processes. One is a proven BCL process that produces 120,000 bbl/d of liquefied oil, another is Advanced BCL process that produces 140,000 bbl/d of hydro-treated liquefied oil. As a result, the equipment scale or the number of equipment of the de-watering process can be decreased for the Banko coal compared with the Australian brown coal because of the low moisture content of Banko coal, followed by the reduction of the construction cost becomes possible. The financial analysis of the 30,000 t/d coal liquefaction plant was carried out using the discount cash flow method in which Indonesian information such as coal price, natural gas price, labor cost was applied. From this applicability study, it is suggested that the commercial coal liquefaction plant in south Sumatra using Banko coal will be feasible because of the excellent characteristics of Banko coal. Further detailed study from the various points of view is requested.

(b) Sampling of foreign coals and survey of coalfield

Five ton of coal at Banko area was collected for the experiments using BSU and autoclaves at Takasago Research Laboratory of Nippon Brown Coal Liquefaction Co., Ltd. The sampling point was in the central Banko coalfield. For the collection of the coal samples and the site survey, Indonesian Government gave a wholehearted support to us. The information on the oil refineries, port facilities at Palembang, situation of the infrastructures to Banko coalfield, the construction cost of pipeline and the transportation cost for the coal was collected.

(c) Characterization and liquefaction reactivity of foreign coals

The liquefaction reactivity of the Indonesia Banko coal was examined using autoclave, so it was confirmed that the optimum reaction condition for Banko coal was 450-460°C, 15MPa. The test results using BSU showed about 71wt% oil yield with the yield of CLB less than 1wt% under the condition as follows : the amount of pulverized γ -FeOOH catalyst:1wt% on mafc as Fe, temperature:450°C, pressure:15MPa, reaction time:1.5 hours, recycled gas:3.3Nm³/kg on mafc and recycled CLB:75wt%.

Moreover, the settling characteristics of solid materials such as the minerals and catalyst, etc. contained in the CLB derived from the Banko coal was examined using BSU in order to compare with that of CLB from Yallourn coal. As a result, the equation of sedimentation velocity for Yallourn coal can be applied to the CLB from Banko coal. And by adjusting the solubility of de-ashing solvent, the sedimentation velocity can be same to that of 50t/d PP. Also, it was confirmed that the naphtha made from Banko coal liquefaction can be used as de-ashing solvent.

The secondary hydrogenation characteristics of THFS (DAO, de-ashed oil) of CLB made from Banko coal were also investigated with Ca-Ni-Mo/Al₂O₃ catalyst in order to confirm the applicability of two stage liquefaction technology to Banko coal. As a result, DAO obtained from Banko coal showed the same reactivity and selectivity as that of DAO from Yallourn coal. It was judged from this result that two stages coal liquefaction process can be applied to Banko coal liquefaction.

The quality of liquefied crude oil could be improved by the two steps in-line hydro-treatment. At the first step, the de-nitrogenation ratio was 85-98%, finally the concentration of nitrogen and sulfur in the hydro-treated oil was 1-7ppm, 1-16ppm, respectively at second step. By this hydro-treatment, the stability for the storing was improved. On the other hand, the combustion characteristics such as smoke point and the cetane index, etc. of light gasoline (b. p. <100°C), kerosene (b. p. 150-240°C), and light oil (b. p. 240-300°C) made from second in-line hydro-treatment did not fill

the JIS standard on the fuel evaluation. The up-grading depending on the usage is necessary.

(2) International collaboration, exchange of information and survey of coal liquefaction technology

Based on the MOU between NEDO and BPPT on coal liquefaction, the third expert meeting was held to report the result of the research cooperation. Two Indonesian engineers training were executed for about six weeks. Also, the technical assistance was done for the operation of 5L autoclave and gas analysis etc. installed in LSDE, Indonesia.

On the other hand, four kinds of the Russian brown coal sample of Kansk-Achinsk coalfield were obtained and an analytical evaluation was done. The characteristics of Russian brown coal were high ash content and volatile matter and low moisture content. And the result of the research about these coal samples was presented at the Kansk-Achinsk brown coal liquefaction conference, April 1996 and the information of coal liquefaction research situation of Russia was gathered.

Future Tasks

Further detailed study shall be done for the applicability study of Banko coal liquefaction in order to offer the information for the future development schedule in accordance with the second MOU. Moreover, the exchange of information with the foreign countries that are proceeding the research of liquefaction will be continued to improve the liquefaction technology of Japan.

Preliminary survey on the Mongolian Coal

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Objectives

This survey is , as a part of the feasibility study of the coal liquefaction facilities in the foreign countries, to investigate the status of resources and energy, infrastructure, organization of research and development, and selection of the most suitable coal conversion process in Mongolia. Moreover, the necessity of the guidance for improvement and diffusion of coal utilization technologies is also investigated. In addition to these survey, it collects information by the coal utilization situation of the coal resources country and which has economy and technology , being developing.

Work program

- 1) Investigation of the Governmental policy for energy , resources and the technical potentiality.
- 2) Evaluation tests of Mongolian coal
- 3) Evaluation of the applicability of coal utilization technology
- 4) Cooperation of improvement and diffusion for the coal utilization technology
- 5) Visiting Mongolian related organizations for survey of present situation
- 6) Energy situation of other coal resources countries

Summary (1993 - 1995)

1. Up to FY1995

In 1993, resources, energy status, suitable coal conversion technologies and requirement of technical assistance were studied based on published literature and on the spot survey. Moreover, coal analysis as preliminary tests were conducted over the coals provided by Mongolia.

In 1994, coal analysis, and liquefaction with autoclave and low temperature carbonization tests were conducted as preliminary study for evaluating liquefaction characteristics of Mongolian coals, besides, two Mongolian research engineers were invited and visited national and private research organizations for discussing coal utilization technologies. Moreover, the spot survey was conducted for investigating recent energy status and visiting related organization in Mongolia.

In 1995, as the spot survey, present situation of the coal production and utilization could be obtained by visiting Baganuur coal mine and N0.4 Ulaanbaatar power station. As for Mongolian coal evaluation test, ultimate, proximate and petrographic analyses were carried out on the Mongolia selected Togrognuur and Tsaidamnuur as sample coals. Liquefaction test was conducted with continuous micro reactor system using Uvdughudag coal and same oil yields were obtained as Wyoming coal.

As the diffusion cooperation of the technology, two Mongolian engineer were invited and visited research and development organization about the coal utilization technology to improve their technical potentialities.

2.For FY 1996

In this year, the summary are as follows.

(1) The investigation about the energy policy, resources technical potentiality As the energy policy, to strengthen social economic basis, "the Mongolian state development plan" including the development of science and technology, new plan of energy development and coal processing were settled on. There is a lot of coal reserves(50 billion tons) as resources and 16 mines are operating now. The technological level about the coal utilization are not too high but possessing technical potentiality.

(2) Evaluation test of Mongolian coal

a) Proximate and Ultimate analyses

Ultimate, proximate, and petrographic analyses were carried out about two kinds of Togrognuur(N31,N41), four kinds of Tsaidamnuur (N3, N5, N23, N27), which were selected by Mongolia The result is shown in table1 and table2.

Table 1. Proximate Analysis (Equilibrium Moisture basis wt %.)

Kind of coal Item	Togrognuur		Tsaidamnuur			
	N34	N41	N3	N5	N23	N27
Moisture	16.9	17.6	15.6	12.4	16.4	13.6
Ash	6.4	6.5	7.2	32.8	16.5	36.2
Volatime Matter	39.2	37.5	39.0	26.2	34.2	24.3
Fixed Carbon	37.5	38.4	38.2	28.6	32.9	25.9
Clorific Value daf base (cal/g)	6,570	6,650	6,340	6,260	6,380	6,210
Total Sulphur	0.77	0.94	1.33	0.96	1.37	0.82

Table 2. Ultimate Analysis (daf coal basis wt %)

Kind of coal Item	Togrognuur		Tsaidamnuur			
	N34	N41	N3	N5	N23	N27
Carbon	627.28	70.79	68.85	68.85	69.24	68.16
Hydrogen	4.73	4.32	4.83	4.89	4.63	4.58
Nitrogen	1.11	1.02	0.79	0.81	1.26	1.14
Oxigen	26.8	23.56	24.74	24.44	24.32	25.65
Combustion Sulfur	0.77	0.3	0.79	1.01	0.55	0.48

From the result of the above ultimate analysis, it was proved that Tsaidamnuur was contained much ash except N3 and ash content in Togrognuur was less than 10%, and that Togrognuur is comparatively little sulfur content.

b) The Maceral analysis and the reflectance

Maceral component analysis result and reflectance are shown in Table 3. It shows that the reactive value of Tsaidamnuur N3,N23 and Togrognuur exceed 80%, so these coal will be easy to be liquefied from the point of component only.

Table 3. Petrographic analysis and Reflectance

Kind of coal Maceral	Togronuur		Tsaidamnuur			
	N34	N41	N3	N5	N23	N27
Vitrinite						
Collinite	50.1	20.6	39.2	27.4	49.2	44.0
Telinite	16.3	13.0	15.7	20.0	14.3	17.8
Degradinite	22.2	8.6	27.6	10.0	20.4	17.5
Exinite						
Sporinite	1.3	0.0	0.2	0.0	1.9	0.2
Cutinite	0.0	0.0	0.0	0.0	1.3	0.7
Resinite	0.0	0.5	0.2	0.0	3.0	2.9
Suberinite	0.4	0.0	0.2	0.4	0.2	0.0
Total Reactives	90.3	42.7	83.1	57.8	90.3	83.1
Inertinite						
Micrinite	1.3	0.0	1.7	0.4	1.1	3.4
Macrinite	0.6	0.3	2.2	0.4	1.3	2.9
Sclerotinite	0.6	0.0	0.0	0.0	0.4	0.0
Fusinite	1.5	6.2	0.7	5.3	1.7	5.0
Semifusinite	0.6	1.6	0.2	0.4	0.8	1.0
Inertdetrinite	0.0	24.1	0.0	6.8	0.0	0.0
Mineral Matter	5.1	25.1	12.1	28.9	4.4	4.6
Total Inerts	9.7	57.3	16.9	42.2	9.7	16.9
Reflectance						
Mean	0.34	0.34	0.39	0.41	0.40	0.41
Minimum	0.27	0.28	0.29	0.33	0.22	0.29
Maximum	0.46	0.49	0.5	0.54	0.54	0.58

As for the coal samples of Togrognuur N31 and N41, the average reflectance is 0.40, 0.41 respectively and the Maceral is wealthy in Collinite which belongs to Vitrinite. Either of total reactives are equal to or more than 80% and are wealthy in the reactivity.

Moreover, the existence of Inertodetrinite was confirmed in N41 sample but without counting.

As for the core samples of Tsaidamnuur N3, N5, N23 and N27, the average reflectance of N3 and N5 are 0.34 and the coal rank is rather low compared with Togrognuur. Inertodetrinite is admitted in N5 and N27 sample, it becomes 24.1% in N5 and accounts for 45% of total Inerts. Also, the mineral matter content in N5 and N27 is 25.1% and 28.9 % respectively. Inert quantity was relatively high contained and approximately 11% observed except for the mineral matter.

c) Liquefaction Test

To compare with the former liquefaction test, in this test, liquefaction test were conducted autoclave reactor under the non-catalytic condition expecting contribution of sulfur content in Uvdughudag coal. however the oil yield was not so high as expected. Unconverted coal and product gas was increasing and coal conversion rate was less than 95 wt%. As for Tsaidamnuur N26, the oil yield was 57.85 wt % but product gas was higher than the case of Uvdughudag under the catalytic condition. However, there were little preasphaltene and asphaltene generation, Tsaidamnuur showed the best liquefaction characteristics in Mongolian coal which examined up to now. When comparing the ratio of the oil yield to the unit hydrogen consumption, Tsaidamnuur N26, Uvdughudag and Uvdughudag: were 12.2, 14.2, and 13.8 respectively.

In case of Uvdughudag* (noncatalytic), the oil yield to the hydrogen consumption is higher than that of other case of coal, but it is possible to evaluate nothing because the no property of oil was

analyzed. Liquefaction test results are shown in the table 4 and table 5.

Table 4. Liquefaction product yield (wt% daf coal basis)

Kind of coal Products	Tsaidamnuur26 (catalytic)	Uvdughudag (non catalytic)	Uvdughudag* (catalytic)
Product Gus	20.11	22.31	17.53
Product Water	16.05	15.00	14.91
Product Oil	57.85	48.65	55.56
Asphaltene	5.67	7.03	10.12
Preasphaltene	2.17	4.44	1.57
Unreacted Carbon	2.72	5.99	4.33
Total	104.57	103.42	104.02
Hydrogen Consumption	4.57	3.42	4.02
Conversion Rate	97.28	94.01	95.67

Note: Uvdughudag* : Test result in 1996

Table 5. Composition of Product Gas (mol %)

Kind of coal Item	Tsaidamnuur26 (catalytic)	Uvdughudag (non catalytic)	Uvdughudag* (catalytic)
CH ₄	29.53	29.76	32.33
CO	15.36	8.34	11.30
CO ₂	25.76	34.98	24.83
C ₂ H ₆	12.97	12.42	12.27
C ₃ 's	6.81	6.07	6.72
C ₄ 's	1.75	1.61	1.86
H ₂ S	7.82	6.82	10.70
Total	100.00	100.00	100.00

The content of CO₂ in the product gas of Tsaidamnuur N26 was less than that of Uvdughudag, so when using product gas as fuel, Tsaidamnuur N26 will be favorable.

(3) Evaluation of the applicability of coal utilization technologies

Being based on the results of proximate analyses, using coal property such as Volatile matter, ash content, total sulfur and calorific value, evaluation study was conducted what field of utilization applicable for these coal. As a results, Togrognuur and Tsaidamnuur N26 were possible to apply liquefaction technology. But Tsaidamnuur N5, N23, N27 were considered to be available for only as the pulverized combustion, the light industry and the household fuel. Judging from the autoclave test, it is possible to apply liquefaction technology about Uvdughudag and Tsaidamnuur N2.

(4) Cooperation of improvement and diffusion for the coal utilization technology

The provision of technical literature of coal utilization and so on besides Japanese development status in this field were explained. Technical discussion was held on the matter of analyses and autoclave test results in Mongolian coal. Two Mongolian research engineers were invited to Japan and visited private company entrusted by NEDO which is implementing coal utilization technology development. Through observation of research facilities, acquisition of technical information, and practice the liquefaction test by autoclave, more or less their technical ability were improved.

(5) Visiting Mongolian related organizations for spot survey of present situation

Spot survey was conducted on September 21st. to October 2nd, 1996 and visited related organization

to discuss the coal utilization technology development status and development program of energy and so on. Also, lectured the former tests results entitled "Liquefaction characteristics of Mongolian coal" in Mongolian coal forum of the JAPC sponsorship Energy status and Development plan are as follows.

a) Energy situation

Coal is used about 80% Of domestic energy and all petroleum products are imported from Russia. The production rate of coal are tend to decrease. Coal production rate recorded its peak(8.6million tons) in 1988 and then has showed decrease tendency. In 1994, it depressed 4.9million tons but in 1995 the production was recovered in 5.12 million tons. As for the trend with energy price, since September 1st, the government decided that the price of coal and electric was raised to 45% and 60% respectively.

b) Development program

The Mongolian state development program including the coal liquefaction program could get the approval of the cabinet in May,1996. This plan divide in 3 periods until 2020 and the contents consist of the following items.

① Developing plan of science and technology

- Science and technology development----how to use coal and petroleum
- New energy development----Solar, wind and nuclear energy development

② Development plan of economic society

- Establishing domestic production and supply system of energy----Exploring oil resources
- Establishing coal processing and coal chemistry----liquid fuel and chemicals from coal

(6) Energy situation in the other coal resources countries

Such as India, Czech and Poland, economical developing countries with abundant proved coal resources are investigated on the present energy status. The workable coal resources of each countries are 69.9 billion tons of India, 42.1 billion tons of Poland, 5.4 billion tons of Czech. And in 1995, the annual coal production was 246 million ton of India, 85 million ton of Czech, 200 million ton of Poland , respectively. The coal share rate to the primary energy was 47% of India, 55% of Czech, 75% of Poland.

Concluding Remarks

When ending preliminary study on the Mongolian coal this time, the following is generalized.

As the energy policy for the development of Mongolia, the promotion of coal energy utilization is indispensable. However, from the Mongolian economic circumstances, to execute alone is a very difficult situation and needs economical and technical aid from the advanced foreign countries.

In the future, the individual cooperation and assistance for the following items are necessary by the invitation of researcher, sending technical expert and so on.

a) The aid of the making repletion program for the coal utilization technology development.

- The advice to the purchase plan for the experimental apparatus and instruments The drafting assistance for the research and development program suited resources in Mongolia

b) The diffusion of the technology to the researcher and engineer In order to level-up technical

performance of the research engineer. The following items are necessary

- The provision of the related technical information
- Training aid to of the researcher and the engineer

5. RESEARCH AND DEVELOPMENT OF COAL HYDROGASIFICATION TECHNOLOGY

(1) Research Using Experimental Apparatus

(2) Elemental and Supporting Research

① Supporting Research

② Research on Social Adaptability

Research Using Experimental Apparatus
Seo Tomoyuki, Director, Clean Coal Technology Center
New Energy & Industrial Technology Development Organization
Contractor : K. Ito, The Japan Gas Association

Objectives

In view of the possibility that supplies of natural gas will become increasingly scarce in the future, our ultimate objective is to establish a coal hydrogasification technology allowing a high-quality substitute for natural gas to be provided inexpensively, in a stable manner and in large quantities, from the raw material coal, which is more or less equally abundant all over the world. The aim of this research and development project is to develop the principal elemental technologies required for evaluating the possibilities for bringing the coal hydrogasification technology into practical use, and using a range of experimental apparatus.

Work Program

1. Developing a coal hydrogasifier

(1) Data acquisition using a small-scale experimental apparatus

Our small-scale experimental apparatus is a continuous reactor allowing us to study the reaction between coal and hydrogen at high temperatures and high pressures, and to acquire material balance data for different retention times of coal particles or gas. In this apparatus, experiments can be carried out under the following conditions.

- (a) Temperature: 700 to 1,000°C
- (b) Pressure: 3.0 to 7.0 Mpa
- (c) Retention time: 1 to 20 sec
- (d) Hydrogen/coal ratio: 0.15(kg/kg) or higher

Using this experimental apparatus, we acquire gasification data for the 3 modes of the ARCH (Advanced Rapid Coal Hydrogasification) process: SNG yield maximum, thermal efficiency maximum, and BTX yield maximum. This data are used to improve our reaction model.

This apparatus had been up and running about 10 years. With a view to carrying out tests efficiently and reliably for this project, a wide-ranging program of refitting and remodeling was carried out in FY 1996 on the main body of the reactor, and also on the peripheral apparatus.

(2) Developing an injector

The injector is an aggregate combining a coal feed nozzle with hydrogen/oxygen burners. To enable it to support operation in the 3 modes of the ARCH process (SNG yield maximum, thermal efficiency maximum, and BTX yield maximum), it has to have 3 functions:

- (a) steady feeding of hot hydrogen and coal into the gasifier;

(b) mixing of hydrogen and coal:

(c) ensuring the momentum needed to sustain fluidity inside the gasifier.

The hydrogen/oxygen burner forming part of the injector needs to supply hot hydrogen in a stable manner at 1,200°C in order to support the BTX yield maximum mode characteristic of the ARCH process, and it also needs to heat the coal with the hot hydrogen and ensure a temperature of approximately 900°C in the first reaction zone.

In FY 1996, we planned to develop the hydrogen/oxygen burner to be used in the Pilot Plant (PP), and to formulate a plan for developing an injector incorporating burners and mixing hot hydrogen with coal.

(3) Hot model experiment

The purpose of the hot model experiment is to confirm the performance of the injector that mixes coal particles with hot hydrogen, causing the coal to undergo rapid pyrolysis. To be more specific, it has the following two objectives:

(a) to confirm that the coal particles do not agglomerate excessively under the PP operating conditions, and

(b) to prospect heat resistance and durability of the injector after 1,000 or so operating hours.

In FY 1996, we intended to draw up the basic design for the hot model experimental apparatus, and the full plan for the hot model experiment.

(4) Cold model experiment

The cold model experimental apparatus allows us to observe visually the fluid dynamics inside the gasifier, which is difficult to do in the case of a real gasifier, and to measure the fluidity. The PP for this project processes coal at a rate of 50t/d. The object of the exercise is to arrive at a proposal for the optimum gasifier structure able to accommodate the 3 above-mentioned modes of the ARCH process, by measuring and analyzing the fluid dynamics using a cold model experimental apparatus of the same size, owned by BG plc.

In FY 1996, we planned to run a fluid dynamics simulation, formulate the plan for the cold model experiment, set up the cold model experimental apparatus, perform preliminary tests, and draft a facility repair plan for the execution of the test plan.

2. Developing peripheral technologies for the gasifier

(1) Developing char discharge technology with fluidized cooling

We are investigating means for removing the hot char in a stable manner from the bottom of the high-temperature high-pressure gasifier, and fluidizing and cooling it. To this end, we need to evaluate how the fluidization and heat transfer properties of the char are affected by factors such as the positioning of the cooling pipes inside the fluidized cooler, the shape of the distribution plate, and the retention time. We also need to decide on the optimum operating conditions that would allow us to discharge the char in a stable manner. In order to evaluate the fluidization and heat transfer

properties of the char, we plan to carry out a "char fluidized bed heat transfer properties experiment", and to determine the right conditions for continuous and stable discharge of char, we plan to carry out a "char discharge circulation experiment".

In FY 1996, we worked on the basic plan and basic specification for these two experiments.

Summary (1990 - 1996)

1. Up to FY 1995

Over the five years starting in FY 1990, coal hydrogasification technology research was carried out by NEDO. This research resulted in the establishment of a new concept in coal SNG manufacturing processes. This new process is highly efficient, flexible in terms of operability, excellent in economic terms, and its raw material is coal, which is still plentiful, and stable in price.

The new coal SNG manufacturing process is known as the ARCH (Advanced Rapid Coal Hydrogasification) process. Using ARCH, methane is manufactured directly, by gasifying coal using hydrogen at high temperatures (850 to 1,200 °C) and high pressures (3 to 7MPa); BTX is also produced. The by-product, char, is gasified by the conventional process of partial combustion, and becomes a source of hydrogen.

The gasifier uses the pressurized entrained circulation flow system with two-stage hydrogasification. The upper part of the gasifier becomes a rapid-heating zone due to the hot hydrogen, while the lower part becomes an isothermal reaction zone with draft tubes to produce internal circulation. This allows the 3 operating modes (SNG yield maximum, thermal efficiency maximum, and BTX yield maximum) to be accommodated in a single gasifier.

At present, coal SNG is more expensive than LNG. However, considering that LNG is likely to rise in price more than coal, coal SNG will probably become competitive with LNG in price by the year 2010.

2. For FY 1996

(1) Developing a coal hydrogasifier

(a) Data Acquisition using a small-scale experimental apparatus

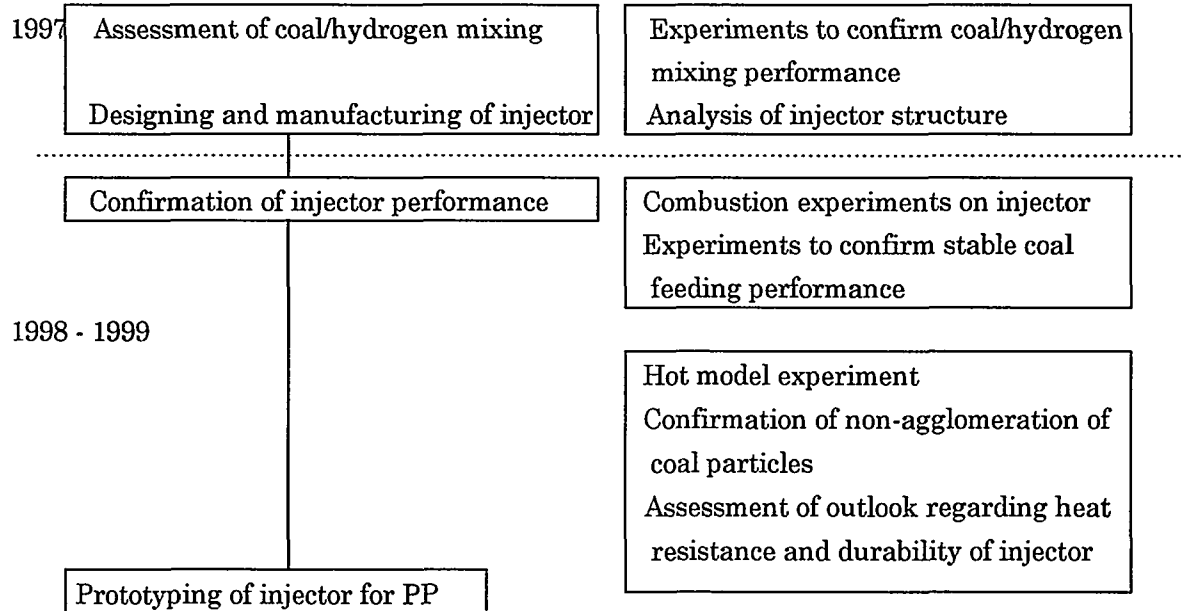
- (i) We carried out remodeling to control the two-stage reaction (this included dividing up the electric heater and installing a service flange), and remodeling to improve operability (this included remodeling the injector and installing a load cell).
- (ii) The performance of the load cell was checked in combination with carrying out the coal feed test, and it was confirmed that coal could be fed in at a rate of 3.0 to 5.2kg/h.

(b) Developing an injector

- (i) Regarding the design conditions for the hydrogen/oxygen burner in the PP (oxygen 5%), the temperature range at the hydrogen outlet at the tip of the burner became

clear to make it possible to use a self-ignition system.

- (ii) We performed a comparative study of burner structures, by running combustion simulations for an external-mixing burner where a diffused hydrogen/oxygen flame forms on the outside of the burner, and for an internal-mixing burner, which has an internal mixing chamber inside the tip of the burner: diffused flames are formed in this chamber, and the burning gas is sprayed out of the nozzle.
- (iii) Using the 1/10 scale burner used in the PP, selected on the basis of the studies described above, 3 external-mixing types and 1 internal-mixing types were selected and combustion experiments were carried out accordingly. Regarding the ignition temperature range, it was confirmed that both self-ignition and flame retention could be possible with both the external and the internal mixing types, and that combustion was stable in all cases.
- (iv) We adjusted our combustion calculations in the light of the results of our high-pressure combustion experiments with the 1/10 scale burner. Besides confirming the oxygen consumption distance for the external mixing types under the PP conditions, we also confirmed that both the internal and the external mixing types could provide hydrogen hotter than 1,200°C with no residual oxygen.
- (v) We formulated a plan for the development of the injector from 1997 onwards, as follows.



(c) Hot model experiment

- (i) We decided that the hot model experiment would focus on the main body of the injector and the first-stage reaction zone directly underneath it, where the coal would be rapidly pyrolyzed at approximately 1,173K (900°C). We also decided to carry out an experiment whereby we would install an injector having the same dimensions as in the PP, to be designed and manufactured during the development of the separately-implemented injector.

- (ii) The scale of the hot model experimental apparatus was decided on as follows: the coal processing rate would be 5.7t/d, and the experimental pressure would be 0.79MPa (=7.0kgf/cm²G).
 - (iii) We decided on the design conditions of the hot model experimental apparatus, the process flow, the material balance, the specifications for each item of apparatus, and so on.
 - (iv) To check whether the coal particles would agglomerate, we decided to perform an experiment in which parameters such as the coal processing rate would be varied, under conditions matched as closely as possible to those of the PP in terms of coal heating speed and coal space density, these being thought to be the principal factors influencing coal agglomeration. The object of this exercise is to confirm that, within the operating conditions envisaged for the PP, the coal particles would not clump together or stick to the inside walls of the gasifier, hindering the operation of the gasifier.
 - (v) It was decided that the outlook for the thermal resistance and durability of the injector would be tested by means of an experiment in which the operating conditions would include high temperatures, cumulative times of several hundred hours, and several tens of starts and stops. The aim is to assess the resistance of each part of the injector to thermal fatigue.
- (d) Cold model experiment
- (i) Efficient fluid dynamics simulation
In order to screen the optimum structure of the ARCH gasifier, we have created a man-machine interface making it easier for data - such as diagrams of likely gasifier structures, analysis conditions and so on - to be input into the simulation software "stream". The object of this exercise is to reduce the labor required by the fluid analysis operation.
 - (ii) Studying simulation technologies, including particle dynamics modeling
As a preliminary study for the particle fluid dynamics model scheduled for development starting in 1997, we have reviewed the current state of general-purpose computational fluid dynamics technologies, including particle dynamics modeling. We have also reviewed analytical techniques using proprietary software belonging to BG plc.
 - (iii) Clarification of the technological level of current fluid dynamics simulations
We have evaluated current fluid dynamics simulations by comparing them with measurement data from our cold model experimental apparatus.
 - (iv) Formulation of a remodeling plan for our current cold model experimental apparatus
In order to perform experiments on the possibilities of the 2-stage reaction using BG's cold model experimental apparatus from FY 1997 onwards, we have looked at remodeling the following 3 aspects of the cold model.

- (A) First-stage reactor
 - (B) Quench gas feed system
 - (C) Oxygen feed system
- (2) Developing peripheral technologies for the gasifier
- (a) Developing char discharge technology with fluidized cooling
- (i) In the "char fluidized bed heat transfer properties experiment" and the "char discharge circulation experiment", we decided to use imitation particles of a similar diameter and density to char, instead of actual char.
 - (ii) We decided that, in both experiments, the experimental apparatus would be at room temperature, and since the conditions envisaged for the PP (temperature: 623K, pressure: 7.0MPa, H₂ atmosphere) would be different from the experimental conditions (temperature: 300K, pressure: 0.1MPa, CO₂ atmosphere), we decided to preserve equivalence in terms of fluidization properties by using the same Ar and Re numbers in the experiments as in the PP.
 - (iii) In the "char fluidized bed heat transfer properties experiment", we decided to monitor the fluidization status and change in temperature, and to find out the fluidization and heat transfer properties, using the following parameters: bulk velocity, bed height, heat-transfer tube structure, retention time, distribution plate mesh and fluid gas used.
 - (iv) In the "char discharge circulation experiment", we decided to (A) establish a method for controlling the level of char inside the fluidized cooler, (B) find out the conditions under which char could be conveyed without causing a blockage, and (C) find out the durability of the entire system, and get an idea of the whole control system including the operation start and finish times.
 - (v) In order to find out the best conditions for discharging hot char in the PP, we decided to measure the angle of repose of the char at high temperatures.
 - (vi) We have formulated the principal specifications for the char fluidized bed heat transfer properties experimental apparatus, drew up the plans, system diagrams, and apparatus list, and completed the structural plans and principal specifications for the char discharge circulation experimental apparatus.

Future Tasks

1. Developing a coal hydrogasifier

(1) Data acquisition using a small-scale experimental apparatus

We intend to use a small-scale experimental apparatus to investigate the relationship between the temperature and retention time, and the product.

(2) Developing an injector

We shall be designing and manufacturing an injector to be installed on our hot model experimental apparatus. We shall also be designing and manufacturing an experimental apparatus for injector combustion experiments.

(3) Hot model experiment

We shall be designing the experimental apparatus and building part of it. We shall also be making a simulation program for the mixing and heating of coal with hot hydrogen.

(4) Cold model experiment

We shall be running fluid dynamics simulations for different sets of conditions, including gas/gas mixes, and carrying out gas circulation tests, and tests where injection gas is mixed with circulation gas, using the cold model experimental apparatus.

2. Developing peripheral technologies for the gasifier

(1) Developing char discharge technology with fluidized cooling

We shall be designing and building the char fluidized bed heat transfer properties experimental apparatus, and performing fluidization experiments and the like. As for the char discharge circulation experimental apparatus, we are going to design the apparatus, build part of it, and also carry out data-acquisition experiments for the purposes of fine-tuning the design.

(2) Developing a technique for conveying coal particles in dense phase

We shall be studying techniques for conveying coal particles in dense phase, and drawing up a detailed design for an experimental apparatus.

Industrial property rights, technological instruction, publication of papers, oral presentations and other fruits of this research

Presentation	Audience (host organization)	Presenter	Date of presentation
Development of Coal Hydrogasification Technology	Town Gas Symposium Annex (The Japan Gas Association)	Kojiro Katsukura and 2 others	October 14, 1996
Development of Coal Hydrogasification Technology	Osaka Gas R&D Forum (Osaka Gas)	Fuyuki Noguchi and 1 other	October 22-24, 1996
Development of Coal Hydrogasification Technology	Japan-China Symposium on Environmental Science (Japan-China Environmental Technology Exchange Association)	Fuyuki Noguchi and 1 other	November 23, 1996

SUPPORTING RESEARCH

T. SEO

Director of Clean Coal Technology Centre

New Energy and Industrial Technology Development Organization(NEDO)

Contractor: M. KUMAGAI, Institute of Research and Innovation

Objectives

To carry out detailed research on the mechanisms of hydrogasification of coal, whereby contributing the development of coal hydrogasification technology.

Work Program

1. Research of the detailed mechanisms of coal hydrogasification

(1) Survey

Literature survey is carried out on the mechanisms of coal hydrogasification and the behaviour of hetero-elements during gasification.

(2) Hydrogasification experiments

Since the property of coal varies widely depending on the location produced, it is of particular importance to know the correlation between the basic property and the gasification efficiency of coals. This year, coal samples are collected and their basic properties are analysed, and preliminary hydrogasification experiments are carried out with an available apparatus of a laboratory scale to establish experimental conditions.

(3) Design of an experimental gasification apparatus

Specification of a new experimental apparatus of a capacity of gram order for the present investigation is examined with the design in detail.

Summary(FY 1996)

1. Literature survey

Survey on coal hydrogasification was carried out on the JICST data base, which included 8.8 million records from 1981 to 1996, and we found about 60 related papers on the apparatus design and the behaviour of hetero elements in coal.

Experimental apparatuses are classified into three types as

1)Free-fall reactor

continuous, sample of g/hr

2)Constant rate heating reactor

batch experiment, sample of gram order

3)High pressure Curie-point pyrolyzer, or wire-mesh one

batch experiment. sample of mg order

Fig.1 shows the apparatus used by Sugawara et. al. The reactor is made of quartz with the inner diameter of 36mm and the length of 300mm, heated by 5 separate electric heaters controlled independently. Coal samples are fed at 0.2g/min from the top and the hydrogen gas flows from the bottom to the top at 2.0NL/min.

The pressure is limited to around the atmospheric pressure due to the material, but the temperature can be elevated up to 1000°C. The temperature profile is shown in the same figure.

Analysis showed a quick increase in temperature of the hydrogen gas at the inlet. The temperature of a coal particle is controlled by the radiation, with a little contribution from the endothermic decomposition reaction.

Fig.2 shows the free-fall reactor made of Incoloy at Tomita laboratory at Tohoku University. The coal feed rate was 0.1-2g/min. The reactor size is 6×22×1830mm. Experimental conditions up to 5MPa and 850°C are reported.

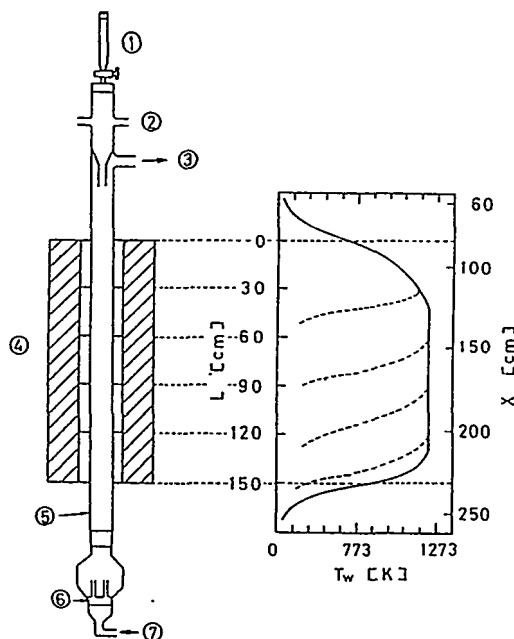


Fig.1 Free fall pyrolyzer made of quartz and an example of temperature distribution

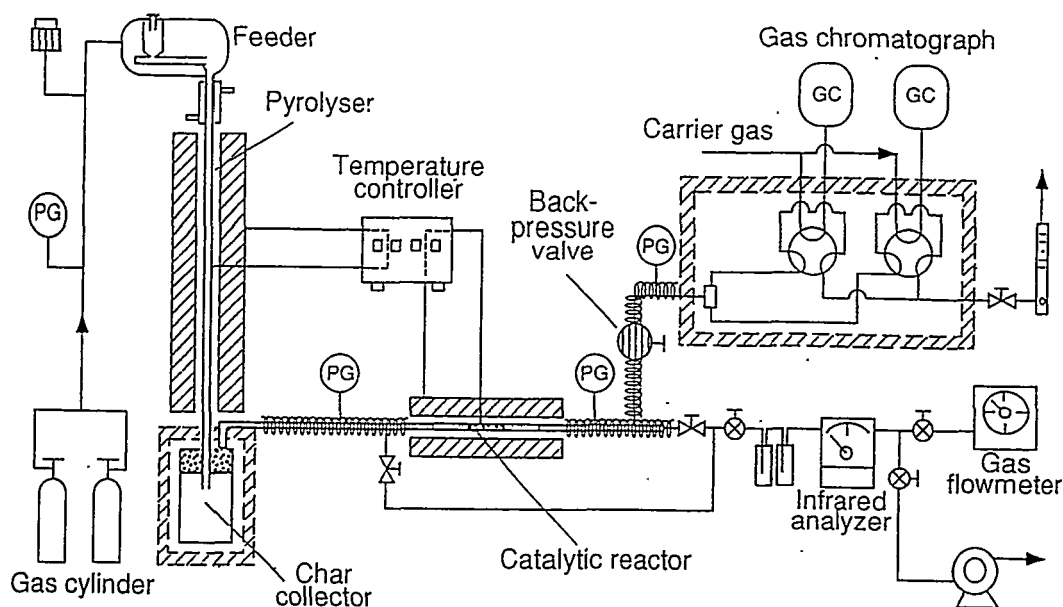


Fig.2 Free fall pyrolyzer made of Incoloy

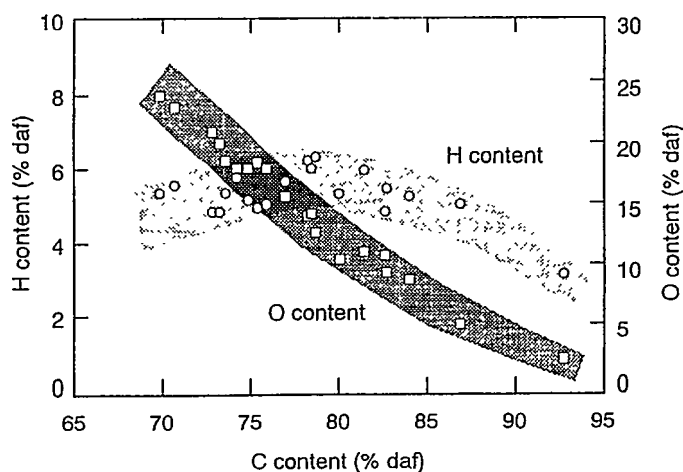


Fig.3 Composition distribution of coal samples

2. Hydrogasification experiments

Considering that the basic properties of coals vary widely depending on their origin, it would be necessary to elucidate the correlation between the hydrogasification behaviour and the basic properties. Fig.3 shows the results of the properties of 20 coal samples collected in 1996. Using six samples, we have carried out constant-rate heating experiments in the pressurised hydrogen atmosphere.

(1) Methods

The reactor is made of SUS304 with the inside diameter of 4.3mm and the outside diameter of 6.3mm. The sample was pulverised to 30/42mesh and the aliquot of 100-300mg was served to experiment without drying. The hydrogen pressure varied between 1-50atm, and the temperature was raised at 5°C/min up to 900°C.

(2) Results

Methane

As show in Fig.4, methane formation did not depend on the pressure at temperatures below 550°C, but above this temperatures it depended markedly on the pressure.

The methane formation curves have three peaks at all pressures, suggesting that three different forms of carbonaceous matters may be involved in the

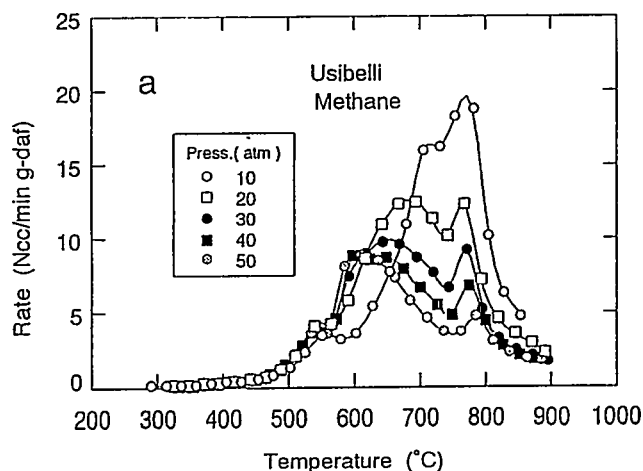


Fig.4 Pressure dependence of methane formation from Usibelli coal

methane formation.

Carbon dioxide

This was evolved almost completely at 550°C, and no apparent effects of pressure was detected. This means that the hydrogen is not fully activated under this temperature.

Effects of coal species

Six coal samples of different origin were compared at the hydrogen pressure of 50atm. Methane and ethane release curves are shown in Fig.5. A common behaviour is that both the gases evolved most actively at around 550°C.

Fig.6 shows the carbon conversions to methane, gaseous hydrocarbon and carbon oxides. The conversion to the gas is at most 50%, whereas the total conversion reaches above 90%. The difference of these values is equal to the conversion to liquid hydrocarbons. Under the rapid heating condition, the liquid hydrocarbons may be again decomposed and hydrogenated to yield gaseous hydrocarbons, meaning that the relative yield of each fraction may differ from this results.

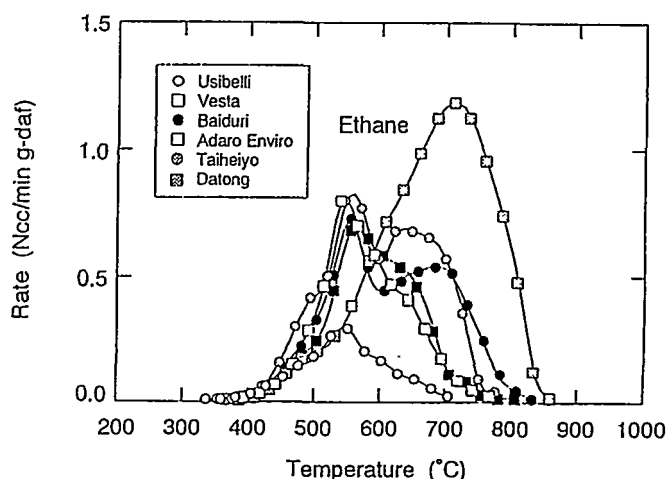
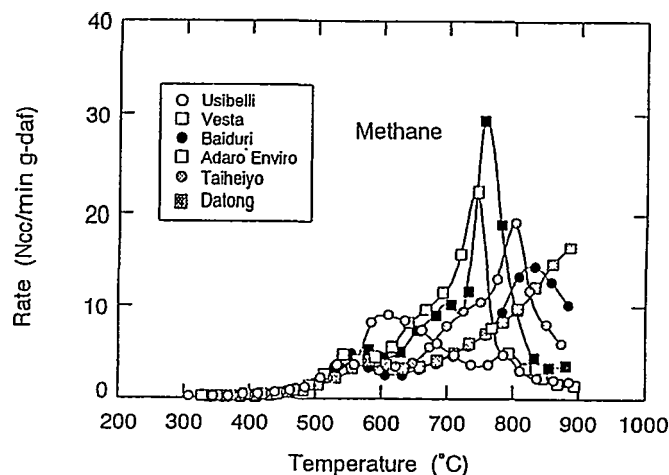


Fig.5 Methane and ethane formations from various coals (50atm)

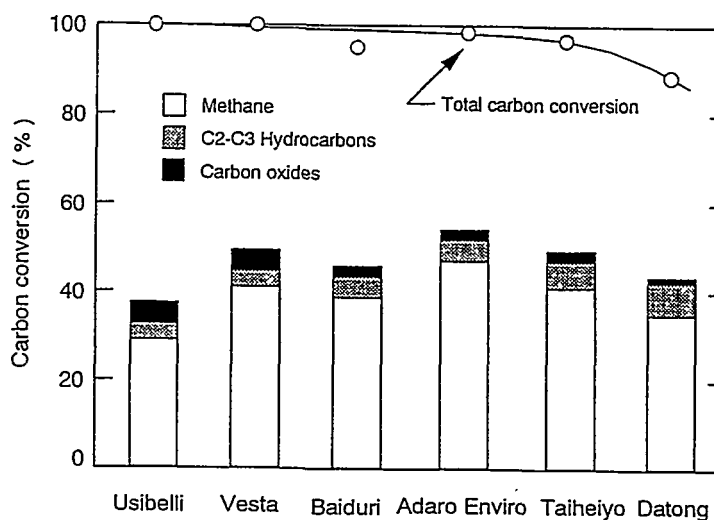


Fig.6 Carbon conversions of various coals

3. Design of apparatus

Requirements for an experimental apparatus would be

- (1) Reaction conditions in the apparatus should be as close as the prototype reactor,
- (2) Behaviours of hetero elements in coal can be analysed,
- (3) The apparatus can be applied to any species of coal,
- (4) Experiments can be carried out with sufficient stability and safety,
- (5) High temperature and high pressure hydrogen can be treated safely,
- (6) Scale of the apparatus should be proper so that many experiments can be handled with limited resources.

Considering these requirements, we have selected a free-fall gasification reactor, because this has been applied by many workers and the shape is similar to the prototype reactor.

The basic specifications of the reactor were decided as

Sample	pulverised coal(-100 μ m)
Feed rate	5-30g/hr
Feed gas	hydrogen and methane
H ₂ /coal	0.2-0.5(weight)
Gas flow rate	0.2-2Nl-H ₂ /min, 0-13Nl-CH ₄ /min
Pressure	0.1-7MPa
Temperature	650-900°C
Residence time	1-10sec
Reactor size	10 ^{id} × 1200mm
Heater	divided into three
Char trap	300-350°C

Future Tasks

In FY 1997, the literature survey will be continued on the behaviour of hetero elements in coal, and the gasification apparatus is to be constructed and operated with some basic data. Extensive researches on the detail mechanisms of coal and gasification and the research on porous material for separation and conversion of BTX are to be carried out.

Design of an actual plant needs the knowledge on the properties of hot coal and hot char and on the hydrodynamics and heat transfer in apparatuses, and researches on such subjects are to be set about.

Research on Social Adaptability

T. Seo

Director of Technology Development Department

Clean Coal Technology Center

New Energy and Industrial Technology Development Organization (NEDO)

contractor: Y. Tsuru The Japan Institute of Energy (JIE)

1. Objectives

Coal is widely distributed throughout the world, and is a most hopeful oil-alternative energy source due to its abundant supply. The natural gas supply in Japan depends upon foreign imports in the form of liquefied natural gas (LNG). LNG consumption has been increasing year by year for electric power and city gas for consumer. It has become necessary to develop a substitute natural gas (SNG) production process which features high efficiency, environmental acceptance and low cost, which in the future will help keep LNG prices low. In this point of view, a coal hydrogasification process was studied from FY 1990 to FY 1994 and new coal hydrogasification process (ARCH Process) has been proposed.

To complete this process technology the project for elemental research of this process has started from FY 1996 on. As a link in the chain of this project, to estimate the feasibility of this process, this committee will perform a five-year investigation on social acceptability necessary for feasibility study of coal hydrogasification.

2. Work Program

Do an examination about the development of the technology, and grasp the progress conditions of the development of the opposition technology and the change of energy situation and the improvement of the circumference technology and so on at the same time. Do the evaluation of the executive possibility of the technology at the last step.

Divide it into next items, and do investigation research.

(1) Study on upgrading the process

compare various gas producing facilities / improve the heat efficiency by up-to-date circumference technologies / elemental research for cost reducing / elemental research on social adaptability

(2) Study on social adaptability

research on trends of developments related to LNG, coal source, oil source and so on and expect these prices / research on trends of developments related to methane-hydrate and coal-bed-methane as competing sources

(3) Synthetic feasibility study investigation

have a feasibility study putting together with the results of above mentioned research and the results of "Research by experimental facility" by The Japan Gas Association and of "Supporting research" by the Institute of Research and Innovation

The subjects concerning to above mentioned (1), (2) will be extracted and the future plan will be produced in FY 1997.

The research meeting for the study of the process in the Japan Institute of Energy was composed of the people of learning and experience and specialists. On the other hand, working groups were established and studied the subjects.

3. Summary

(1) Up to FY 1996

NEDO established the Coal Hydrogasification Technology Research Committee in FY 1990 in that inside.

The deliberation of the need of the coal hydrogasification process was done, and the basic plan (ARCH process) of the pilot plant and the realization schedule were proposed in 5 years until FY 1994.

The committee has considered the necessity of the coal hydrogasification and proposed a basic conception (ARCH Process) and a schedule to the commercial plant and so on.

On the other hand, JIE took re-trust from NEDO in the same time, and a "Coal hydrogasification committee" was established inside, and that back the technology calculation of the ARCH process and business such as process evaluation like investigation was done. The committee has tried to verify the calculated results and evaluate the process.

Each result is being put together in the report edited in FY 1994.

(2) For FY 1997

In 1996, to evaluate coal hydrogasification process, investigation of improvement of the process and social acceptability are performed.

For investigation of improvement of process, current status of research and

development activity on coal hydrogasification over the world were summarized and technological achievements were evaluated by the working group consists of young scientists established in Institute of Applied Energy.

Factors and tasks for evaluation of coal hydrogasification was extracted from the results of former feasibility study on coal hydrogasification process performed from FY 1990 to FY 1994 and will be reflected to the future investigation.

Methane (SNG) production process other than hydrogasification of coal is also investigated and will be carefully evaluated.

From the viewpoint of social acceptability, source of raw materials, relationship of methane and competing fuels, price of by-products (BTX), and price of energy are mutually rationalized. Current issues on resources, abundance and potential of supply of fossil fuels such as petroleum and coal are summarized. Purpose and tasks for the prediction in the future were discussed. Issues on conventional and non conventional natural gas resources, a competing fuel to coal based SNG, were extracted. Same kind of investigation was done for LNG as an another competing fuel. As cost of SNG produced by coal hydrogasification process is closely dependant to the price of BTX, by-product of the process, effect and issues of future coal-based BTX supply to the existing market were extracted.

Importance of coal based SNG production and development of hydrogasification technology was discussed from the viewpoint of bargaining power for energy and national security.

The outline of the results are described in the following.

(1) Evaluation of the coal hydrogasification process

① The introduction of the methane producing process from gasificated coal gas

- a. The outline of the coal hydrogasification processes of DOW, SHELL, KRUPPKOPPERS and TEXACO are introduced.
- b. Feeding method, gas flow direction, scaling up method, heat loss and oxygen or air blowing method of this process are evaluated technically.
- c. The heat and material balance of TEXACO type gasification reactor (wet-gas-type) which is now running on stable condition are showed.
- d. The producing efficiency of the methane synthesized with gasificated coal by SHELL or KRUPPKOPPERS gasification process (dry-O₂ blowing) is 65.5% and that of SNG synthesized by Lurgi is 40%.
- e. Future investigation subjects

The heat efficiency and economy of the methane synthesizing process using gasificated coal gas from SHELL or KRUPPKOPPERS gasification process in which

the methane producing efficiency is highest are to be investigated.

② Development of coal hydrogasification process and extraction of development-related factors and subjects

To upgrade the process the reports compiled in from FY 1990 to FY 1995 were examined.

a. The results of investigation concerned to upgrading of coal hydrogasification

The process has to be designed on the condition with many kinds of coal.

Control, gas purge method when nitrogen will be used, oxygen purity and oxygen making power, tar problem, HCN treatment, economic feasibility of BTX, reliability of gas yield by 2nd step reaction, these subjects have to be investigated.

b. The extraction of the factor and the subject about the optimization of the coal hydrogasification process

Ground of the plant size, refractories for the gasification reactor on high temperature and high pressure condition, adhesions of alkali metal and leaking of hydrogen at the heat exchanger, these subjects have to be investigated.

In the development of the coal hydrogasification process, the method for reducing the heat loss and controlling the carbon combustion and approaching to the reaction (Taiheiyotan : methane yield - 31%, benzen yield - 14%) which is a highest heat efficiency have to be investigated.

- Supposing that coal is completely changed into CO, H₂ in the high temperature territory, do the response balance calculation of the system that H₂O, H₂ were added under various temperatures, the pressure, and do enthalpy calculation together, too.
- The use rate of H₂ and O₂.
- Examination the possibility of that the coal will completely convert to the methane in only one reactor.

(2) The trend of development of fossil energy resources

① Coal

Though acceptable reserves of the whole world of the coal are about 3 ± 0.5 trillion tons, there is an uncertain point in the definition of the reserves.

Furthermore, we have to estimate the amount of annual production in the present condition, the life of the production, the change of the amount of annual production and the amount of export of the main coal production country of the world will be expected from now on.

② Petroleum and natural gas

We have to clear the definition of general ideas of reserves production.

As for the supply ability of the main petroleum production country of the world, the same investigation as the coal is necessary.

③ Unusual natural gas

a. Methane hydrate

It is a unused natural resources being in the limelight recently.

The acceptable amount of resources in the sea stage around Japan is estimated at 2.3 billion kl. The quantity is equal to the one for 43-year of the amount of consumption of the domestic natural gas, the one for about 4-year of the Japanese amount of the 1st energy use.

From now on, we should pay attention to a movement outside the country, and it will be important to work for the collection of the related information.

b. Coal bed methane

It is decided that there are 91~ 160 billion m³ resources when it is estimated from the Japanese coal confirmation reserves. The quantity is equal to the one for 17-30-year of the amount of consumption of the present natural gas comes.

Methane collection from the coal layer is done actively as a future subject in main coal production country of the world from the viewpoint of prevention of warming as well. We have to work for the related information gathering about the development conditions of the various foreign countries.

(3) Social adaptability of the coal hydrogasification process

① The supply and demand and price movement of the coal seen from the raw material side

We want to advance an examination based on the data on the nature of coal which conforms to the process.

How to expect the price of the coal was explained.

The FOB and CIF price of the coal to Japan from each country, the correlation of the price of the coal and the petroleum and the natural gas have to be examined. Furthermore,

the collection of the materials for the future change of the price of the coal is necessary.

② The supply, demand and price movement of LNG which competes with the coal hydrogasification SNG

It was estimated about the present condition of the supply and the demand of LNG and the natural gas in the world and in Japan. The LNG supply and demand plan of the countries in Asia which contains future Japan and the LNG project of the world have to be paid attentions.

The present condition and the change of the price of natural gas and LNG were examined.

Excepting the case that a crude oil price changes drastically in a short time like a former oil crisis, the LNG price of our country will change in the level which exceeded a crude oil price a little.

When the ratio of the LNG/ crude oil is presumed 1.10~1.20

Crude oil 17 \$/bbl → LNG 165 - 180 \$/ton

Crude oil 25 \$/bbl → LNG 245 - 265 \$/ton

We have to pay attention to the movement of the import crude oil of our country in the meaning of following the price of LNG.

And, the point of view toward LNG of the electric power industries, the price of the one for the industry and the one for the public welfare as well, these items have to be examined.

③ An influence on the market of the aromatic group of BTX

a. The extraction of the factor and the subjects relating to the supply and demand of BTX and the influence by new entering to the market

The uses of benzenes are mainly styrene monomer, cumene and cyclohexane. At present, it is presumed that there will be no change in these big three uses from now on. Correspondence to the movement of the decline of the benzene content in the gasoline is necessary.

The disproportionately treatment of the toluene by the increase of demand of xylene expands recently. Therefore, the benzene that is produced together with xylene has to be paid attentions. And, you must be careful of the demand for octane as a substitution of the benzene in the gasoline as well.

The benzene and the xylene of our country are the export dependence type by the supply and often influenced by the demand and the supply of the overseas market. Moreover, the reserve power of the supply of the benzene is worldwide big, therefore, there are many subjects of new entering.

b. The extraction of the factor and the subjects relating to the cost of BTX and the

influence by new entering to the market

Prospects for the BTX price of the present condition and of the benzene price in future of the United States and our country were examined.

The price of BTX in the United States is being ahead of the world. The movement of the price of United States is a big factor.

The related analysis of the supply and demand balance between and the price of BTX is a future subject. The amount of supply of the benzene from this project will have an influence on the market conditions.

④ Coal hydrogasification SNG in the energy security of our country

The comparison of the problem was done about the security concerned with the coal which was the raw material of LNG and SNG referring to the history of the introduction of LNG to our country.

- a. The political stability of the coal production country and sea lane problem
- b. A problem about the supply interruption
- c. The progress conditions of the LNG project

As a conclusion, the SNG is a converted coal energy and is equal to the coal about the energy security. Moreover, the increase of the amount of SNG will contribute to securing safety of LNG beyond the supply rate toward LNG.

4. Future Tasks

(1) Factory conditions of location

Before this process is materialized, a construction place is a big problem.

In this examination, we do not specify the construction area and will propose the condition to realize this process.

(2) The general idea design of the factory

Hold the design of the general idea of the factory of the coal hydrogasification which contains all of facilities in the circumference as the equipment for environment protection.

(3) Economic evaluation

In the precondition of the promotion of this project, the process has to be constructed in Japan.

Examine the way of the evaluation of profit of the large-scale project which lasts for a long time, to choose the most suitable way of evaluation on the precondition.

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