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NEW ENERGY AND INDUSTRIAL TECHNOLOGY
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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 elucidate the reaction mechanism of coal liquefaction and further to develop more efficient process. For these purposes, studies are conducted on the analysis of physical and chemical structures of coal, the liberation 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 and the analysis of physical properties of coal slurry.

Work Program

1) Study on liquefaction characteristics of various coals

Liberation of non-covalent bonds in coal and its effect on liquefaction reactivity, and the development of highly active and dispersed catalyst for the improvement of coal liquefaction performance.

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

Coprocessing of bitumen/coal oil and bitumen/coal for the elucidation of synergism.

3) Study on engineering aspects of coal liquefaction

Relationship between batchwise and continuous liquefaction data with relation to the scale-up of liquefaction reactor.

Summary (1984-1994)

1. Up to FY 1993

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 1994

(1) Study on liquefaction characteristics of various coals

(a) Effect of alkylation on liquefaction reactivity of high-rank coal

The non-covalent bonds in coal have been considered to be of fundamental importance for full understanding of physical properties of coal. Pretreatment techniques of coal, including selective (O-alkylation) and non-selective (reductive alkylation) techniques, have been investigated to determine the effect of these pretreatments on the reactivity of coal. O-alkylation reacts with hydroxyl and carboxyl functional groups in coal and can disrupt only hydrogen bonds. In the case of reductive alkylation, methyl group is added to not only hydroxyl and carboxyl group but also other active sites in coal. From these pretreatments, we can get the information of hydrogen bonds, ionic bonds and van der Waals interactions in coal molecules. The enhancement degree of reactivity was evaluated by liquefaction using tetralin as a hydrogen donor solvent. Illinois No.6 coal was used as coal sample. Coal conversion was determined based on toluene and THF solubility.

Figure 1 shows FT-IR spectra of raw and alkylated coals. For O-alkylated coal, there is very weak, OH stretching vibration at 3500 wave number compared to the raw coal. The weakness of OH stretching vibration results in disrupting of a part of hydrogen bonds in the sample. In the case of reductive alkylated coal, broad band at 3500 wave number has almost disappeared. This procedure probably disrupts most of hydrogen bonds in coal molecules.

Figure 2 indicates the change in composition of products after the liquefaction of raw and reductive alkylated coals. At 693K, total conversion of coal was drastically increased by reductive alkylation, where the production of oil and gas was promoted. Furthermore, the total conversion of reductive alkylated coal at 693K was much higher than that of raw coal at 723K. The difference in the reactivity between O-alkylation and reductive alkylation corresponds to the degree of disrupting non-covalent bonds in coal molecules. O-alkylation disrupts only hydrogen bonds in coal, but reductive alkylation reaction disrupts not only hydrogen bonds but also ionic bonds and van der Waals interactions. These results indicate that the penetration of hydrogen donor solvent into coal molecules may be very effective in increasing the reactivity of coals, especially at low reaction severity conditions.

(b) Development of highly dispersed iron-based catalyst

The improvement of contact efficiency between coal and catalyst has been tried to increase the catalytic activity and to reduce catalyst loading. The liquefaction of Taiheiyo coal which was impregnated with a sulfate-promoted iron oxide catalyst was conducted under 10 MPa initial hydrogen pressure at 673K, 698K and 723K by use of a 70 ml autoclave. The way to impregnate the catalyst on the surface of coal was that the coal was suspended into a mixture of aqueous solution of ferric sulfate and urea and then heated it up in a water at 370K for 2 h.

Figure 3 shows the effect of loading method of catalyst on coal conversion at 723K over iron oxide catalyst without sulfur as a promotor. The impregnation method gave a higher coal conversion than a mixing method in a range of greater amount of catalyst loaded. The FT-IR spectrum of impregnated coal showed the lower shift in wave number for OH stretching vibration, suggesting that the OH group in coal was strongly associated with the catalyst loaded.

Figure 4 shows the effect of sulfur loading on coal conversion. The active species of iron-based catalyst in coal liquefaction is considered to be pyrrhotite of which needs the coexistence of sulfur. However, the addition of sulfur did not affect the reaction in terms of coal conversion and high activity for the liquefaction of coal was obtained even in the absence of sulfur. These results suggest that the active species of the catalyst developed in this work might be different from pyrrhotite.

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

(a) Coprocessing of coal/bitumen

The coprocessing of oil sand bitumen with coal has been expected as a promising process. It is further reported that the additional enhancement of oil yield, namely synergistic effects, is sometimes observed in the coprocessing. The objective of the present work is to elucidate the mechanism of synergistic interaction in the coprocessing in conjunction with hydrogen transfer between coal and bitumen. These works were studied in two types of reaction systems: the upgrading of bitumen and coal-derived oil, respectively, and the coprocessing of bitumen with either coal-derived oil or coal additive. The coprocessing was performed by use of a 0.1 t/d continuous bench scale test plant.

Figure 5 shows the changes in the composition of products with the concentration of coal-derived oil in the feed when the bitumen is coprocessed at 723K. The yield of distillable oil in the upgrading of bitumen at 723K has already been underestimated as a result of retrogressive reaction and hence the upgrading data of bitumen can not be used for the calculation of additivity. In this work, the addition effect of coal-derived oil on the upgrading of bitumen was evaluated by the comparison with the broken line in the figure which showed the sum of distillable oil fraction from the raw bitumen and coal-derived oil present in the feed. If the coprocessing data is lower than the broken line, it means that the retrogressive reaction of bitumen still occurs even in the presence of hydrogen donor solvent. At 723K, the yield of distillable oil at coal oil concentrations of 13 wt% and 25 wt% was in fair agreement with the broken line in spite of the considerable decrease in oil yield observed at coal oil concentration of 0 wt%. The result shows that the addition of coal-derived oil which is a good hydrogen donor solvent is very effective for the suppression of retrogressive reaction of bitumen and at least approximately 10 wt% of coal-derived oil

is necessary to avoid the retrogressive reaction of bitumen under the present coprocessing conditions.

Figure 6 shows the change in the composition of products with the concentration of coal in the slurry feed of bitumen/coal. Here, the amount of distillable oil in the slurry feed was calculated from its original amount in the raw bitumen added and was illustrated by the broken line in the figure. The yield of distillable oil in the coprocessed products was increased by the addition of coal up to 10 wt% and then decreased with the increase in the concentration of coal. These values were comparable or slightly higher than the broken line at any coal concentrations except for 40 wt%. The result shows that the retrogressive reaction of bitumen is effectively suppressed by the addition of coal and the gap between the yield of distillable oil and the broken line corresponds to the amount of oil formed by the decomposition of bitumen pitch or coal. However, the production of oil from coal is considered to be small, because the gap between the broken line and the yield of distillable oil would be enlarged with an increase in the concentration of coal if some amounts of oil is produced by the decomposition of coal. Actually, the yield of distillable oil came close to the broken line with the increase in the concentration of coal. It is therefore concluded that the apparent enhancement of distillable oil in the coprocessing is mainly due to the suppression of retrogressive reaction which occurred in the upgrading of bitumen alone and/or to the promotion of decomposition of bitumen pitch by the addition of coal, not due to the formation of oil from coal. The coal as well as coal-derived oil probably acts as a hydrogen donor in the coprocessing. In summary, the coprocessing of bitumen with 5~30 wt% of coal was superior or comparable to the upgrading of bitumen alone in terms of production of distillable oil.

(3) Study on engineering aspects of coal liquefaction

The analysis of relationship between batchwise and continuous coal liquefaction data is indispensable for the establishment of liquefaction simulator. In the present work, the liquefaction of Taiheiyo coal with anthracene oil and red mud/sulfur catalyst was conducted by use of a batch reactor and a bench-scale preheater. Rate constants were obtained from the analysis of experimental results with two reactants model. Furthermore, the coal conversion in a continuous liquefaction was estimated by use of these rate constants with a perfect mixed reactor model.

Arrhenius plots of reaction rate constants for less active constituent (k_1) and active one (k_2) of coal obtained in the batchwise experiments are shown in Figure 7. k_1 was approximately 1 order smaller than k_2 in anthracene oil, but was almost comparable to k_2 in tetralin as a solvent. Therefore, it was found that k_1 strongly depended on the hydrogen donorability of solvent, while k_2 did not. In the case of anthracene oil which is first hydrogenated and then donates hydrogen to coal

molecules, its hydrogen donorability is considered to be greatly influenced by hydrogenation degree of the solvent which depends on hydrogen pressure and reactor type. Assuming that the frequency factor depends on hydrogen pressure and reactor type and the activation energy does not for k_1 in the continuous preheater, the model of well-mixed reactor in series was adopted for the analysis of the reaction in the preheater. The reaction rate constant (k_1') for less active constituent of coal in the preheater was larger than k_1 by about one order. The discrepancy between k_1 and k_1' is considered to come from the difference in the concentration of transferable hydrogen in the solvent, resulting from the fact that hydrogen pressure in the preheater is almost 3 times as high as that in the batch reactor. Furthermore, when the well-mixed model was used for the analysis of liquefaction reaction in a reactor, the observed values of coal conversion approximately agreed with the calculated values. Therefore, it was found that the frequency factor of the reaction rate (k_1) varied with both pressure and reactor type, but the activation energy did not. The effect of vaporization of solvent on the residence time of coal slurry in the reactor could be neglected under the present reaction conditions (30 MPa, 723 K), and the residence time was governed only by the gas holdup of reactor.

Future tasks

The following tasks will be required to improve the performance of coal liquefaction process:

- 1) Analysis of distribution of various types of bonds in macromolecular structure of coal.
- 2) Development of highly active and dispersed catalysts.
- 3) Analysis of mechanism of hydrogen transfer and its control at the initial stage of liquefaction reaction.
- 4) Analysis of coal slurry properties such as solubility of coal, phase split in the slurry and so on.

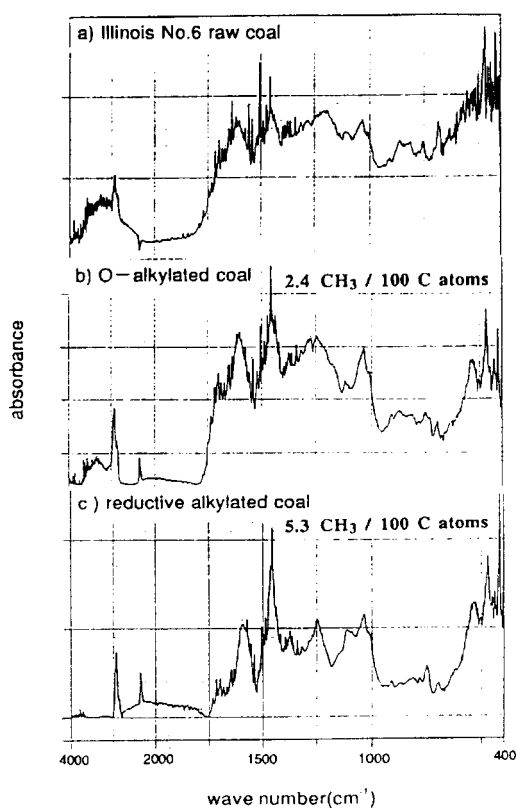


Fig.1 FT-IR spectra of raw and reductive alkylated coal

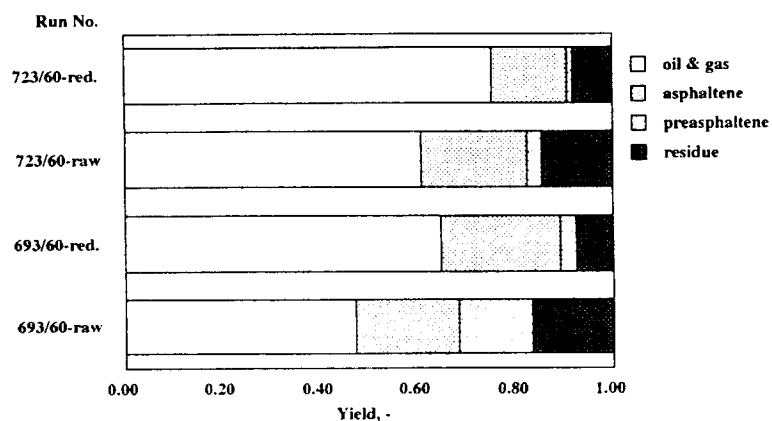


Fig.2 Results of liquefaction of raw and reductive alkylated coal

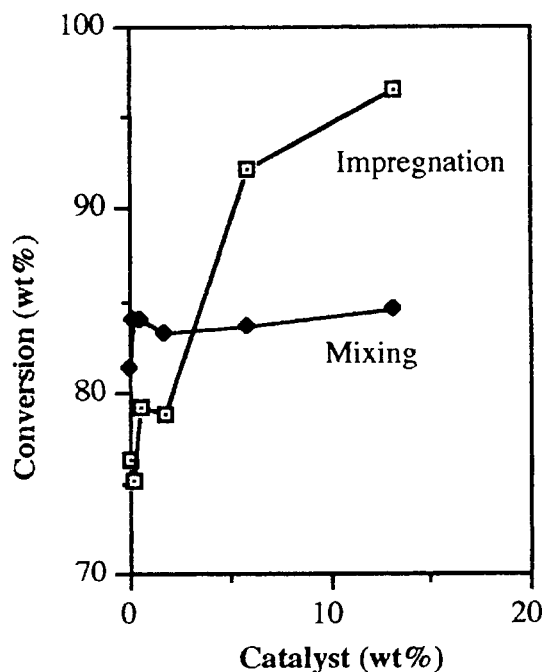


Fig.3 Effect of addition method of catalyst on coal conversion

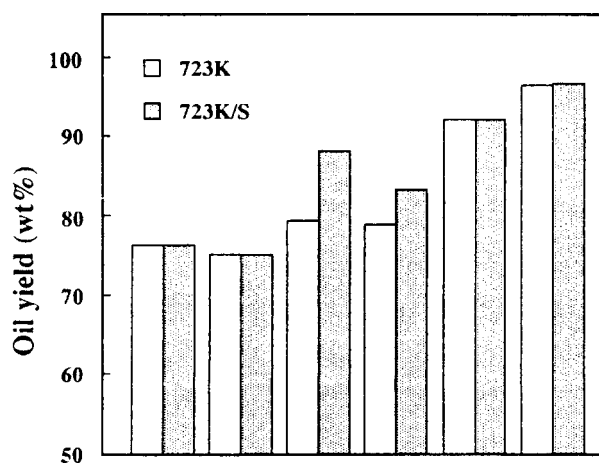


Fig.4 Effect of addition of sulfur on activity of iron catalyst

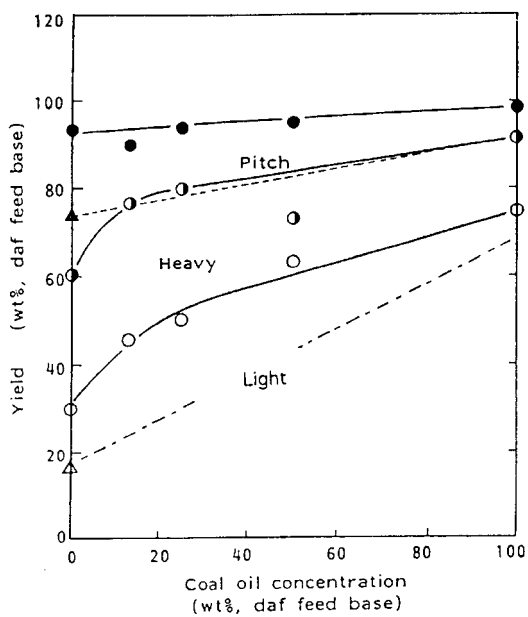


Fig.5 Effect of addition of coal-derived oil on hydrocracking of bitumen

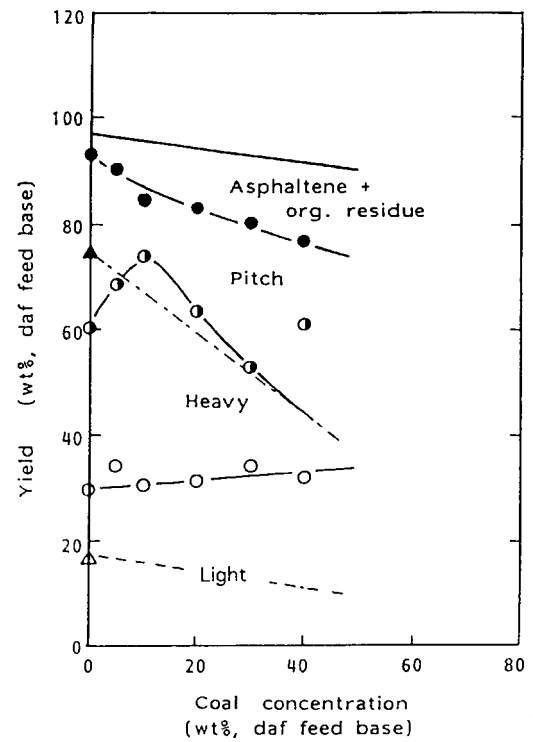


Fig.6 Effect of addition of coal on hydrocracking of bitumen

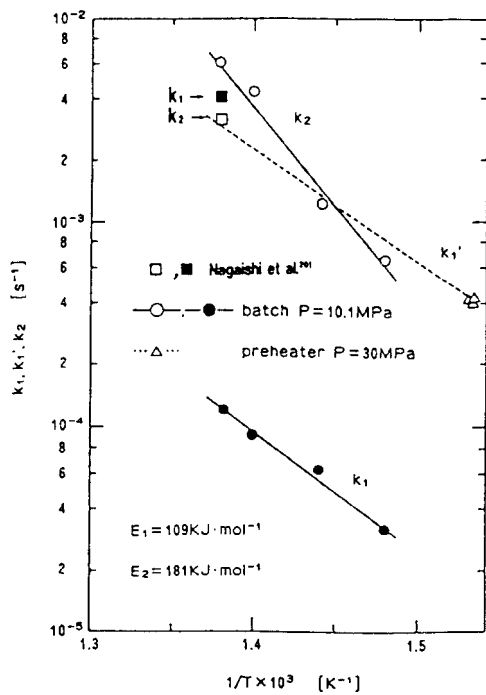


Fig.7 Arrhenius plots of rate constants for Taiheiyo coal liquefaction

STUDIES ON CATALYSTS FOR COAL LIQUEFACTION

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Objectives

Investigation of catalysts which enable to produce liquid fuels from coal and establishment of analytical methods applicable to coal liquefaction.

Work Program

Each of the following subjects is studied based on the results obtained through the years up to FY 1994.

(1) Design and characterization of catalysts

- a. Combination of the hydrogenation and hydrocracking activities is investigated to optimize the catalytic performances of upgrading catalysts.
- b. Mechanism of catalyst deactivation due to metal and carbonaceous deposits and changes in local structures of active metals is investigated to develop a highly active catalyst with a long life.

(2) Mechanistic studies on principal reactions in coal liquefaction

The role of catalyst and solvent in coal liquefaction is investigated by the detailed characterization of original coals and coal-derived liquids.

(3) Studies on systems for catalyst reaction

Preparation of catalyst and reaction system of catalyst are investigated to improve catalyst performance.

Summary (1980-1994)

1. Up to FY 1993

(1) Design and characterization of catalysts

- a. Nickel-tungsten catalysts were designed and prepared based on understanding of fundamental research.
- b. The nickel-tungsten catalysts were more active than the conventional nickel-molybdenum catalysts for upgrading coal-derived liquids.
- c. Oxygen-containing compounds and dissolved molecular oxygen in coal-derived oils deactivated the sulfided catalysts significantly. Co-refining of coal-derived oils and petroleum oils suppressed this kind of deactivation.
- d. The Y-zeolite/ Al_2O_3 catalysts promoted with some of the active metals, such as Ni, Mo and W, were highly active for cleaving the naphthenic rings with minimal amounts of carbonaceous deposits.

(2) Mechanistic studies on principal reactions in coal liquefaction

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

(3) Studies on systems for catalyst reaction

- a. Evaluation of catalyst performance in fixed bed reactor and complete stirred tank reactor was done. Effects of catalyst particle diameter and hydrogen donorability of solvent were also evaluated.

b. Preparation of fine metal particle catalyst was investigated by using combination of mechanical vibration and chemical reaction.

2. For FY 1994

(1) Design and characterization of catalysts

Two types of hydrotreating catalysts for upgrading coal-derived liquids were designed and prepared based on understanding of thermodynamic analyses, characterization of catalyst properties and functions. Hydrogenation and hydrocracking catalysts prepared in FY 1994 were then used for model test and upgrading reactions in order to evaluate catalytic performance of the catalysts. Results obtained from fundamental and practical investigations concerning hydrogenation and hydrocracking activities and catalytic performance of the catalysts are as follows.

a. Hydrogenation catalyst

Deactivation mechanism of the Ni-W catalyst which was prepared and used for upgrading coal-derived liquids for 2,000 h in FY 1993 was investigated to improve catalytic performance of the Ni-W catalyst. Based on understanding of catalyst deactivation behavior (changes in local structures of active metals during reaction such as crystal growth of WS_2 like structure and release of Ni from W), a new Ni-W catalyst was designed and prepared by optimizing physical and chemical properties of alumina support and active metal loading. Then metal sulfiding of the Ni-W catalyst was controlled to give the highest hydrogenation activity.

Model test reactions revealed that this newly prepared catalyst possesses the highest hydrogenation activity among other Ni-W catalysts prepared up to FY 1993 and commercially available catalysts. Upgrading reactions of coal-derived liquids were then carried out over the new Ni-W catalyst. Accelerated aging tests of the catalyst were also performed to evaluate catalytic performance. This newly prepared catalyst gave considerable improvements in overall activities (aromatic saturation, HDN and HDS) and initial deactivation as compared to the Ni-W catalyst prepared in FY 1993.

b. Hydrocracking catalyst

We selected a mixture of a crystalline Y-zeolite and amorphous double oxide support as the support component of hydrocracking catalysts because of the highest hydrocracking activity for naphthenic ring cleavage. Up to FY 1993 the basic synthesized zeolites (NaY, Si/Al ratio = 5) were highly modified because the Y-zeolite must be thermally stable and nitrogen-tolerant. In FY 1994 high silica NaY zeolites (Si/Al ratio = 7) were synthesized for developing a new hydrocracking catalyst with a superior activity and long life. Then H-form of zeolites was prepared by NH_4^+ ion exchange. The protonated form was obtained after calcination of the NH_4^+ -form at 550 °C. The high silica Y-zeolites were much more stable during the ion exchange. Na was more easily removed from the high silica NaY-zeolite without loss of crystalline structure compared to commercially available NaY-zeolite (Si/Al ratio = 5). The high silica HY-zeolites showed higher hydrocracking activities in the model test reactions at lower temperature than commercially available HY-zeolite, indicating that new hydrocracking catalysts prepared using the high silica zeolite possesses superior hydrocracking activity as well as longer life.

(2) Mechanistic studies on principal reactions in coal liquefaction

a. The role of catalyst and solvent in coal liquefaction

Taiheiyo coal has been liquefied at 410, 430, 450 and 470 °C with 1-methylnaphthalene (1-MN) or tetralin as vehicle and either with presence or absence of FeS_2

catalyst. The roles of catalyst and solvent in the reaction were investigated by analyzing the liquid and solid products in detail. The liquefaction was considered to involve two types of reaction: very rapid reaction and the successive slow reaction. A recombination of radical intermediates to form tetrahydrofuran-insoluble fraction (THFI) seems to proceed during the former reaction stage and the resulted THFI showed lower reactivity for the secondary cracking. The successive degradation of residual oil and distillable fraction was observed during the latter reaction stage. Tetralin solvent suppressed both the formation of THFI and the secondary cracking of produced oil (Fig. 1). The existence of the catalyst resulted in the suppression of recombination to a significant extent.

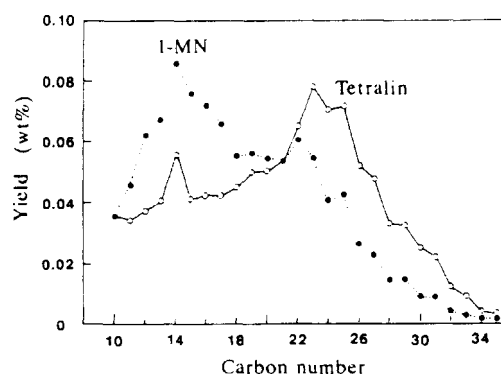


Fig. 1 Effect of Solvent on the Yields of *n*-Paraffins without catalyst

b. Clarification of structural changes during coalification process

Cellulose (CEL), Japanese red pine (AKA) were thermally decomposed in water at 200 °C for 50 h, and the chemical structures of the solid products (CEL50, AKA50) were investigated. The solid state ^{13}C -NMR spectra of the samples (Fig. 2) showed that cellulose and Japanese red pine were converted into brownish materials which have similar structures to Morwell brown coal (MOR) and Morwell coalified log (MLG), respectively. The six samples shown in Fig. 2 were hydrogenated over $\text{Ni-Mo}/\text{Al}_2\text{O}_3$ for the further consideration of their structures. While gases and light liquid were predominant in the hydrogenated products from CEL and AKA, toluene-insolubles and heavy oil were produced in a large amount from the hydrogenation of the hydrous pyrolysis residues (CEL50 and AKA50) as shown in Fig. 3. Major products from cellulose were hexane,

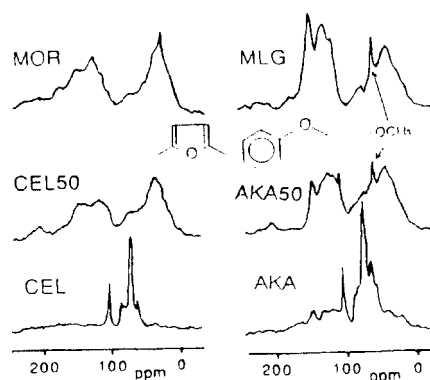


Fig. 2 CP/MAS ^{13}C -NMR Spectra: CEL; cellulose, AKA; Japanese red pine CEL50 and AKA50; hydrous pyrolysis residues of CEL and AKA. MOR; Morwell brown coal. MLG; Morwell coalified log

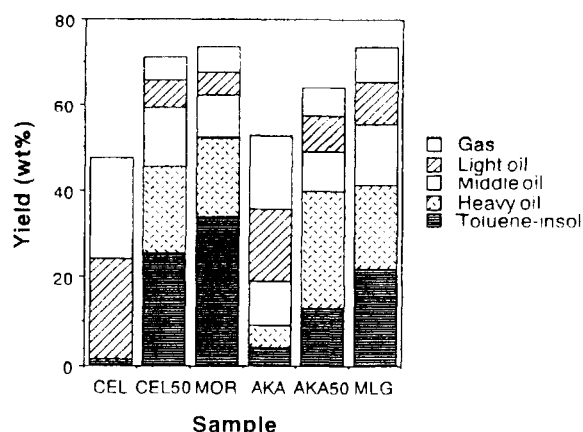


Fig. 3 Distribution of Hydrogenated Products of CEL, AKA, CEL50, AKA50, MOR and MLG

methylcyclopentane and C1-C5 hydrocarbons, and the hydrous pyrolysis residue (CEL50) provided a significant amount of cyclohexanes and polycyclic compounds of which yields were similar to those from Morwell brown coal (MOR). These results would show that cellulose were converted into Morwell coal-like structure after the thermal degradation in water for 50 h at 200 °C.

(3) Studies on systems for catalyst reaction

a. Synthesis of ultra fine catalyst particle

Ultra fine metal sulfide particles were synthesized by arc-discharge methods and catalytic activity of these metal sulfide particles were investigated. The metals used were Co, Ni, Fe and alloy of Fe and Co. The average diameter of these metal particles were 20 nm and these fine metal particles were sulfided by H_2S . The catalytic activity of these fine metal sulfide particles were examined by using model compound. The experiments were carried out in a 50 ml stainless steel autoclave at 400-450 °C under the initial hydrogen pressure of 7.9 MPa.

Figure 4 shows results of experiment. Hydrogenation activity of these ultra fine metal particles per weight were as follows, $Co > Ni > Fe$. The structure of sulfided Co was Co_9S_8 , but that of sulfided Ni was mixture of Ni_xS_y ($x > y$). We didn't find any synergy effect of Fe and Co in the case of alloy of Fe and Co. We are now applying these catalyst to the liquefaction of Wandoan coal.

b. Effect of type of Mo catalyst on coal liquefaction.

Various types of Mo catalyst were examined to investigate the role of Mo catalyst in the coal liquefaction reaction. Following type of Mo catalyst were examined, (a) oil soluble Mo catalyst dispersed in liquefaction solvent, (b) impregnation of coal with oil soluble Mo catalyst, (c) Co-Mo/ Al_2O_3 catalyst, (d) powder of Co-Mo/ Al_2O_3 catalyst. Molybdenum dioxyacetylacetonate ($MoO-AA$) was used as oil soluble Mo catalyst. Cyanamid HDS1442A was used as Co-

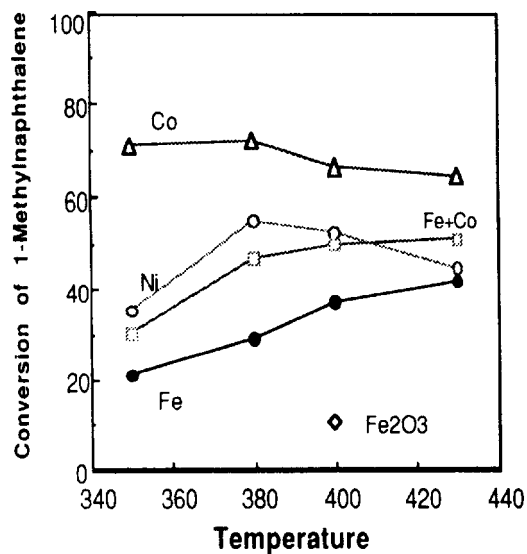


Figure 4 Relationship between temperature and conversion of 1-methylnaphthalene reaction time=60min, $PH_2=7.9$ MPa, catalyst%=5 wt%

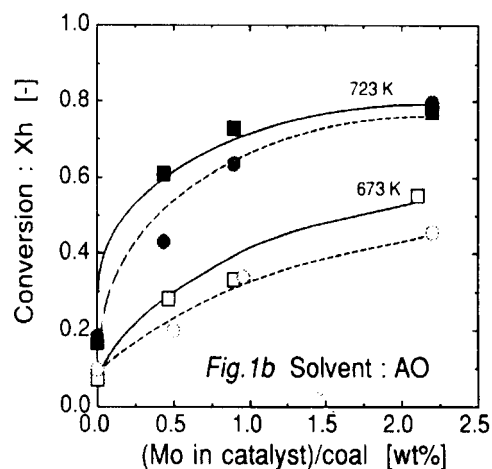
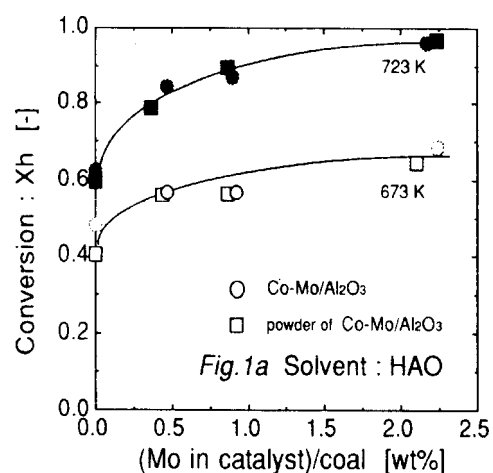


Figure 5 Liquefaction of Taiheiyo coal by using supported Mo Catalyst. (□,■): catalyst(a) (Original Co-Mo/ Al_2O_3 catalyst). (○,●): catalyst(b) (powder of Co-Mo/ Al_2O_3 catalyst, average diameter=2.5 μ m)

Mo/Al₂O₃ catalyst. Powder Co-Mo/Al₂O₃ was prepared from combination of Co-Mo/Al₂O₃.

Liquefaction experiments were done by using 50 ml autoclave at 400°C and 450°C, hydrogen pressure (initial) was 9.8 MPa. We used Taiheiyo coal and anthracene oil (AO) and hydrogenated anthracene oil (HAO) as liquefaction solvent (coal/solvent = 3/7). Mo metal concentrations were 0.5wt% - 2wt% of coal. Figure 5 shows results of experiment of catalyst (a) and (b). Figure 6 shows results of experiment of catalyst (c) and (d). The results showed that catalyst activity (yields of hexane soluble) of Mo had little concern with the type of Mo catalyst in the both HAO and AO, and catalyst activities were correlated to the total amount of Mo metal in the reactor. From comparison of catalyst (a) and (b) in the AO solvent, Mo catalyst did not catalyze hydrogenation of solid coal. From comparison of catalyst (a), (c) and (d) in the AO solvent, dispersion of Mo metal in the solvent was important to improve catalyst performance. We suppose that contact of Mo metal and solvent is essential in the liquefaction reaction.

Future Tasks

- (1) Optimization of calcination/sulfidation conditions to control the catalyst activity/selectivity.
- (2) Preparation of highly stable Y-zeolites for developing a new hydrocracking catalysts with a long life.
- (3) Full understanding of the role of catalyst and solvent in coal liquefaction
- (4) Preparation of highly active ultra fine particle catalyst.
- (5) Utilization and development of catalyst based on chemical structure of coal.

Major publications in FY1994

“Structural change of supported Ni-Mo sulfide catalysts during the hydrogenation of coal-derived liquids”

N. Matsubayashi, H. Shimada, T. Sato, Y. Yoshimura, M. Imamura, and A. Nishijima, *Fuel Processing Technol.*, **41**, 261 (1995).

“Catalytic functions of molybdenum sulfide catalysts supported on alumina (Part 3) Effect of active metal and metal loading on catalytic activities”

T. Kameoka, T. Sato, Y. Yoshimura, H. Shimada, N. Matsubayashi, and A. Nishijima, *Sekiyu Gakkaishi*, **37**, 497 (1994).

“Structural stability of binary sulfide catalysts during the hydrotreating of coal-derived liquids”

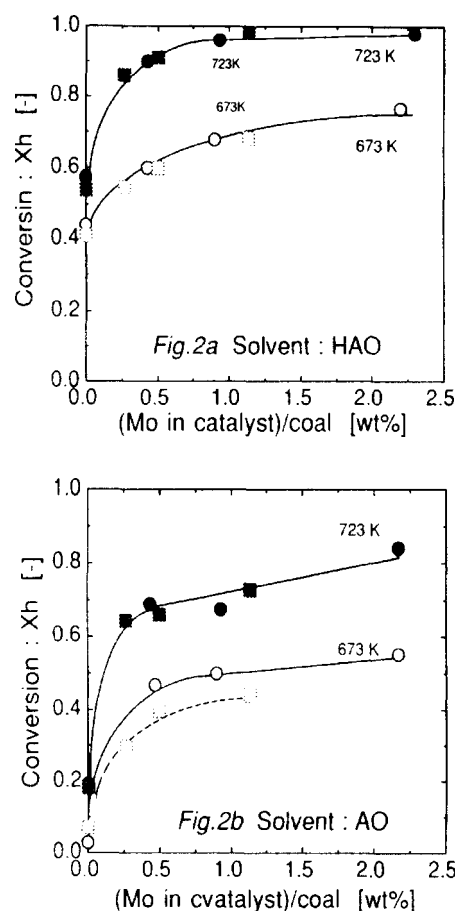


Figure 6 Liquefaction of Taiheiyo coal by using Oil soluble Mo. (○,●):catalyst (c) (dispersed in liquefaction solvent). (□,■): catalyst(d) (impregnation of coal with MoO₂-AA).

H. Shimada, N. Matsubayashi, M. Imamura, T. Sato, Y. Yoshimura, T. Kameoka, K. Masuda, and A. Nishijima,
Bull. Soc. Chim. Belg., **104**, 353 (1995).

“Hydrodesulfurization and additional reaction of thiophenic compounds”

Y. Miki, Y. Sugimoto,
Sekiyu Gakkaishi., **37**, 386(1994).

“Compositional analyses of lignin- and coal-derived liquids by GCMS chromatograms”

Y. Sugimoto, Y. Miki,
J. Fuel Soc. Jpn., **73**, 333(1994).

“Hydrocracking of acenaphthene over a sulfided Ni-Mo/Al₂O₃ catalyst”

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“Study on the swelling behavior of the coal by using atomic force microscopy”

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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 the coal liquefaction

(1) Comparative Evaluation of Oil Soluble Metal Compounds as Catalysts for Coprocessing of Coal and Tarsand Bitumen

Comparative catalytic evaluation of oil soluble metal compounds were carried out in coprocessing of coal and tarsand bitumen.

(2) Comparison of Solubilization Behavior of Taiheiyō coal and Yallourn coal in Liquefaction at Mild Conditions by the aid of Super acid

Solubilization of Taiheiyō coal and Yallourn coal at mild conditions using super acid in the presence of isopentane and hydrogen donor without gaseous hydrogen is studied.

(3) Hydropyrolysis of Swollen Coal

Effect of hydrogen pressure and reaction time on hydropyrolysis are investigated and swollen coal by solvents are pyrolyzed to study an influence of the structure of coal on hydropyrolysis.

(4) Liquefaction Behavior of Finely Pulverized Coal

The effect of the Fe_2O_3 -sulfur catalyst concentration on the liquefaction of finely pulverized coal and conventional particle size coal (-100 mesh) was experimentally compared.

2. Hydrotreatment of Coal Derived Liquid

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

Effect of solvent extraction conditions on the extraction yields are carried out to obtain the fundamental data for solvent extraction method to separate phenol and its derivatives from coal liquids.

(2) Dearomatization of coal liquids

The performance of some shape selective adsorbents which showed good result in FY1993 are studied and the preparation conditions for such adsorbents are also investigated.

SUMMARY (1975-1994)

1. Up to FY 1993

(1) Fundamental Study on the 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. TFMS (trifluoromethanesulfonic acid) completely solubilized Taiheiyō coal in the presence of isopentane or n-pentane at 150°C for 3h without gaseous hydrogen. On the hydropyrolysis of coal, the effects of hydrogen pressure and swelling with tetralin on the conversion were significant for finely pulverized coal. In the case of finely pulverized coal liquefaction, the HS yield increased to 52.4 wt% by 0.5wt%/slurry addition of nonion mixed with anion surfactants.

(2) Hydrotreatment of Coal Derived Liquids

The degrees of hydrogenation, desulfurization, denitrogenation and

deoxygenation of coal derived liquids have been evaluated using continuous apparatus equipped with fixed bed tubular reactor. On color stability of raw coal liquids, it was clarified that coal liquid was colored by the oxidation of mainly nitrogen compounds. A continuous apparatus for methanol-water extraction of phenolic compounds was designed and operated. High pressure crystallization technique was also applied to isolate the nitrogen containing compounds from model coal liquids. Several commercial adsorbents and prepared adsorbents were tested to evaluate the separation ability of aromatic compounds.

(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 1994

(1) Fundamental Study on the Coal Liquefaction.

(a) Comparative Evaluation of Oil Soluble Metal Compounds as Catalysts for Coprocessing of Coal and Tars and Bitumen

In the coprocessing of coal and heavy oil (bitumen), the feedstocks of both are upgraded simultaneously by catalytic hydroconversion. The catalysts for coprocessing is very important for efficient oil production. The evaluation of oil soluble metal compounds (Mo, W, V, Ni, Co and Fe) as catalysts for coprocessing of Taiheiyo coal and Cold Lake tars and bitumen were studied. The catalysts used here are shown in Table 1. The catalytic activity of oil soluble metal compounds for coprocessing was evaluated by the conversion of hexane insolubles and toluene insolubles in the feedstocks. The results are shown in Fig. 1. Mo compounds showed higher activity than any other oil soluble metal compounds. The order of catalytic activity of oil soluble metal compounds was $\text{Mo} > \text{Ni} > \text{Co} > \text{Fe}$. W and V compounds did not exhibit catalytic activity for the coprocessing. Molybdenum dithiocarbamate (MoDTC) which contain sulfur atoms in the molecule showed the highest activity among the Mo compounds. The addition of elemental sulfur in reaction mixture gave significant increase of catalytic activity of Mo compounds other than MoDTC, since Mo compounds were converted under the reaction conditions to MoS_2 which is effective for coal liquefaction. No synergic effects of Mo and Ni compounds were found in this study.

(b) Comparison of Solubilization Behavior of Taiheiyo coal and Yallourn coal in Liquefaction at Mild Conditions by the aid of Super acid

TFMS (Trifluoromethanesulfonic acid) was found to solubilize lignite and subbituminous coal in the presence of isopentane at temperature as low as 150°C for three hours under autogeneous pressure of 6.1-6.9 MPa without hydrogen. Yallourn coal gave 63 wt% pyridine soluble fraction after reaction and required more TFMS to achieve the maximum solubility, but the treated Taiheiyo coal could be solubilized in pyridine to the extent of 90% by the same reaction with TFMS (Fig. 2). Acid catalyzed depolymerization with TFMS would be inadequate, because the lignite has many oxygen containing functional groups. The average molecular weight of benzene soluble and THF soluble fraction from the treated Yallourn coal decreased, and their aromaticity increased with the increase of TFMS concentration (Table 2). In contrast, average molecular weight of soluble fraction from the treated Taiheiyo coal was unchanged, and their aromaticity decreased with the increase of TFMS concentration. It is suggested that TFMS plays an important role in

depolymerization of the coal molecules for Yallourn coal solubilization, and accelerate alkylation and hydrogenation in the Taiheiyo coal solubilization.

(c)Hydropyrolysis of swollen coal

Taiheiyo coal under 100 mesh was mixed with tetralin, pyridine and 5,6,7,8-tetrahydroquinoline (5THQ), respectively at weight ratio 1:7. Swelling was carried out under 5.0MPa of nitrogen gas at 200°C for 60min. Swollen-dried coal was prepared by heating swollen coal under vacuum condition at 110°C. Remodeled Curie point pyrolyzer for high pressure was used. The sample was wrapped by a foil and heated at 764°C and 920°C for 5-360sec under 0.1MPa and 6.0MPa of hydrogen and helium. Relationships between conversion and reaction time are shown in Fig. 3. Conversion of coal increased significantly as reaction time until 10 sec. It was 43% at 764°C under 0.1MPa of helium at 10sec. However, slight increase of conversion was observed more than 10sec. Under 0.1MPa of hydrogen, conversion at 60 sec was 47%. Conversion of coal at 10 sec under 6.0 MPa of helium was 38%, remarkable increase of conversion was not observed more than 10sec. On the other hand, under 6.0MPa of hydrogen gas, conversion at 10sec was almost same as that under helium gas and it increased up to 47% at 60sec. This implies that extremely fast reaction of pyrolysis completed until 10sec and relatively slow reaction with hydrogen gas were carried out during hydropyrolysis. The reaction with hydrogen gas was accelerated under high pressure of hydrogen. At 920°C, conversion under 0.1MPa and 6.0MPa of hydrogen were 53% and 73% respectively. This indicates the reaction with hydrogen was enhanced at high temperature. Increases of volume after swelling by tetralin, pyridine and 5THQ were 14%, 83% and 63% respectively. Solvents that have nitrogen in aromatic ring swelled coal effectively. Remarkable increases of conversion were not observed for swollen coal by tetralin and pyridine. High conversion of swollen coal and swollen-dried coal by 5THQ indicates that 5THQ modified structure of coal by swelling effectively.

(d)Liquefaction Behavior of Finely Pulverized Coal

The effect of the Fe_2O_3 -sulfur catalyst concentration on the liquefaction of finely pulverized coal and conventional particle size coal (-100 mesh) was experimentally compared. Finely pulverized Taiheiyo coal (average particle diameter : $4\mu\text{m}$) was prepared using a recently developed slurry jet mill. Experiments were conducted in a 200ml magne drive autoclave in the presence of a coal-derived recycle solvent and Fe_2O_3 catalyst at initial hydrogen pressure of 8.5MPa and temperature of 440°C. Liquefaction of a conventional particle size coal (-100 mesh) was performed under the same reaction conditions for comparison purpose. Conversions of the two coals, on a daf basis, calculated from THF insolubles, were similar (95-96wt%) in either cases. However, the finely pulverized coal showed a much higher HS yield of 45.1wt%, while the conventional particle size coal had only 39.5wt% HS yield at catalyst concentration of 4.4wt%, daf coal as shown in Fig. 4. Similar differences in HS yield were seen at lower concentration of iron catalyst. The higher HS yield obtained with the finely pulverized coal sample may be attributed to the enhanced contact among the components of the coal-catalyst-solvent slurry, resulting in lower amounts of retrogressive products. To examine the effective dispersion among the components in the slurry for liquefaction, the effect of surfactant addition on the yield of liquid product and the conversion from liquefaction was examined. In the case of finely pulverized coal, the HS yield increased to 52.4wt% by 0.5wt%/slurry addition of nonion mixed with anion surfactants, while the HS yield, obtained without surfactant, was 45.1wt%. The increased conversion and HS yield from the -100mesh coal with the surfactant were also observed as similar as the finely pulverized coal. Finely ground coal with few micron in average particle

diameter have attracted attention because of its favorable liquefaction behavior, etc. Since finely ground coal is prepared through coal-water mixture and seemed to be easily oxidized during the preparation process, the gas production behavior during pyrolysis that reflects the oxidation degree of coal was studied. The gas production behavior of finely ground coal during pyrolysis in nitrogen atmosphere was almost same as that of raw coal with few hundred micron in diameter (Table 3). In hydrogen atmosphere, finely ground coal, however, produced less amount of hydrogen sulfide in relatively high temperature range than raw coal. The change in hydrogen sulfide production indicates small degree of oxidation of finely ground coal.

(2) Hydrotreatment of Coal Derived Liquid

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

The methanol-mediated extraction has been performed by the mixing methanol to the samples of coal liquid distillates and following addition of water to the resulting mixture. The samples which have been used for the extraction are generally dissolves with methanol at any proportion to afford homogeneous mixtures of the oil and methanol. However, mixing a naphtha distillate of Wyoming coal derived liquids with methanol gave a heterogeneous mixture at the naphtha/methanol ratio of 1/4 to 8/4. This phenomena would be caused by the lower contents of aromatic compounds in the oil. To determine the suitable method for the extraction of such heterogeneous mixture of a Wyoming naphtha distillate and methanol, we have compared the results of the extraction of a Wyoming naphtha distillate by two methods, Method A and B. Thus, a naphtha distillate of Wyoming coal liquid was mixed with methanol at the naphtha/methanol ratio of 1/4 to 8/4 to give two layers. One is an oil layer which is saturated with methanol and a methanol layer which dissolves a slight amount of phenolic compounds. In the Method A, water was added to each layer and the each mixture was shaken with a shaker. After the mixture was settled until it separated in two layers clearly, the extracted samples were analyzed to determine extraction yield of phenolic compound with GC. In the Method B, water was added to the heterogeneous mixture and the resulting mixture was shaken for 10 min. The mixture was settled until it separated in two layers clearly, the extraction yield was determined by GC analyses of the extracted samples. Generally, both methods of Method A and Method B gave the similar results in the extraction yield of phenol as shown in Table 4. And the selectivity of phenol in the Method B was higher than that in Method A. From the extraction procedures of Method A and B, Method B is more simple and easy to be performed. Therefore, Method B is better for the treatment of a heterogeneous mixture of a naphtha and methanol with water at the points of its simple handling and the selectivity of phenol.

(b) Dearomatization of coal liquids

Two kinds of adsorbents having 0.9 and 1.0 nm in pore diameter, which showed good result on screening test, was compared their adsorption ratio by static method using the adsorbents and 10 times of this amount of monoaromatics-heptane solution (about 1 wt%). Both adsorbents adsorbed monoaromatics without exception (Fig. 5), but the adsorbent having 0.9 nm in pore diameter slightly less adsorbed o-ethyltoluene than the other. This variation was only observed at low concentration. The amounts of ultimate equilibrium adsorption were estimated using several monoaromatics-heptane solutions. They were about 2 mmol/g for both adsorbents. As the molecular weight of the monoaromatics were 100-130, Both adsorbents had relatively large amounts of ultimate equilibrium adsorption of 20-25 wt.%. The adsorption tests were done using model gasoline by static method and oil/adsorbent ratio of 2. The model gasoline consisted of 49.8, 21.8, 12.8 and 15.6 wt.% of n-

paraffin, iso-paraffin, naphthene and monoaromatics, respectively, but free from polar compounds. This ratio was determined the analysis of coal liquid naphtha fraction. After adsorption, aromatic content was decreased while other fractions did not varied(Fig. 6). This result indicates that the adsorbents were effective to remove aromatics.

Future Tasks

1.Fundamental Study on the Coal Liquefaction

- (1)Study the chemical desulphurization behavior in the liquefaction at mild conditions by the aid of super acid.
- (2)Study the optimization of solvent in liquefaction coprocessing.
- (3)Study the reactivity of coal surface with H_2 in hydrolysis.
- (4)Study the effect of catalyst pulverization and various catalysts of fine powder in the coal liquefaction.

2.Hydrotreatment of Coal Derived Liquids

- (1)Study the reaction of phenolic compounds during the hydrotreating of coal liquids.
- (2)Study the extraction behavior of nitrogen containing compounds from coal liquids in solvent extraction.
- (3)Study the effect of solvents and selectivity of adsorbents.

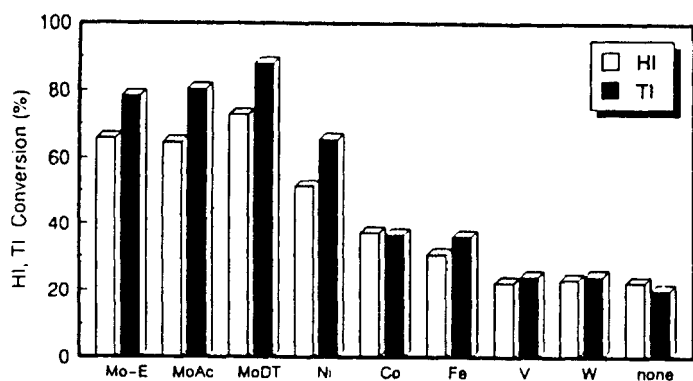


Fig.1 Catalytic activity of oil soluble metal compounds.

Reaction conditions: Cat. : 0.2wt% as metal/coal TSB/coal : 2wt/wt
 H_2 : 10 MPa, 430°C, 60min

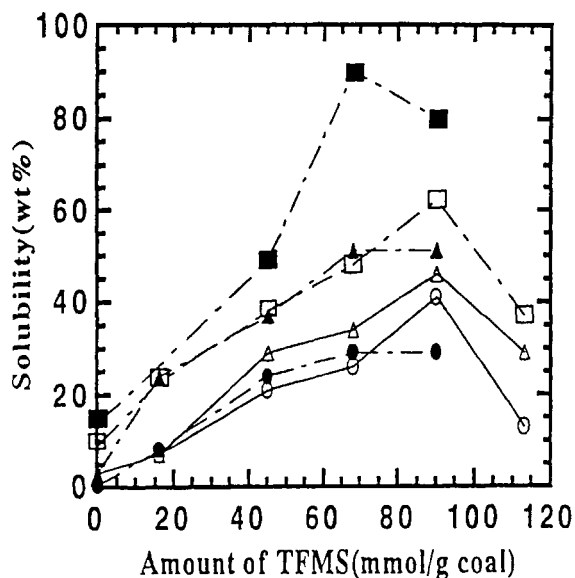
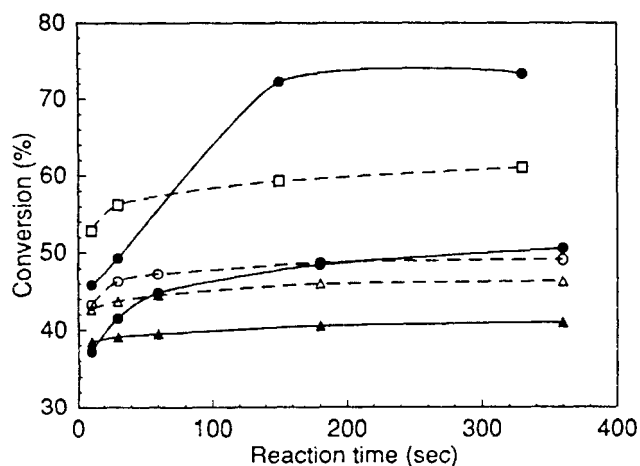


Figure 2 Effect of trifluoromethane sulfonic acid concentration on coal conversion.

●:BS(Taiheiyo) ▲:THFS(Taiheiyo) ■:PS(Taiheiyo)
○:BS(Yallourn) △:THFS(Yallourn) □:PS(Yallourn)



○ T=764°C, P=1 atm(H2) ▲ T=764°C, P=60 atm(He)
● T=764°C, P=60 atm(H2) □ T=920°C, P=1 atm(H2)
△ T=764°C, P=1 atm(He) ● T=920°C, P=60 atm(H2)

Fig. 3 Conversion of hydropyrolysis

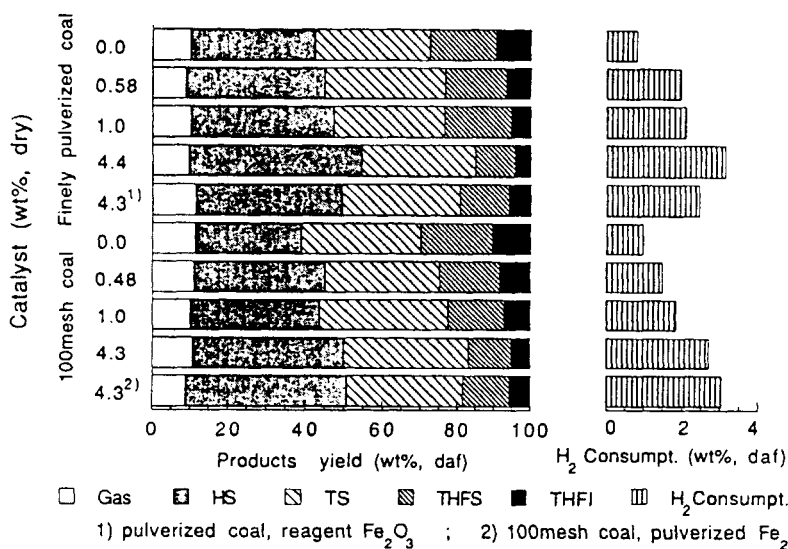


Fig. 4 Effect of Catalyst Concentration on the Yield of Products, Conversion and Hydrogen Consumption.

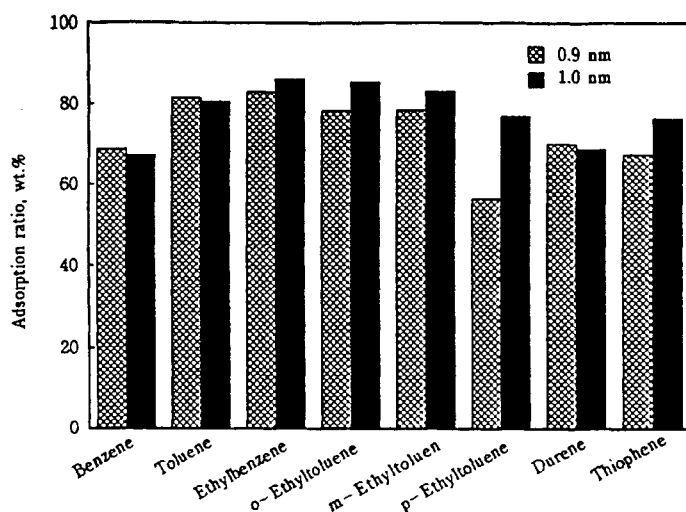


Fig. 5 Adsorption of some monoaromatics on molecular sieves having 0.9 and 1.0 nm in pore diameter

Experimental condition

Solution : 1 wt.% sample in heptane

Solition/adsorbent ratio 10/1

Adsorption time: overnight

Adsorption ratio = Adsorbed amount/charged amount $\times$ 100

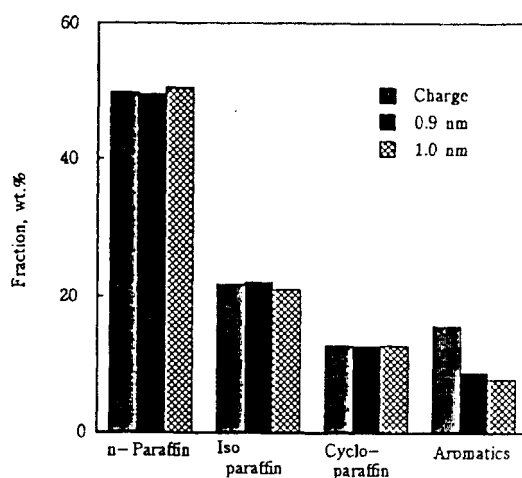


Fig. 6 Recoveries of component types of a model gasoline by two kinds of molecular sieve adsorbents

Recovery: based on charge, wt.%

Oil/adsorbent ratio 2/1

Table 1 Oil Soluble Metal Compounds

Formula			Decomp. Temp. (°C)
Mo:			
Mo-E	$((C_6H_{17})_3N)_4H_2Mo_2O_7$		300
MoDTC	$((C_6H_{17})_2NC)_2S_6Mo_2O_2$	Molybdenum dithiocarbamate	310
MoAc	$(C_{10}H_{14}O_4)_2MoO_2 \cdot 2H_2O$	Molybdenum acetylacetonate	200
Ni:			
	$(C_{10}H_{17}O_2)_2Ni$	Nickel(II) 4-cyclohexylbutyrate	300
Co:			
	$(C_{10}H_{17}O_2)_2Co$	Cobalt(II) 4-cyclohexylbutyrate	350
Fe:			
	$(C_{10}H_{17}O_2)_2Fe$	Iron(III) 4-cyclohexylbutyrate	250
V	$(C_{10}H_{14}O_4)_2VO \cdot 2H_2O$	Vanadyl(IV) acetylacetonate	250
W	$W(CO)_6$	Tungsten hexacarbonyl	150

Table 2 Average molecular weight of soluble fractions.

	molecular weight	
	BS(wt%)	BI-THFS(wt%)
Y-I-68	620(26)	1357(8)
Y-I-90	428(41)	1145(5)
Y-I-113	383(13)	694(16)
T-I-45	451(24)	708(13)
T-I-68	454(29)	751(22)

():amount of BS and BI-THFS fractions in treated coals, respectively.

Table 3 The amount of gas production by pyrolysis

	H ₂	CO	CH ₄	CO ₂	H ₂ S	COS
	mol/ g-coal			mmol/ g-coal		
Original Coal	5.81x10 ⁻³	1.8x10 ⁻³	1.2x10 ⁻³	0.8x10 ⁻³	2.69x10 ⁻²	6.99x10 ⁻⁴
Pulverized Coal	6.0x10 ⁻³	2.0x10 ⁻³	1.1x10 ⁻³	0.8x10 ⁻³	1.90x10 ⁻²	3.58x10 ⁻⁴

Table 4 Extraction yields of phenolic compounds from naphtha fraction of Wyoming coal derived liquids

M e O H	H ₂ O					
	1	2	4	8	10	16
2	90.00	87.50	78.14			
	(89.48)	(84.81)	(76.98)	(69.05)	(74.24)	(77.23)
3	90.74	89.44	89.08			
	(92.68)	(90.43)	(85.36)	(79.16)	(77.74)	(80.70)
4	93.16	93.87	91.27			
	(93.97)	(91.71)	(88.69)	(84.99)	(84.60)	(83.53)

Upper figure in each box was obtained from method A (separation by settling method)
Lower figure in each box was obtained from method B (separation by vibration method)

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 (1981-1994)

1. Up to 1993

Benzyl phenyl ether as was hydrogenated using stabilizes 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.

The synthetic pyrite showed the ability of hydrogenation of ethylene and cracking C-C bond between aromatic ring and aliphatic side chain, and higher activity at the temperature higher than 450 C depending on the structure of sample.

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

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. The C₂-fragment or C₂-side chain might play an important role in producing condensed aromatics.

A great deal of solvent soluble materials in coal can be extracted by the relaxation of entangling structure at the higher temperature.

A fraction of FCC residual oil could be used as a solvent of coal liquefaction.

The semi-coke was shown to form from the thermally cracked fragments at the initial reaction stage without sufficient external hydrogen supply. A generalized reaction model containing the retrogressive reaction paths was deduced. Coking characteristics was experimentally examined for preasphaltene derived from Akabira coal liquefaction. Coal conversion at temperature of a preheater was supposed to be 60 to 70 %.

2. For FY 1994

(1) Reaction mechanism of coal liquefaction: Hydrogenolysis of model compound using synthetic pyrite as catalyst (4)

Benzylphenol and diphenylmethane were reacted to discuss the effect of OH group on methylene-bridged bonding in the presence of synthetic pyrite as catalyst. The reaction was

carried out in similar procedure to the previous report, i.e. 50ml autoclave, sample 1.25mmol, decalin as solvent 6.25mmol, 10 wt % catalyst of the sample, initial hydrogen pressure 3MPa, 400-500 C of reaction temperature, 15min of reaction time. The results are shown in **Table 1** and **2**. In the case without catalyst, benzylphenol was not easy to cleave. In the presence of catalyst the conversion increased at any reaction temperature compared with the ones without catalyst. However, the conversion was less than 50% at 500 C. The reactivity of benzylphenol was much lower than benzyl phenyl ether. The main products were toluene and phenol, but phenol obtained in somewhat larger amount because of the formation of diphenylmethane and dibenzylphenol from decomposed benzyl group. Diphenylmethane was more difficult to cleave compared with benzylphenol. The conversion was only 9% at 500 C. The difference from the stability of radicals formed during reaction of benzylphenol and diphenylmethane would be one of the reason not to split methylene bond of diphenylmethane.

(2) Upgrading of coal liquid. (2) Non-catalytic thermal hydrodealkylation of alkyl-phenol with hydrogen in the presence of methanol

The reactions of o-ethylphenol and thiophenol were carried out in the presence and absence of methanol in flowing H₂ (64 mmol/h) at 850 C. A methanol solution of 0.7~0.9 g was injected into the reactor by means of a micro feeder for 1 h in a controlled flow of hydrogen at normal pressure. Liquid products were collected in a trap cooled with liquid nitrogen and gases in a reservoir. Gaseous and liquid products were analyzed and identified by GC and GC/MS. The methanol solution was prepared with a 1/1 weight ratio of methanol to o-ethylphenol or thiophenol. The results are shown in **Table 3**. The results for ethylbenzene and phenol are also included in Table 3. For the reaction of ethylbenzene in the presence of methanol in H₂, the yield of benzene increased, and the condensed products and carbon decreased compared with the result of the reaction in H₂ without methanol. For the reaction of o-ethylphenol, the benzene yield was somewhat lower than that for the reaction of ethylbenzene, and the condensed products decreased. Phenol was also obtained by dealkylation of ethylphenol. For the reaction of phenol itself the conversion was lower than those of ethylphenol and thiophenol. Hydroxyl group was not easier to cleave than ethyl- or mercapto-group. Water formed during the reaction of phenols may prevent proceeding the reaction. Products from o-ethylphenol included about 80% of dehydroxylated products (benzene, toluene and styrene). It means that dehydroxylation is easy to occur for phenol substituted with alkyl group compared with for phenol itself.

(3) Extent of coal liquefaction at process preheating conditions

In an effort to evaluate axial distributions of the extent of coal dissolution into solvent during their residence in preheater of a coal liquefaction process, coal liquefaction experiments were carried out in a 50cm³ micro-autoclave which was heated at a rate equivalent to that in a continuous process preheater (50K/min for heating and 150K/min for cooling). In the present experiments Tanitoharm coal was used as a coal sample in stead of Wandoan coal employed in the last FY and was liquefied with the recycle oil and the synthesized pyrite catalyst from 1t/d NEDO PSU process under 10.1MPa H₂ gas atmosphere. Products were analyzed by the same method and procedure as described in our previous report. In **Fig.1** the coal conversion ($1-y_R$) and the yields (y_i) of liquefaction product are plotted against temperature. It is seen from the figure that the conversion increases rapidly with temperature when temperature exceeds 600K, resulting in an increase of the yields. The preasphaltene yield, y_P , attains a maximum at about 700K while the yields of asphaltene, y_A , and oil & gas, $y_{O\&G}$, gradually increase with temperature. **Fig. 2** shows changes in the conversion and the yield with time after the autoclave temperature was held at 723K. As can

be seen, the rate of increase of the conversion deteriorates with time and the conversion levels off at about 0.90. It is also seen that y_p slowly decreases with time whereas y_A gives a maximum value at 10 to 20min and $y_{O\&G}$ a monotonous increase. These characteristic changes are much the same as for Wandoan coal employed in the last FY. Thus, in the next FY a reaction model is developed to explain the data for both coals, on the basis of which kinetic parameters are analyzed.

Future Tasks

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

Table 1 Effect of the reaction temperature on the product yield from p-benzylphenol

Temp. (°C)	FeS ₂	Conversion (mol %)	Product Yield ¹⁾ (mol%)						
			Toluene	Phenol	o-BP ²⁾	Benzene	DPM ³⁾	DBP ⁴⁾	Others
400	—	4.2	0.2	—	—	tr	0.5	—	3.5
400	+	10.3	2.1	3.6	0.6	0.1	0.6	1.6	2.2
450	—	3.3	0.7	0.5	—	0.2	1.0	—	0.9
450	+	37.0	12.7	15.0	1.8	0.4	3.4	0.7	3.0
500	—	9.1	1.5	1.3	—	0.3	1.1	0.1	4.8
500	+	50.2	14.5	15.3	1.3	1.0	1.3	0.8	16.9

1) based on p-Benzylphenol, 2) o-Benzylphenol, 3) Diphenylmethane, 4) Dibenzylphenol

Table 2 Effect of the reaction temperature on the product yield from diphenylmethane

Temp. (°C)	FeS ₂	Conversion (mol %)	Product Yield ¹⁾ (mol%)				
			Benzene	Toluene	DB ²⁾	MDM ³⁾	Others
450 ⁴⁾	—	tr	tr	tr	—	—	—
450 ⁴⁾	+	5.7	2.7	2.9	—	—	0.1
500	—	7.9	2.1	0.9	0.4	0.1	4.9
500	+	6.1	2.5	0.8	0.3	0.1	2.4

1) based on Diphenylmethane, 2) Dibenzyl, 3) Methylidiphenylmethane, 4) H₂ 10MPa

Table 3 Product yields in the reaction¹⁾ of ethylbenzene, o-ethylphenol, thiophenol and phenol

Substrate	MeOH	Conversion (mol %)	Product Yield ²⁾ (mol%)				
			Benzene	Toluene	Styrene	PhOH ³⁾	Others ⁴⁾
EB ⁵⁾	—	100	86.7	0.5	0.7	—	5.9
"	+	100	93.1	0.7	0.4	—	3.1
o-EP ⁶⁾	—	100	78.7	5.0	0.3	2.0	8.7
"	+	100	70.4	4.9	0.2	3.3	6.0
PhSH ⁷⁾	—	100	92.2	tr	—	—	4.7
"	+	100	88.9	tr	—	—	1.6

1) Reaction conditions: 850°C, 87~107 mmol/h H₂, 2) Based on substrate, 3) Phenol, 4) Naphthalene, Dibenzyl, Acenaphthylene, Fluorene and others. 5) Ethylbenzene, 6) o-Ethylphenol, 7) Thiophenol

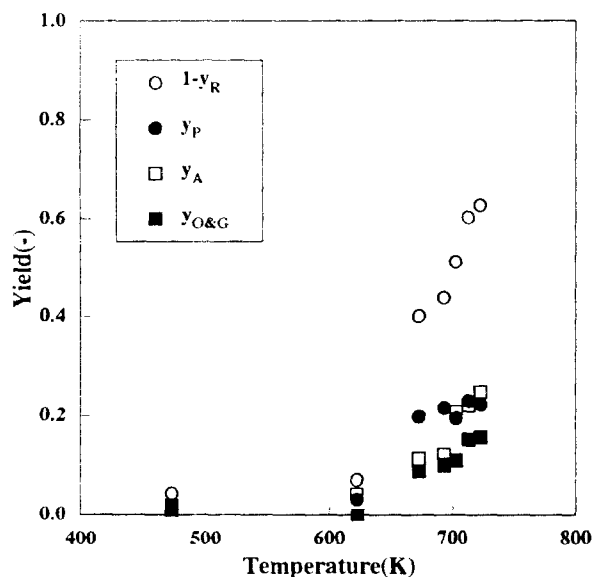


Fig.1 Changes in coal conversion and product yields with temperature.

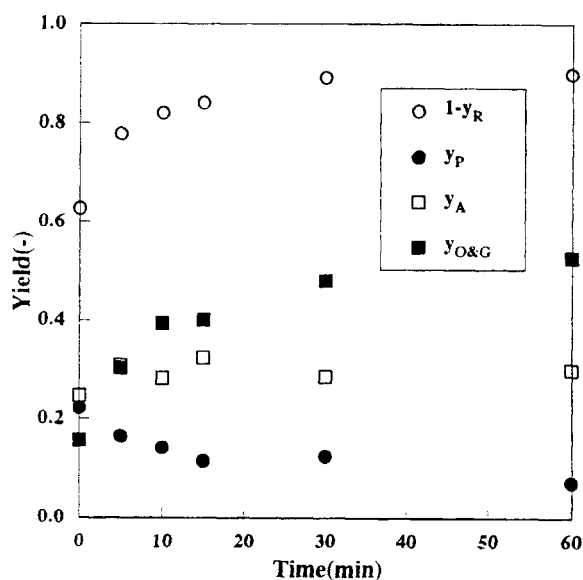


Fig.2 Changes in coal conversion and product yields with time at 723K.

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

Etsuo Niki
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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 dissolution reaction of various coals in the presence of hydrogen-donating hydroaromatic solvents and development of effective catalysts. This year, our objectives were to investigate three points of pyrite FeS_2 catalyst for the 150 tons/day pilot plant of NEDOL Process as a Japanese national project: 1) Oxidation of synthetic pyrite FeS_2 catalyst for the pilot plant of NEDOL Process under atmosphere between room temperature and 200°C; 2) Effects of pyrite FeS_2 catalyst oxidation under atmosphere on hydrogenation of 1-methylnaphthalene; and 3) Reactivation of pyrites FeS_2 catalysts deactivated with addition molecular solid sulfur.

Work Program

- (1) Oxidation of Pyrite FeS_2 Catalyst with Oxygen under Atmosphere between Room Temperature and 200°C.

Pyrite FeS_2 catalyst is one of catalysts used for NEDOL Process in primary hydroliquefaction stage of 150 tons/day coal liquefaction pilot plant, which is a national project in Japan. Oxidation of pyrite FeS_2 catalyst is one of very important factors in basic studies of industrial handling, such as grinding and mixing and storage of the catalyst. The oxidation of synthetic pyrite FeS_2 catalyst under atmosphere is tested at room temperature, 80°C, 150°C and 200°C. The weight change of pyrite oxidation contacted with oxygen in air is measured at 150°C and 200°C.

- (2) Effects of Pyrite FeS_2 Catalyst Oxidation under Atmosphere on Hydrogenation of 1-Methylnaphthalene.

Catalyses of oxidized pyrite FeS_2 catalysts are tested on the hydrogenation reaction of 1-methylnaphthalene as the most basic model reaction in coal hydroliquefaction reaction. Activities and selectivities of pyrite FeS_2 catalysts oxidized under various oxidation conditions are investigated in detail.

- (3) Reactivation of Pyrite FeS_2 Catalysts Deactivated with Addition of Molecular Solid Sulfur.

To develop more highly active iron catalysts, deactivated pyrite FeS_2 catalysts with oxidation under atmosphere is designed for the reactivation of the oxidized pyrites by the addition of excess molecular solid sulfur to the 1-methylnaphthalene hydrogenation system.

Summary (1974 - 1994)

1. Up to FY 1993

Various coals were thermally treated under different conditions in order to settle the most suitable reaction conditions. The sample coals were various ranks of coal such as Ohyubari, Akabira, Taiheiyo, Liddell, Wandoan, and a number of solvents for coal liquefaction has been evaluated as well as the effect of several sorts of additives such as phenols. Effect of mineral matters present in the coal was studied for both coal liquefaction and hydrolypyrolysis 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.

The relative reactivity of hydrogen donating solvents did not change in the liquefaction of different ranks of coal. Strong hydrogen donors were confirmed to be more reactive than tetralin toward free radicals. It has been shown that SRC promotes the hydrolypyrolysis 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 hydrolypyrolysis of Wandoan coal-derived SRC. Highly active iron catalysts for coal hydroliquefaction and phenanthrene hydrogenation in the presence of solvents have been obtained by CO pretreatment of inexpensive iron oxides and iron ores suspended in hydrocarbon solvents as a new preparation for activation. Some different rank coals were liquefied in the presence of the active and inexpensive iron ores. With increase in carbon content, both coal conversion and hydrogen consumption decreased. Partial oxidation of coal has a negative effect on coal liquefaction because coal conversion decreases in spite of increased solvent consumption. In the oxidation of coal at low temperature, however, the gaseous products were produced about ten times as much as those for the thermal treatment at the same temperature. Compared with the oxidation of Yallourn coal, gaseous products were formed at a half rate in the oxidation of Akabira coal. In comparison with the liquefaction of raw coal, depressing effect by oxidation was observed to a greater extent for Akabira coal. Humic acids, which were produced by oxygenating the coal suspended in aqueous alkaline solutions at 130°C, were photooxidized with high pressure mercury arc in aqueous alkaline solutions. An interesting finding obtained is that humic acids are easily photooxidized at room temperature.

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 the Fe and Ni-Mo catalysts for the hydrolypyrolysis of di(1-naphthyl)methane. It has also been shown that the Fe-S-catalyzed hydrogenation of naphthalene-rings is promoted by methyl-substitution of the ring, but Ni-Mo-S catalyzed one is decreased. In the presence of Fe-S or Ni-Mo-S catalysts, hydrogenation of the naphthalene-ring is retarded by isopropyl group substitution.

2. For FY 1994

In this year, we particularly investigated the relations between oxidation of pyrite and activity and selectivity for the pyrite FeS_2 catalysts to the hydrogenation of 1-methylnaphthalene (1-MN). Pyrite FeS_2 catalyst is one of catalysts used for NEDOL Process in primary hydroliquefaction stage of coal liquefaction pilot plant of 150 t/d, which is a national project in Japan. The most important key points of exact evaluation for coal liquefaction is the catalyst used in primary hydroliquefaction stage of coal liquefaction process.

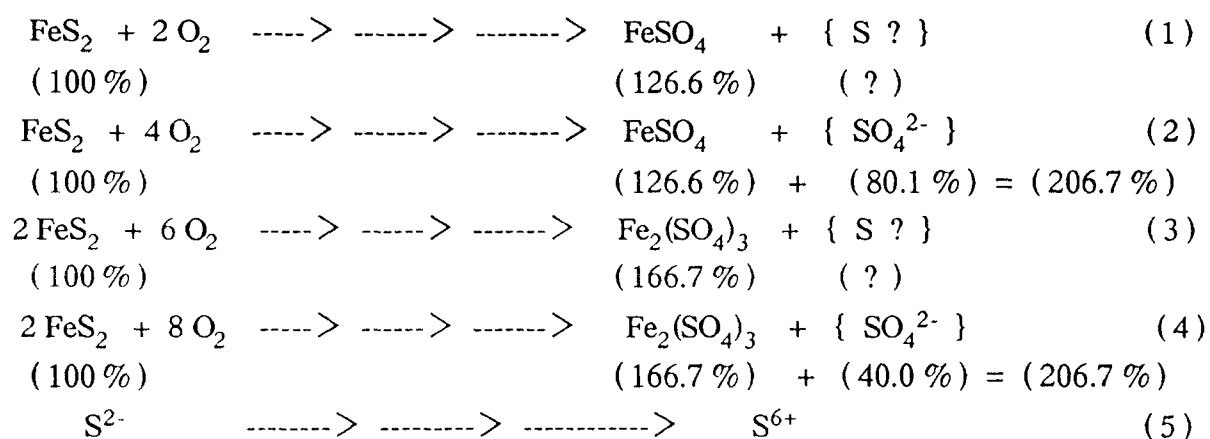
(1) Oxidation of Pyrite FeS_2 Catalyst with Oxygen in Atmosphere Between Room Temperature and 200°C.

Oxidation of pyrite is one of very important factors in basic studies of industrial handling, such as grinding and mixing and storage of the catalyst. A symposium on iron-based catalysts for coal liquefaction was held at the 205th ACS National Meeting (Denver), March 28 - April 2, 1993. Some of those papers have been published in special issue of Vol 8 (No. 1) of *Energy & Fuels*, 1994. In the same time, reviews of the development of catalysts for coal liquefaction in same time were also published in special issue of Vol. 73 (No. 1) of *Journal of the Japan Institute of Energy*, 1994. The first-stage reactor in direct coal liquefaction requires a catalyst that is both inexpensive and disposable in order to develop an economically viable technology. We reported that catalysis of iron-sulfide catalyst was strongly affected by the S/Fe ratio in the reaction system, the activity was increased with pyrrhotite formation and was accelerated by the presence of excess hydrogen sulfur (H_2S) in the system. And also we reported that activity of pyrite for phenanthrene hydrogenation decreased with storage under atmosphere in 1989 and Hirano and co-workers reported that the activity of natural ground pyrites for coal liquefaction decreased with storage under atmosphere in 1993.

The oxidation of pyrite under atmosphere is tested at room temperature, 80°C, 150°C and 200°C. Catalyst pyrite FeS_2 used was synthesized by Asahi Chemical Industry Co. Ltd. The synthetic pyrite FeS_2 was stored in a desiccator in an atmosphere of argon. Before the oxidation, synthetic pyrite used in this paper was a black powder with a specific surface area of 12 m^2/g . Pyrite was exactly weighed out about 0.25 g of pyrite in glass-vessels of bottom area 3 cm^2 , and then each sample pyrite was oxidized at decided temperature between room temperature and 200°C. After sampling of about 1.0 g of pyrite in glass-vessels of bottom area 10 cm^2 , weight change profiles on oxidation of pyrites under atmosphere in drying-oven controlled at 150°C and 200°C are shown in Fig. 1.

Oxidation of pyrites is considered to proceed as shown from eqs. (1) to (4). Increases of weight in the both case of eqs. (1) and (3) were calculated as 27 wt% and 67 wt%, respectively, without excess sulfate anion or/and sulfur. The results in Fig. 1 suggest that pyrite was oxidized to ferrous sulfate, not ferric sulfate, but the excess sulfur in ferrous sulfate formation from pyrites was missing.

XRD patterns of oxidized pyrite showed different XRD patterns even under mild oxidation conditions such as exposure to air at room temperature. These XRD results



showed that oxygen in air was diffused from the gas phase into the very stable pyrite lattice, and the pyrite crystal lattice was destroyed and combined with oxygen to other structure, i.e., the crystal lattice of pyrite consisting of iron and sulfur atoms was transformed to a exactly different crystal form. This clearly shows that iron and sulfur atoms in the strict pyrite structure of a regular crystal lattice were moved and rearranged even at room temperature.

(2) Effect of Pyrite FeS₂ Oxidation under Atmosphere on Hydrogenation of 1-Methylnaphthalene.

Catalyses of oxidized pyrite FeS₂ catalysts are tested on the hydrogenation reaction of 1-methylnaphthalene as the most basic model reaction in coal hydroliquefaction reaction. It is well known that large conglomerates of pyrite ore maintain a golden color for a long time on exposure to air. Activities and selectivities of pyrite FeS₂ catalysts oxidized under various oxidation conditions are investigated in detail.

Materials: The compounds used as substrate 1-methylnaphthalene (1-MN) and solvents were commercial reagents and were purified by conventional methods if necessary. The catalyst pyrite FeS₂ used was synthesized by Asahi Chemical Industry Co. Ltd. **Procedure:** In a typical reaction, 1.0 g of 1-MN, 0.25 g of FeS₂ and 30 ml of decalin (DHN), and a prescribed amount of sulfur (S/Fe ratio = 2.0) if necessary, were placed in a 150 ml stainless steel (SUS 316), magnetically stirred autoclave. After pressurization with 10 MPa of hydrogen or argon, the autoclave was heated to at 350°C and maintained for 1 hr. It was then immediately cooled in an ice-water bath. **Analysis:** The reaction products were identified by GC-MS (Shimadzu, Model GCMS QP-1000, equipped with a 0.24 mm (I.D.) x 50 m (L.) glass capillary column chemically bonded with OV-1) and quantified by GC (Shimadzu, Model GC-15A, equipped with the same capillary column). **Oxidation of FeS₂:** FeS₂ was oxidized at room temperature, 80°C, 150°C and 200°C for the desired time by atmospheric oxygen. FeS₂ oxidized was analyzed using XRD (Rigaku Denki, Model RINT 2400) and XPS (Perkin-Elmer, Model PHI 5500), and was tested for 1-MN hydrogenation.

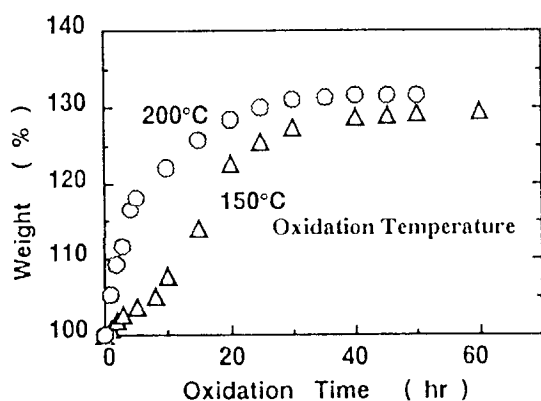
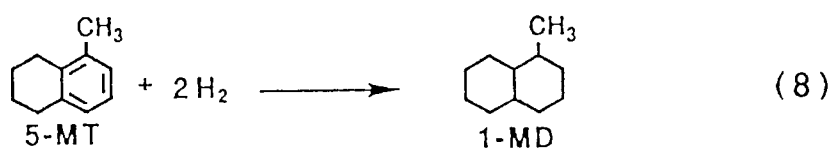
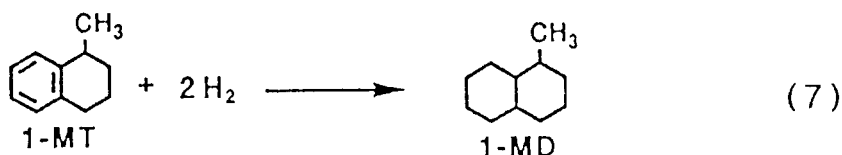
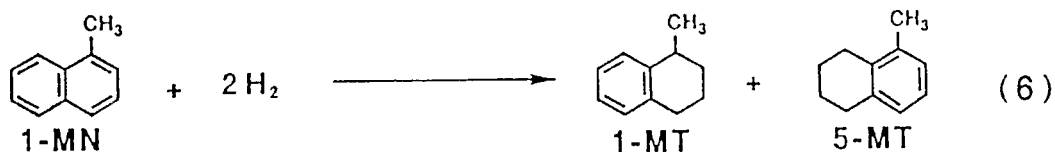


Fig. 1 Oxidation of FeS₂ Catalyst under the Atmosphere at 150°C and 200°C.

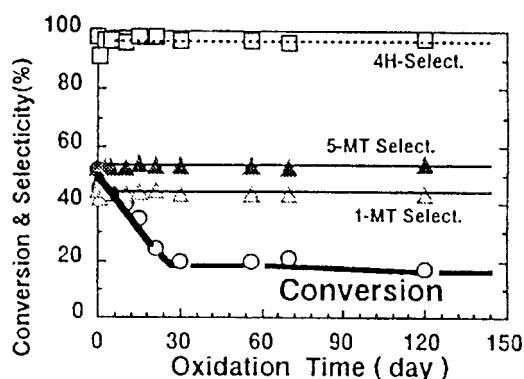


Fig. 2 Effect of Oxidation of FeS₂ Catalyst at Room Temperature on the Hydrogenation of 1-Methylnaphthalene.

1-MN 1.0 g, FeS₂ 0.25 g, DHN 30 ml, PH₂ 10 MPa, 350°C, 1 hr.

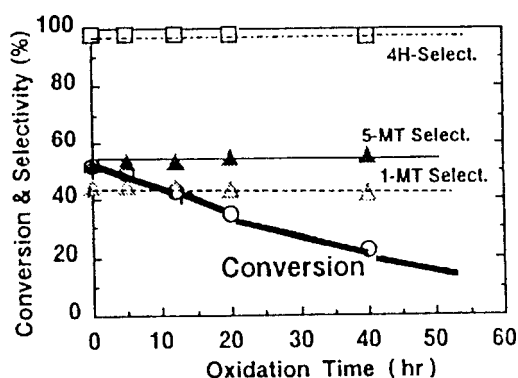


Fig. 3 Effect of Oxidation of FeS₂ Catalyst at 80°C on the Hydrogenation of 1-Methylnaphthalene.

1-MN 1.0g, FeS₂ 0.25g, DHN 30 ml, PH₂ 10 MPa, 350°C, 1 hr.

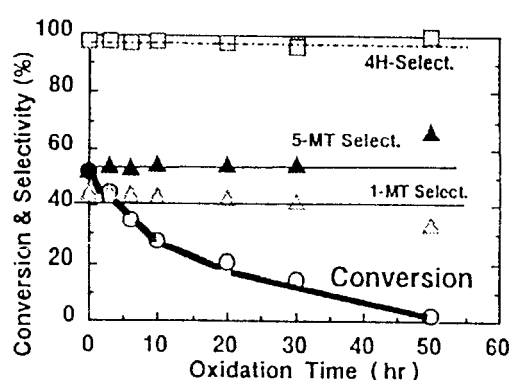


Fig. 4 Effect of Oxidation of FeS₂ Catalyst at 150°C on the Hydrogenation of 1-Methylnaphthalene.

1-MN 1.0g, FeS₂ 0.25g, DHN 30 ml, PH₂ 10 MPa, 350°C, 1 hr.

Hydrogenation of 1-MN is negligible in the absence of catalyst at 400°C. As shown from eq. (6) to eq. (8), 1-MN was hydrogenated to 1-methyltetralin (1-MT) and 5-methyltetralin (5-MT) with selectivity of over 97% in the presence of FeS₂ catalyst.

Hydrogenations from methyltetralins to methyldecalins as shown in eqs. (7) and (8) were very difficult.

Effects of pyrite oxidation on catalytic activity and selectivity on hydrogenation of 1-methylnaphthalene(1-MN) are shown in Figs. 2 ~ 4. Catalytic activity decreased almost linearly for the initial one month of storage/oxidation at room temperature, and then the activity was gradually reduced. The deactivation of pyrite was accelerated by raising the temperature of oxidation that is, exposure to air. Pyrites oxidized at room temperature for 500 days and at 150°C for 50 hrs had very low activities, and the color changed from black to dark gray and gray, respectively. All pyrites oxidized under any oxidation conditions below 150°C show about the same selectivity for 1-MN hydrogenation. These results suggest that the oxidation of pyrites decreases the number of active sites, and the nature of residual active sites is almost the same as that before oxidation. On the other hand, commercially available ferrous sulfate and ferric sulfate showed very low activity in the hydrogenation.

(3) Reactivation of Pyrites FeS_2 Catalysts Deactivated with Addition of Molecular Solid Sulfur.

To develop more highly active iron catalysts, deactivated pyrite FeS_2 catalysts with oxidation under atmosphere is designed for the reactivation of the oxidized pyrites by the addition of excess molecular solid sulfur to the 1-methylnaphthalene hydrogenation system. Catalytic activity of pyrites was greatly decreased with oxidation/exposure to air as shown in Figs. 2 ~ 4. It was found that the oxidized lowly active pyrites were reactivated by addition of excess solid molecular sulfur to the reaction system as shown in Figs. 5 ~ 7. These results are particularly exciting in view of the fact that pyrites deactivated by air oxidation were reactivated to almost the same or a higher level than before oxidation by fresh addition of sufficient sulfur at S/Fe ratio of 2 to the reaction system. As shown evident from the pyrite FeS_2 formula, the S/Fe ratio of original pyrite crystal is 2.0. Under reaction

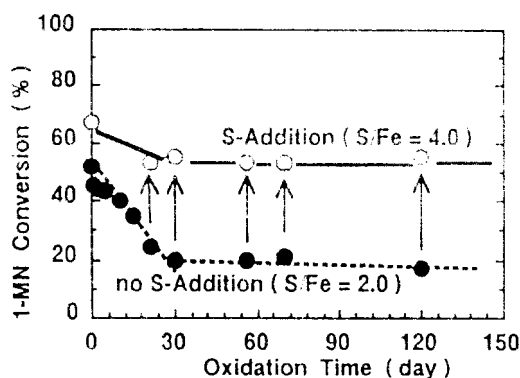


Fig. 5 Additive Effect of Sulfur to Conversion of 1-MN Hydrogenation by Oxidized FeS_2 Catalysts at Room Temperature.

1-MN 1.0g, FeS_2 0.25g, DHN 30 ml, PH_2 10 MPa, 350°C, 1 hr.

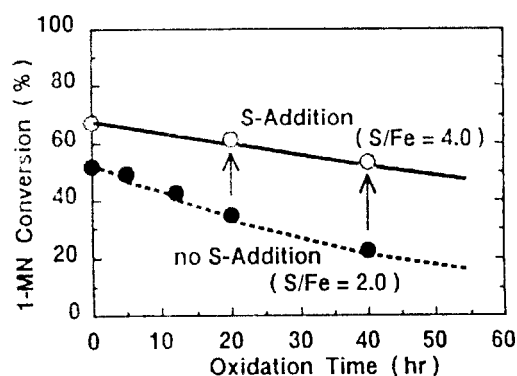


Fig. 6 Additive Effect of Sulfur to Conversion of 1-MN Hydrogenation by Oxidized FeS_2 Catalysts at 80°C.

1-MN 1.0g, FeS_2 0.25g, DHN 30 ml, PH_2 10 MPa, 350 °C, 1 hr.

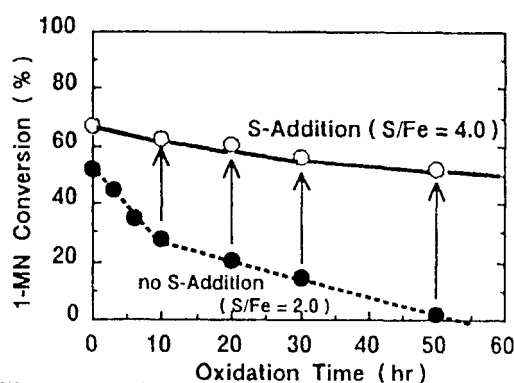
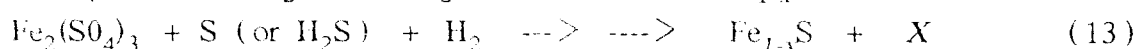
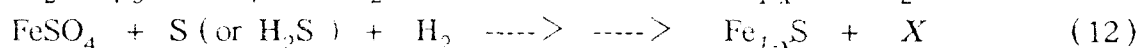
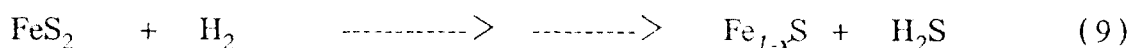


Fig. 7 Additive Effect of Sulfur to Conversion of 1-MN Hydrogenation by Oxidized FeS₂ Catalysts at 150°C.

1-MN 1.0g, FeS₂ 0.25 g, DHN 30 ml, PH₂ 10 MPa, 350°C, 1 hr.



conditions of 350°C for 1 hr and initial hydrogen pressure of 10 MPa and decalin, original pyrites and oxidized pyrites in the presence of excess sulfur were completely transformed to a pyrrhotite Fe_{1-x}S structure according to XRD analysis as shown in eqs. (9) and (12).

Effects of oxidation of pyrite catalyst under air for the hydrogenation of 1-methylnaphthalene were investigated under coal hydroliquefaction conditions. It suggests that pyrite was oxidized to ferrous sulfates even at room temperature under atmospheric oxygen, and the catalytic activities of FeS₂ oxidized decreased by increasing the storage time. The deactivation of pyrites was enhanced by raising the atmospheric temperature for the oxidation. It was proved that pyrites deactivated by air oxidation were reactivated by addition of sufficient sulfur to the reaction system.

Future Tasks

- (1) Solvent Effects on the non catalytic thermopyrolysis of aromatic hydrocarbons at high temperature.
- (2) Role of hydrogen on the pyrolysis of coal related model compounds at high temperature.
- (3) Relationship between reaction temperature and catalysis on the hydroconversion of coal related model compounds.

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(1975-1994)

1. Up to FY 1993

- (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 the extensive hydrogenation at $<400^{\circ}\text{C}$ and the effective hydrocracking at around 430°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) Three kinds of polycondensed aromatic hydrocarbons, pyrene(Py), fluoranthene (FL), and anthracene(An), were investigated in combination with 4HFL in the hydrogen-transferring liquefaction, in order to clarify their roles as nondonor solvents.
- (10) 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.
- (11) 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.

- (12) Complete conversion of Australian brown coal was achieved by the multi stages of deashing pretreatment, hydrogen transfer, and catalysis.
- (13) Liquefaction catalysts can be recoverable by designing functional supports such as ferromagnetic particles and extremely light carbon blacks of hollow sphere.

2. For FY 1994

(1) Design of Recoverable Catalysts for a Multi-stage Coal Liquefaction Process

Introduction

Coal liquefaction has been rather extensively investigated for more than several decades to provide clean liquid fuel from coal in order to meet the increasing demand of transportation fuel expected in early next century. However, the cost of the liquid fuel is still too high to substitute the petroleum products. Several breakthrough ideas on the process simplification as well as the better catalyst are strongly desired to cut the cost currently estimated.

A large quantity of FeS_2 derived from iron ore, dust and natural pyrite is usually applied due to its low activity. Its cost and disposal cannot be overlooked. NiMo or CoMo on alumina which has been applied in the ebullating bed suffers the deactivation by coke and mineral depositions and hence its turnover is limited to force its purge with unreacted coal and minerals.

The present authors proposed basic ideas to recover the catalysts from inorganic residue which are originated from the feed coal. According to natures of inorganic residue, three approaches can be designed, 1) removal of inorganic residue such as carbonates and chlorides, 2) recovery of the ferromagnetic catalysts from the diamagnetic residue, and 3) gravimetric recovery of the catalysts supported on light materials of fine particles. The present authors have reported that NiMo supported on Ketjen Black(KB), which is one of unique carbon blacks of hollow sphere, exhibited the higher activity for the hydrogenation of 1-methylnaphthalene (1-MN) than a commercial NiMo supported on alumina. Its hollow sphere of the low gravity provides the possibility of its gravimetric recovery.

In the present paper, the activities of KB supported NiMo catalyst was studied for the liquefaction of Wyoming coal under some conditions in terms of hydrogen pressure, reaction temperature and heating rate. Several supporting procedures were also studied to find the best activity. The flotation separation scheme of KB-based catalyst was examined to utilize the low specific gravity and hydrophobic surface of KB.

Experimental

Some properties of Ketjen Black(KB) JD provided by Mitubishi Chemical Co. are summarized in Table 1. Ni and Mo salts were supported on KB JD by successive impregnating methods of Mo and Ni in this order using Mo dioxoacetylacetonate ($\text{MoO}_2\text{-AA}$) and $\text{Ni}(\text{OAc})_2$ as metal salts in methanol. Other kinds of NiMo/KB catalysts were also prepared from the

water-soluble metal salts such as $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ and $\text{Ni}(\text{NO}_3)_2$ by simultaneous or successive impregnating methods. The catalyst precursor was dried at 120°C for 12 h in vacuo and presulfided in 5% $\text{H}_2\text{S}/\text{H}_2$ flow at 360°C for 3 h prior to the reactions. A commercially available $\text{NiMo}/\text{Al}_2\text{O}_3$ (<60mesh), provided by Nippon Ketjen Co., and synthesized pyrite (<60mesh), provided by NEDO, were also examined for the comparison.

Catalytic single-stage liquefaction was carried out in an electromagnetic-driven autoclave of 50 mL capacity at the prescribed temperatures ($380 \sim 460^\circ\text{C}$). The ground Wyoming coal (3.0g), the solvent (tetralin; 4.5g) and catalyst (0.09g) were charged into the autoclave. After replacing the air in the reactor with nitrogen and hydrogen gas, hydrogen of the prescribed pressure was introduced to the autoclave at room temperature. Heating rate to the prescribed reaction temperatures was ca. 11 or $22^\circ\text{C}/\text{min}$. The reaction time was counted after the temperature reached to the prescribed temperature. After the reaction, the products remaining in the autoclave were recovered with THF, and extracted with hexane, acetone and THF in this order after the evaporation of THF. The hexane soluble(HS), hexane insoluble but acetone soluble(HI-AcS), acetone insoluble but THF soluble (AcI-THFS) and THF insoluble(THFI) substances were defined as oil(O), asphaltene(A), pre- asphaltene(PA), and residue(R), respectively. The gas(G) yield was calculated by the difference between weight of the initial coal (dry ash free base) and recovered products.

Results

Figures 1 and 2 illustrate product distributions with 3wt% of the catalyst(based on coal) at $380 \sim 460^\circ\text{C}$ under the hydrogen pressure of 10 and 13 MPa, respectively. The oil yield under 10 MPa increased with raising reaction temperature, being 47% of maximum yield at 440°C . Higher temperature of 460°C decreased the oil yield. The oil yield under higher hydrogen pressure (13MPa) increased with raising reaction temperature upto 460°C , providing the highest yield of ca. 55%, although the maximum yields of oil plus asphaltene was achieved at 440°C . Gas yield was slightly suppressed under the higher hydrogen pressure. It should be noted that the yields of PA and R stayed basically the same level at 440 and 460°C .

Figure 3 summarizes the product distributions with variable reaction times by the heating rate of $22^\circ\text{C}/\text{min}$ at 440°C , 13 MP H_2 . The reaction time of 40 min provided slightly higher yields of oil and oil plus asphaltene than those obtained by the heating rate of $11^\circ\text{C}/\text{min}$. The longer reaction times of 60 and 90 min increased the oil yield to 54 and 58%, respectively with the reduced yields of A and PA. It is of value to note that the yields of PA and R were as low as 5% at the reaction time of 90 min. Further longer reaction time of 120 min decreased the oil yield with increased yields of G and R, suggesting the shortage of hydrogen at the longer reaction time.

Figure 4 illustrates the O+A yield obtained with reduced amounts of the catalyst at 440°C , 60 min, 13 MPa and $22^\circ\text{C}/\text{min}$. The catalysts of 3, 1, 0.5wt% provided the (O+A) yields of 69, 65 and 63%, respectively. The yield increased by the catalyst appears not to be proportional to

Table 1 Some properties of catalysts

	NiMo/Al ₂ O ₃	NiMo/KB JD
Surface area (m ² /g)	273	1270
Particle size (nm)	-	30
Apparent density (g/l)	-	115
Ni (wt%)	2.4	2
Mo (wt%)	10	10

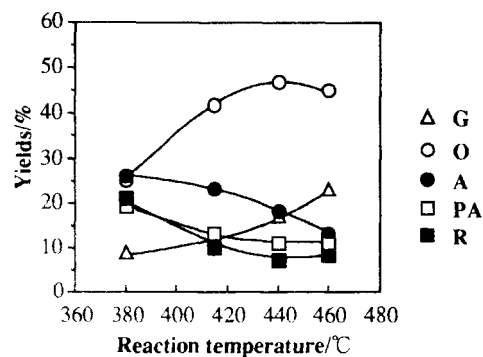


Figure 1 Effect of reaction temperature on the liquefaction yields of Wyoming coal with Ni-Mo/KB JD as the catalyst.

Reaction conditions

solvent(tetralin)/coal=1.5
 reaction temperature : 380~460℃
 reaction pressure : 10MPa
 reaction time : 40min
 heating rate : 11℃/min
 catalyst : Ni-Mo/KB JD
 (3wt% addition to coal)

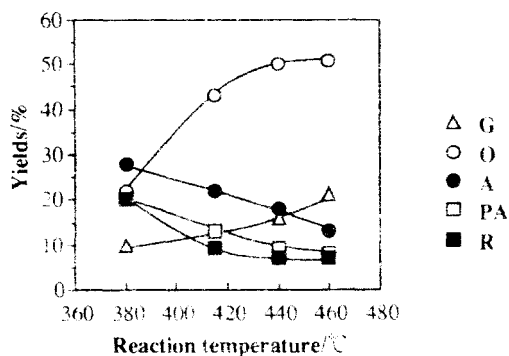


Figure 2 Effect of reaction temperature on the liquefaction of Wyoming coal at 13.0MPa with Ni-Mo/KB JD catalyst.

Reaction conditions

solvent(tetralin)/coal=1.5
 reaction temperature : 380~460℃
 reaction pressure : 13 MPa
 reaction time : 40min
 heating rate : 11℃/min
 catalyst : Ni-Mo/KB JD
 (3wt% addition to coal)

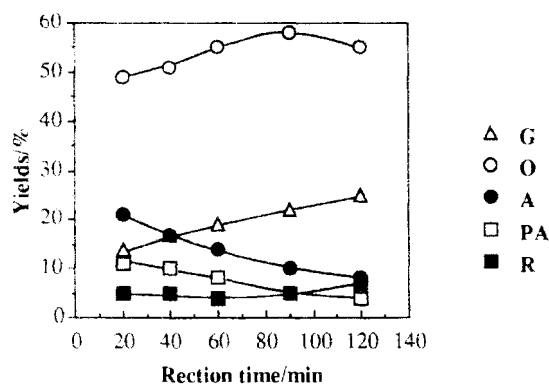


Figure 3 Effect of reaction time on the liquefaction yields of Wyoming coal with Ni-Mo/KB JD catalyst.

Reaction conditions

solvent(tetralin)/coal=1.5
 reaction temperature : 440℃
 reaction pressure : 13MPa
 reaction time : 20~60min
 catalyst : Ni-Mo/KB JD
 (3wt% addition to coal)

the amount of the catalyst. The saturation of the liquefaction or catalyst concentration is suggested.

Figure 5 shows the liquefaction yields without and with NiMo/Al₂O₃ and FeS₂ catalysts at 440°C, 13 MPa, 60 min and 22°C/min. The oil yields were 37, 45, 48% without catalyst and with FeS₂ and NiMo/Al₂O₃, respectively. Excellent activity of NiMo/KB is definite. Other types of NiMo/KB catalysts prepared from water-soluble metal salts exhibited the similar activity for the liquefaction of Wyoming coal, although the NiMo/KB catalyst((d) in Figure 5, principally examined in the present study) showed the highest hydrogenation activity as previously reported.^{2,3} Although the yields of R were much the same regardless of the catalysts, lower yields of G, A and PA reflected the higher yield of O. The conversion of asphaltene and preasphaltene into oil without gas formation appears to depend on the catalyst activity, while coal dissolution leaving residue does to depend on the heating rate with the presence of sufficient amount of the donor solvent.

According to the conversion of tetralin into naphthalene after the liquefaction of 60 min at 440°C, 13 MPa, NiMo/KB allowed only 21% conversion, indicating the effective hydrogenation of dehydrogenated tetralin, whereas NiMo/Al₂O₃ and FeS₂ provided 32 and 38% of conversions. Higher hydrogenation activity of NiMo/KB is definite.

Figure 6 illustrates the recovery scheme of KB-supported NiMo catalyst after the coal liquefaction reaction. KB-supported NiMo catalyst floated at the interface of hexane and water, while the PA and R including minerals sank to the bottom of the flask when methanol, hexane and water were added to the whole product in this order to disperse the products and catalyst and settle them for the gravimetric separation. The oil and asphaltene were dissolved in the organic phase. The catalyst thus recovered gained the weight by twice as the amount of added catalyst, which may include small amounts of PA and R. It is suggested that KB-supported catalyst can be recovered at the liquid/solid separation procedure to be recycled in the practical liquefaction process, because it is dispersed well in the liquid phase.

In the present experimental procedures, the catalyst was recovered as THF insoluble fraction with organic and inorganic residues. The weight of thus recovered catalyst was 0.4g after THF washing, 0.09g of the catalyst added before the reaction, being assumed to be contained. Figure 5 also shows the activity of the recovered NiMo/KB as THFI to compare its activity with that of the virgin NiMo catalyst. Much the same yield of oil was obtained with the recovered catalyst, although the yield of asphaltene was slightly higher than that of the virgin NiMo/KB.

Future Tasks

- 1) Further modification and activation of ferromagnetic supported catalysts
- 2) Higher dispersion of active metals supported on Ketjen blacks to reduce the catalyst amount required for the high distillate yield
- 3) Design of catalyst recovery and regeneration in the multi-stage liquefaction process

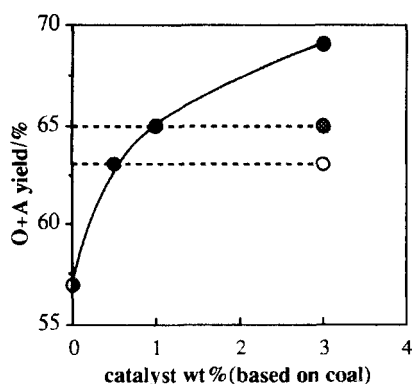


Figure 4 Effect of catalyst amount and comparison of Ni-Mo/KB JD and commercial catalysts on the O+A yield.

- no catalyst ● Ni-Mo/Al₂O₃
- Ni-Mo/KB JD ○ FeS₂

Reaction conditions

reaction temperature : 440℃
 reaction pressure : 13.0MPa
 reaction time : 60min
 heating rate : 22℃/min
 catalyst : Ni-Mo/KB JD
 (0.5~3wt% addition to coal)
 solvent(Tetralin)/coal = 1.5

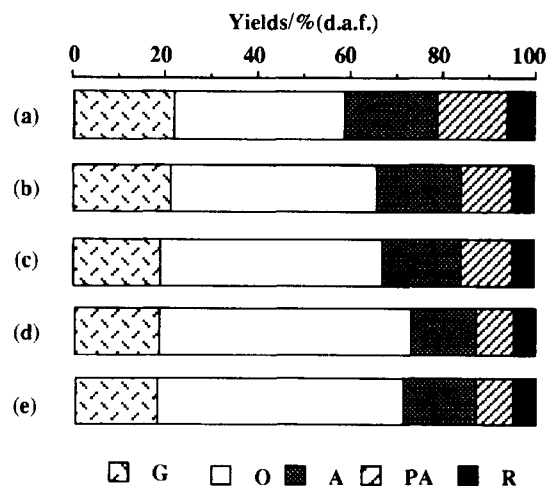


Figure 5 Effect of catalyst species on the liquefaction yields of Wyoming coal at 440℃

- (a) no catalyst
- (b) Synthesized FeS₂
- (c) Commercial Ni-Mo/Al₂O₃
- (d) Ni-Mo/KB JD
- (e) Recovered THFI(NiMo/KBcatalyst 0.09g in THFI (0.4g)), resulfided in 5% H₂S/H₂ at 360℃ for 3 h

Reaction conditions

solvent(tetralin)/coal = 1.5
 reaction temperature : 440℃
 reaction pressure : 13.0 MPa
 reaction time : 60 min
 catalyst ; 3wt% addition to coal

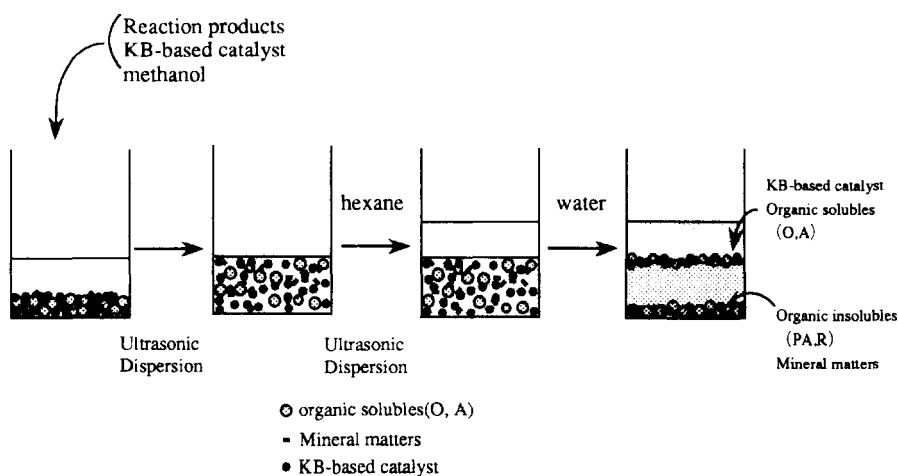


Figure 6 Recovery scheme of KB-based catalyst

2. RESEARCH AND DEVELOPMENT OF COAL GASIFICATION TECHNOLOGIES

(1) Basic Research on Gasification Characteristics of Various Coal

(2) Fundamental Studies on Improvement of Efficiency of Coal Gasification

BASIC RESEARCH ON GASIFICATION CHARACTERISTICS
OF VARIOUS COAL
K.KITANO

Hokkaido National Industrial Research Institute

OBJECTIVES

The utilization of wide variety of coals is the key subjects to develop coal gasification process in Japan. Therefore appropriate estimation of properties of various coals and their change during gasification reaction is an important subject. This research aims to elucidate the gasification mechanism of various coals and their derivatives. The most suitable application of each coal for gasification process will be investigated.

WORK PROGRAM

1. Gasification mechanism of various coals

The gasification rate determined factors such as carbon structure, surface active sites, metal catalysis in ash and temperature have been studying.

2. Characteristic of coal ash at high temperature

The data of melting point for various coals have been accumulating. The fusion mechanism of ash at high temperature was studied.

3. Gasification of coal liquefaction residue

The reactivity and ash properties were investigated.

4. Experiments with bench scale gasifier

The gasification tests were carried out to check the behavior of coal in gasifier.

SUMMARY(1975-1994)

1. Up to FY 1993

The multi-stages pressurized fluidized bed was developed from 1975 to 1985. It was found that the perforate disk plate between first and second stage enhances segregation of coal particles and medium. This improved the carbon conversion of gasifier. The spouted bed gasifier was constructed in 1985 and has been operated with smaller size coal particles and higher temperature than fluidized bed gasifier. Various coals and their derivatives, such as liquefaction residues and low grade coal, have been tested using these gasifiers. Systematic gasification rate measurement of various coals with a high pressure TGA and a laboratory scale reactor have been carried out. It has become apparent that the three important characteristics of coal char strongly affect gasification reactivity. The first is surface structure such as pore size distribution and the number of active sites. The second is carbon structure such as contents of graphite. The third is catalytic effects of metal components in coal ash such as CaO.

It was found that mineral components of coal ash are the most suitable presumptive factor for the behavior of ash melting.

2.For FY 1994

The limiting step change for reactivity of coals, the melting points' estimation base on mechanism of ash fusion and the entrainment phenomena of fine particle for fluidized bed gasifier will describe in the following report.

(1)Gasification mechanism of various coals

The operating temperature of gasifier is quite wide. It is in the range of about 1100K to 1900K for partial oxidation type gasifier. We have studied the difference of the reactivities of coals with surface active sites. The chemical reaction is the limiting step of entire gasification of coal under about 1300K. Therefore, the active sites on surface of char particle become a dominant factor at low temperature. However, it is well known that the diffusion of molecule shows the more important role at higher temperature. In this study the apparent reaction rates of CO₂ gasification were measured by high pressure TGA in the range of 1100K to 1600K. Figure 1 shows the results for Taiheiyu coal char and Ebenezzer coal char. The data presented in this figure are correlated by straight line in a Arrhenius plot with two slopes for each coal. The values of activation energy are calculated from the slopes. These are 127 KJ/mol below 1173K and 45.3 KJ/mol above 1173K for Taiheiyu coal char and 147 KJ/ mol below 1273K and 72.2 KJ/

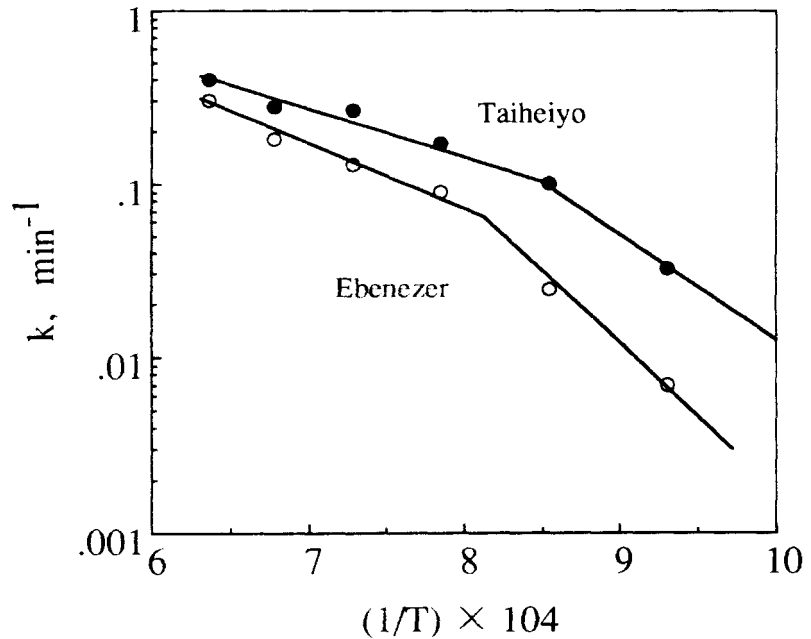


Figure 1 Arrhenius plot of reaction rate

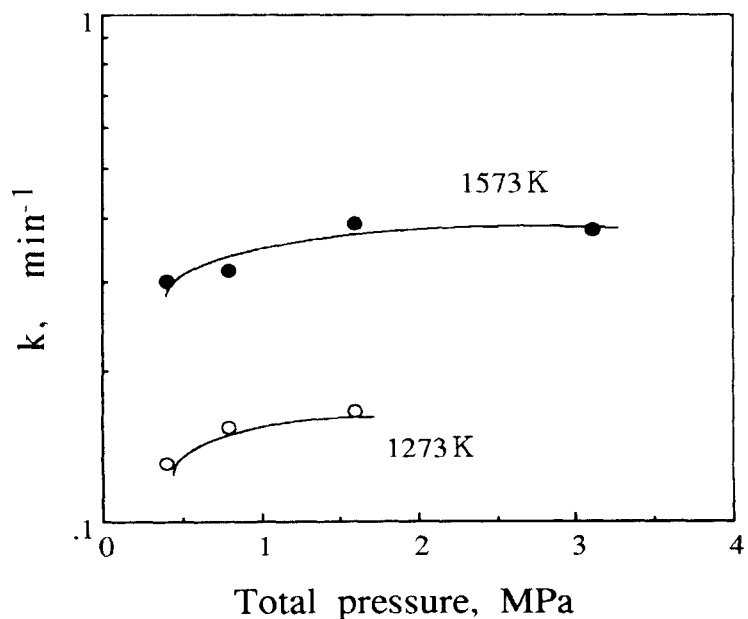


Figure 2 The effect of pressure on reaction rate

mol for Ebenezer coal char. These results mean that the rate controlling step of reaction change from chemical reaction controlling to diffusion controlling at 1173K for Taiheiyo coal and 1273K for Ebenezer coal. There are two possible types of diffusion controlling. One is the film diffusion controlling and the other is the pore diffusion controlling. The molecular diffusion coefficient applies to former condition. The Knudsen diffusion coefficient applies to the latter. The molecular diffusion coefficient is inversely proportional to the pressure while the Knudsen diffusion coefficient is independent from pressure. Figure 2 shows the effects of pressure on apparent reaction rate. The pressure has not much effect on reaction rate at high temperature. The apparent activation energy is estimated as a half of intrinsic value under pore diffusion controlling condition. This is introduced from the relationship between the effectiveness factor and the Thiele modulus. The detailed derivation will be omitted in this report. According to the experimental results, the value of activation energy at high temperature is almost half of it that is observed at low temperature. It may be concluded that the rate-controlling step at high temperature is pore diffusion. This conclusion suggests that the increasing of relative velocity between char particles and gasification reagent has not much effect on increasing of reaction rate. The enlargement of pore size may have more effects on it.

(2)Characteristic of coal ash at high temperature

(2.1)The presumption of melting point

The important role of mineral components in coal ash on fusion behavior has been pointed out in this study. The 43 kinds of coals were investigated. The fluxing minerals are Feldspar, Hematite, Anhydrite and Barite. The refractory minerals are Quartz, Kaolinite, Mullite and Ti oxides. The figure was presented to estimate the melting points of ash from the mineral components mentioned above in the report of last year. However, it is not easy to estimate the contents of minerals in coal ash. The special skill is required to do it by several techniques such as X-ray diffraction, DTA and microscopic morphology as well as chemical analysis. Therefore we tried to develop the easier way to presume the melting point using only chemical analysis. Figure 3 shows the result. The major chemical components, such as TiO_2 , Al_2O_3 , SiO_2 , Fe_2O_3 and CaO , were chosen for correlation. The factors on each chemical component are calculated by the estimation of average contents of each element in refractory minerals of 43 kinds of coals. For example, SiO_2 in Feldspar acts as fluxing mineral while SiO_2 in Quartz works as refractory mineral. About 70% SiO_2 is

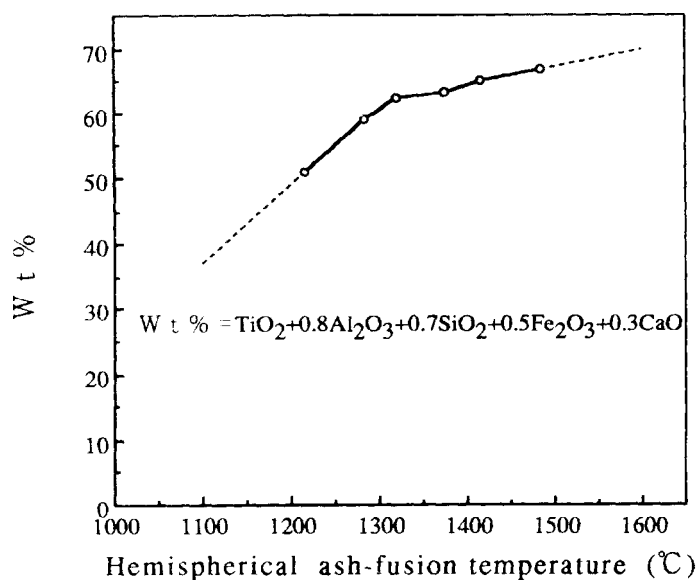


Figure 3 Presumption of melting point of ash based on chemical components

Table 1 Coal rank and chemical components of ash

Rank group	Proximate analysis (as received)	Ultimate analysis (daf)	High-temperature ash analysis	n*
	W VM FC Ash	C H N O S	SiO ₂ Al ₂ O ₃ Fe ₂ O ₃ MgO CaO K ₂ O Na ₂ O TiO ₂ SO ₃	
Low (C _{daf} =62.9~74.3)	10.1 33.7 29.7 26.5	68.9 5.6 1.3 21.3 2.9	49.5 20.89 7.33 2.27 10.21 1.48 0.65 0.95 6.37	12
Medium (C _{daf} =76.4~85.0)	3.2 32.9 47.2 16.7	81.1 5.4 1.2 11.5 0.8	57.42 24.74 5.78 1.36 4.94 1.30 0.95 1.19 2.41	24
High (C _{daf} =85.5~93.5)	2.6 16.5 65.9 15.0	88.7 4.1 1.2 4.7 1.6	54.81 25.28 7.97 1.63 3.87 2.24 0.81 1.29 2.08	7

* number of samples

included in the 43 kinds of coal ash samples as the refractory minerals. This brought 0.7 as the factor of SiO₂ in figure 3. I would like emphasis that the factor in this figure is not determine by average chemical components in ash. It came from consideration of behavior of mineral components in ash. Therefore, I believe the explanation of figure 1 is quit unique and useful correlation to presume the melting points of ash.

(2.2)The general correlation between ash components and coal ash

At least the chemical analysis is necessary to know the coal ash components. The correlation between chemical components and coal rank was examined. The 43 kinds of coals from a wide variety of deposits in the world were chosen as the samples. These samples were divided into tree groups. These are high rank coal that has over

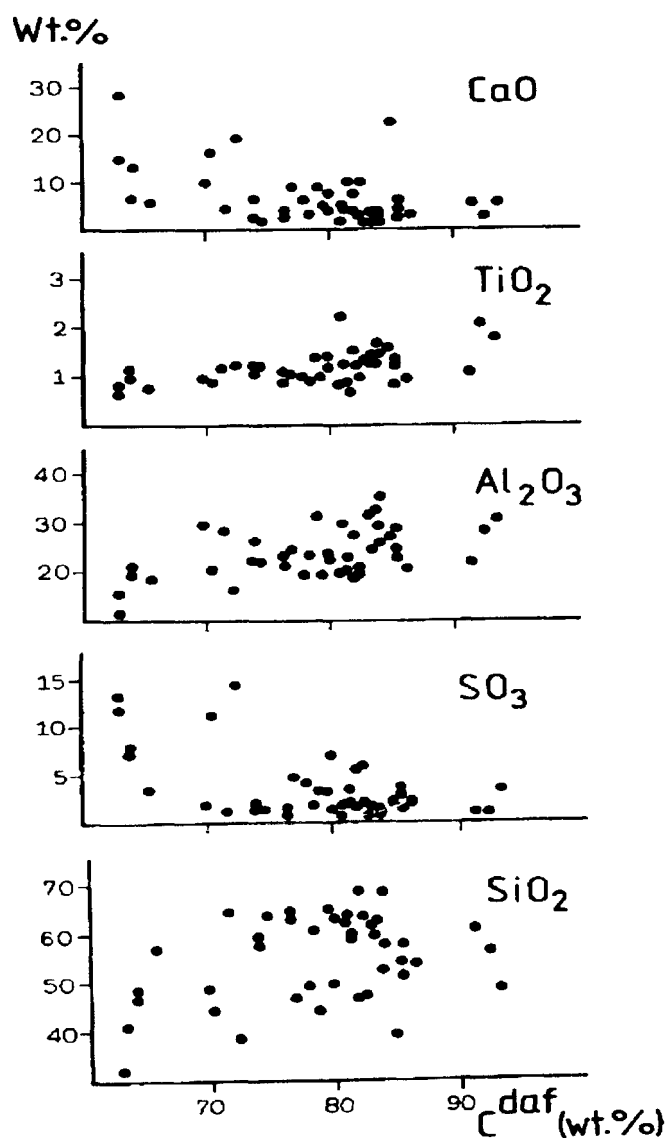


Figure 4 Coal rank and chemical components of ash

85% d.a.f. carbon contents, low rank coal that has less than 75% d.a.f. carbon and medium rank coal. The groups correspond to the approximate carbon values for lignitic-subbituminous coals, subbituminous-bituminous coals and bituminous-anthracitic coals. Table 1 shows the average value of chemical composition of coals. The low rank coals are rich in water, volatile matter, ash, H, N, O, S, MgO, CaO and SO_3 . The higher rank coals are characterized with increased contents of fixed carbon, SiO_2 , Al_2O_3 , Fe_2O_3 , K_2O , Na_2O and TiO_2 . Figure 4 shows the relationship between chemical components and carbon contents. Although this figure shows some scatter, there are some trends. The contents of CaO and SO_3 show the negative correlation with carbon contents while TiO_2 , Al_2O_3 and SiO_2 show positive correlation with carbon contents. These results must have relationship with the geochemical history of coal seam. The genesis of the minerals (authigenic) and introductions of minerals from outside (detrital) during coalification are studying.

(3) Gasification of coal liquefaction residue

The reactivities and handling procedure have been studying

(4) Experiments with bench scale gasifier

The major discharges from fluidized bed gasifier are overflow and entrainment. Figure 5 shows the relationship of the weight fraction of discharged particles to feeding coal and superficial gas velocity in the fluidized bed gasifier.

The OP and EP mean overflow particles and entrained particles respectively. The calculation of weight fraction was based on an ash balance between feeding coal and discharged particles. The carbon contents of discharged particles are also shown in this figure. The increase in superficial gas velocity (U_0) brought decrease of overflow particles and increase of entrained particles. Especially, the effect on the entrainment is obvious. The weight fraction becomes twice when U_0 increase from 0.5m/sec to 0.8m/sec. The carbon contents of discharged particles increase with gas velocity. This means that the increasing of gas velocity reduces the carbon conversion of the gasifier. The carbon contents of entrained particles at 0.8m/sec reached about 0.5. That is close to carbon contents of feeding char particle's carbon that was 0.59. The

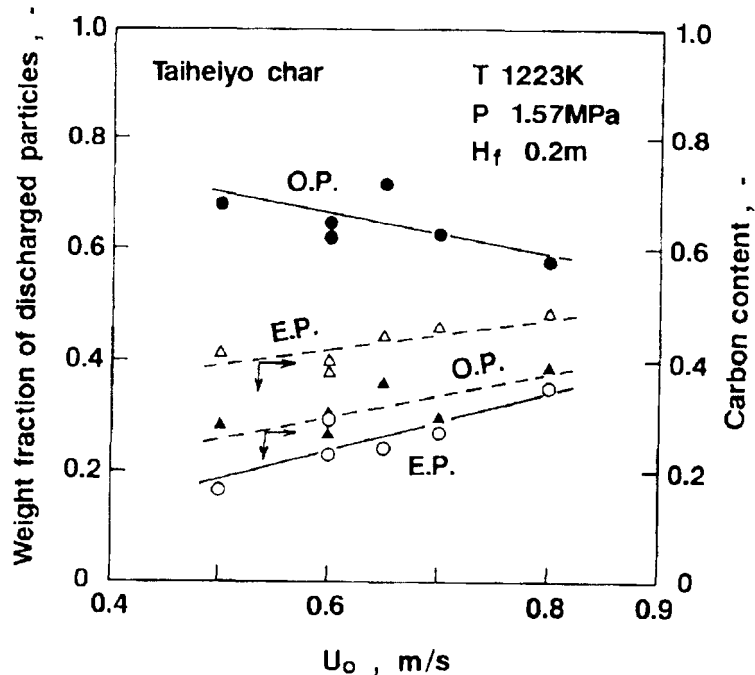


Figure 5 The discharge from fluidized bed gasifier

becomes twice when U_0 increase from 0.5m/sec to 0.8m/sec. The carbon contents of discharged particles increase with gas velocity. This means that the increasing of gas velocity reduces the carbon conversion of the gasifier. The carbon contents of entrained particles at 0.8m/sec reached about 0.5. That is close to carbon contents of feeding char particle's carbon that was 0.59. The

average diameter of entrained particles was 0.11-0.16mm while the feeding particle was 0.6. These experimental results show that the resident time of entrained particle is quit short and gasification reaction didn't progress much. The entrained chars recycle will be required for practical gasifier. Therefore the effect of pressure on entrainment

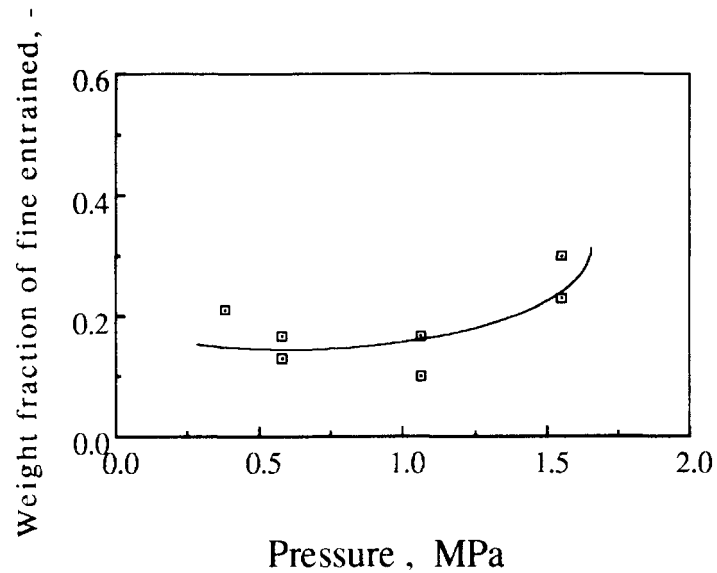


Figure 6 The effect of pressure on entrainment from gasifier

was investigated. Figure 6 shows the measured results. The increase of entrainment was observed at more than 1MPa. The change of minimum fluidization velocity (U_{mf}) is 4.7cm/sec to 4.9cm/sec in the experimental range that shown in this figure. Therefor the bubble flow rate ($U_o - U_{mf}$) changed just little within experimental range. And estimated TDH is 1.7m that is lower than the freeboard length of the gasifier. According to cold model tests, it was found that the shapes of bubble become flatter under higher pressure compare with normal pressure. These phenomena may cause the strong burst of bubble on the surface of fluidized bed and increase the injection of particles to freeboard. This may

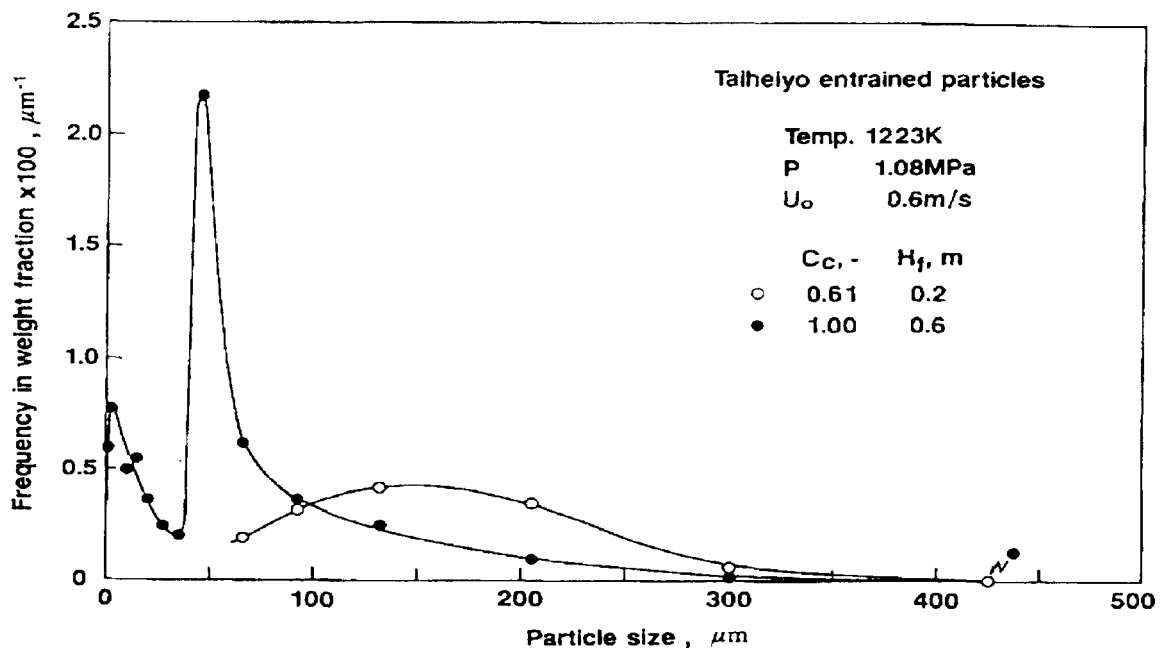


Figure 7 The size distribution of entrained particles

be the reason the increase of entrainment at high pressure.

Figure 7 shows the particle diameter distribution with different carbon conversion (C_c) and bed height (H_f) under same superficial gas velocity. Higher bed height brought higher carbon conversion and generates smaller entrained particles. When Taiheiyoko char particle was gasified to certain conversion, ash layer was established around the unrequited core. The ash layer may generate small particles.

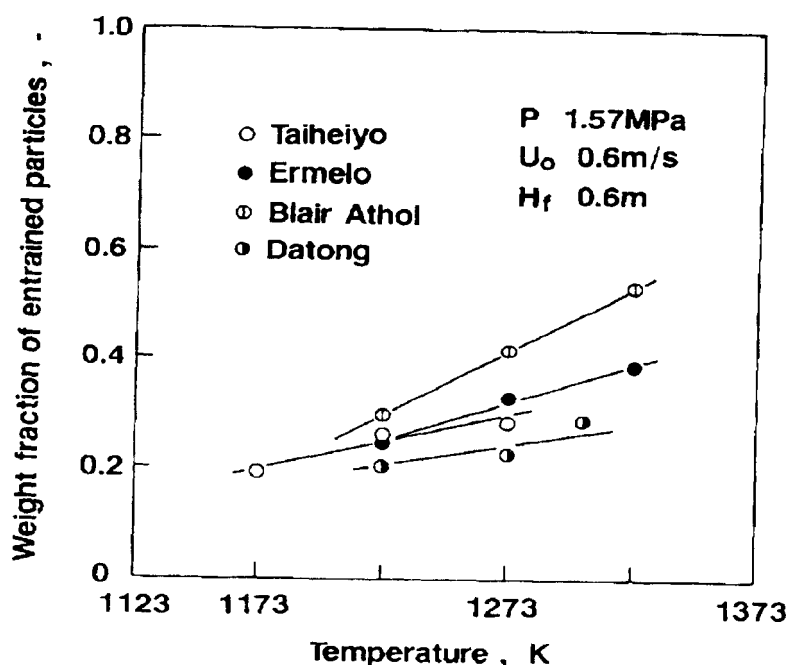


Figure 8 The effect of temperature on entrainment from gasifier

Figure 8 shows the experi-

mental results of gasification tests for four different coals. This figure shows the effects of temperature on the weight fraction of entrained particle. The entrained particles increase with temperature. The minimum fluidization velocities (U_{mf}) decrease with temperature for small particles such as used in these experiments. This increases the bubble flow rate and the amount of particles that were injected to freeboard region. This may be the reason of increase of entrainment with temperature. Blair Athol coal show the most remarkable entrainment. Blair Athol coal is known as the easy pulverized coal by the thermal stress. This may be the reason.

6.Future task

The several factors that govern gasification reactivities have been elucidated. The active modification of coal or its derivatives will be investigated. The mineral matter's behavior for fusion will consider more deeply taking into account the origin of them and change in gasification process. The easier way to estimate the mineral components of ash will be developed. The way to improve the gasifier performance such like in-stu desulfurization will be studied.

FUNDAMENTAL STUDIES ON IMPROVEMENT OF EFFICIENCY OF COAL GASIFICATION

Minoru Shiraishi

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 to produce mainly CO and H₂ at high temperature. Development of advanced technology for high temperature desulfurization including *in-situ* desulfurization in an entrained bed gasifier and hot gas clean-up using a high temperature reactor is also aimed.

Work Program

(1) Analysis and evaluation of coal gasification data

Relationship between material and heat balances of coal gasification was investigated. An equation for calculation of cold gas efficiency was derived based on the stoichiometry of chemical reaction formula. The effect of thermal conditions of pyrolysis on the results of gasification was estimated using the equation derived to evaluate a nature of chars as a raw material of gas production.

For the fundamental research of gasification reactions, step scan FT-IR/photoacoustic spectroscopy(PAS) was applied to depth profiling analyses of coal and gasification chars.

(2) Studies on desulfurization for coal gasification

For the fundamental study of high temperature desulfurization, the sulfur compounds production during coal pyrolysis were pursued by GC-MS. The effect of pyrolysis atmosphere and nitric acid treatment of coal were investigated.

Summary

1 Up to FY 1993

(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 influenced 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(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 1994

(a) Mechanism of moisture retention in coal

Thermal efficiency of coal drying, pyrolysis and gasification process is affected by moisture content. In order to elucidate the moisture retention

mechanism, it seems to be significant to investigate the relationship between the number of water molecule absorbed and those of O and N atoms in coal. To substitute both numbers above mentioned, the values defined by $(\text{moisture}\%) / 18 \times 100$ and $\{ (\text{Oxygen}\%) / 16 \times 100 + (\text{Nitrogen}\%) / 14 \times 100 \}$ were calculated respectively for seventeen kinds of coals and their thermally treated char. Fig. 1 shows that the number of water molecules increased linearly with that of O and N atoms in coal. The slope of linear relationship was found to be 0.20~0.25 for bituminous coal and anthracite. One out of 4 or 5 functional groups containing O or N in these coals is considered to be bound to water. In the case of lignite and subbituminous coal, the slope was estimated at about 1.0. Therefore, the increase in number of water molecules of moisture would be proportional to the increase in that of functional groups in these coal. It seems to be reasonable that almost uniform diffusion of water into coal particle occurred for these young coals instead of surface absorption or capillary condensation.

(b) Analyses of gasification chars using step scan FT-IR/PAS

Step scan FT-IR/PAS was applied to depth profiling analyses of gasification chars. Sampling depth of the instrumental settings used was checked using specially prepared oxidized coal sample. A Biorad FTS-60A/896 step scan FT-IR spectrometer was used for all spectral measurements.

Taiheiyo coal oxidized at 300°C was used for estimation of sampling depth of step scan FT-IR/PAS measurement. Fig. 2 shows depth profiling PA spectra of oxidized Taiheiyo coal with various modulation frequencies and phase angles. PA spectra of unoxidized Taiheiyo coal was used for back ground correction to compare the changes in peaks before and after oxidation. When modulation frequency of 400Hz and phase angle of 90° were selected, layer near coal surface should be detected. Considerable decrease in peaks at 2800~3050cm⁻¹ attributed to CH stretching band was observed. Decreasing phase angle from 90° to 0° to obtain the signals of deeper layer, a peak at around 1700cm⁻¹ attributed to C=O band increased. When modulation frequency is switched to 100Hz, infrared beam is expected to penetrate into deeper layer of coal particle. Applying the phase angle of 90~45°, decrease in CH peaks was observed, while difference between PA spectra of oxidized and unoxidized samples scarcely be detected with a phase angle of 0°. This indicates that changes in functional groups caused by oxidation occur only in the vicinity of coal surface.

The oxidized Taiheiyo coal samples were used for cross-sectional observation by microscope with reflective lights. Approximately 5μm of bright rim was observed on the edge of coal particles. Unoxidized coal did not show this kind of rim. Thus, actual sampling depth of the spectrometer is estimated at 5μm and

deeper.

The FT-IR spectroscopy is applied to the analyses of gasification char. A Taiheiyo coal char and a Muswellbrook coal char produced by HYCOL entrained bed gasifier are used for the IR measurement. In Fig. 3, phase-separated FT-IR/PA spectra are shown. For better baseline correction, spectra of the char collected at the same time in different two places(cyclones CY-301 and 302) during the operation of HYCOL gasifier using respective coal are mutually compared. Using step scan speed as slow as 10Hz to allow IR beam to penetrate deeply inside char, peaks at 2900cm^{-1} , attributed to CH, and broad peaks centered at 1700 and 3400cm^{-1} could be clearly detected. 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 up to 1600°C . Two kinds of chars showed different depth profile. This profile may reflect the difference of morphology of respective chars. Considering that no obvious absorbance peaks could be detected by the conventional FT-IR spectroscopy, the use of step scan FT-IR/PAS is concluded to be a promising method for the analyses of even high temperature gasification chars as well as coals.

(c) Gasification with simultaneous desulfurization

Four kinds of raw coal samples, Taiheiyo, Datong, Wandoan and Mequinenza, and these samples treated with HNO_3 were pyrolyzed in H_2 or He flow. The amounts of H_2S and COS formed during pyrolysis were analyzed by GC-MS. All raw samples showed a maximum on H_2S production curves around 450°C due to the decomposition of FeS_2 and a part of organic sulfur in coal. While Taiheiyo and Wandoan coals showed almost no production of H_2S above 600°C in H_2 flow, Datong and Mequinenza released considerable amounts of H_2S . The effect of atmosphere during the pyrolysis of Datong is shown in Fig. 4. This result suggests that the sulfur forms in Datong and Mequinenza coals are especially reactive with H_2 above 600°C .

The maximum at 450°C on H_2S production curve for all samples was decreased by HNO_3 treatment, because the inorganic sulfur compounds in coal were eliminated by HNO_3 . Above 600°C , the H_2S production curves in H_2 flow for Taiheiyo and Mequinenza coals treated with HNO_3 were similar to those for raw samples. On the other hand, Wandoan and Datong coals with HNO_3 treatment showed completely different H_2S production curves from those raw samples, in which the two characteristic maxima were observed. Fig. 5 shows the effect of HNO_3 treatment on H_2S production from Wandoan coal. The

organic sulfur form in Wandoan and Datong coals, therefore, seemed to be affected by HNO_3 treatment. FT-IR and ^{13}C -NMR measurements suggested Wandoan coal was slightly oxidized by HNO_3 treatment. The maximum at 450°C on H_2S production curve for Wandoan coal was decreased by air oxidation of sample. The air oxidized Wandoan coal produced H_2S over 600°C , but the production curve was different from one for HNO_3 treated sample. The effect of two oxidation processes for organic sulfur in Wandoan coal seemed to be different.

Future tasks

- (1) Adding gasification data using various kinds of coal to the data base in order to clarify the effect of difference of elemental composition and heating value of coal on gasification reaction.
- (2) Depth profiling analyses of various kinds of gasification chars using step scan FT-IR/PA spectroscopy.
- (3) A further study on the acting mechanism of desulfurization agents.

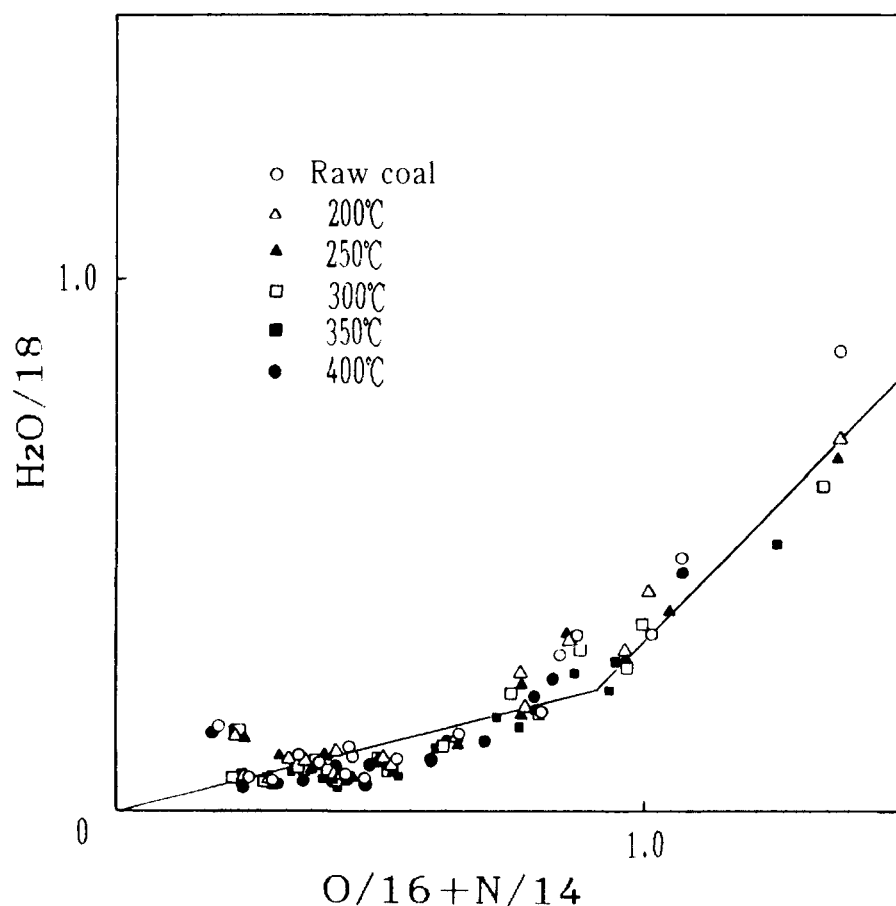


Fig. 1 Relationship between $(\text{O}/16 + \text{N}/14)$ and $(\text{H}_2\text{O}/18)$.

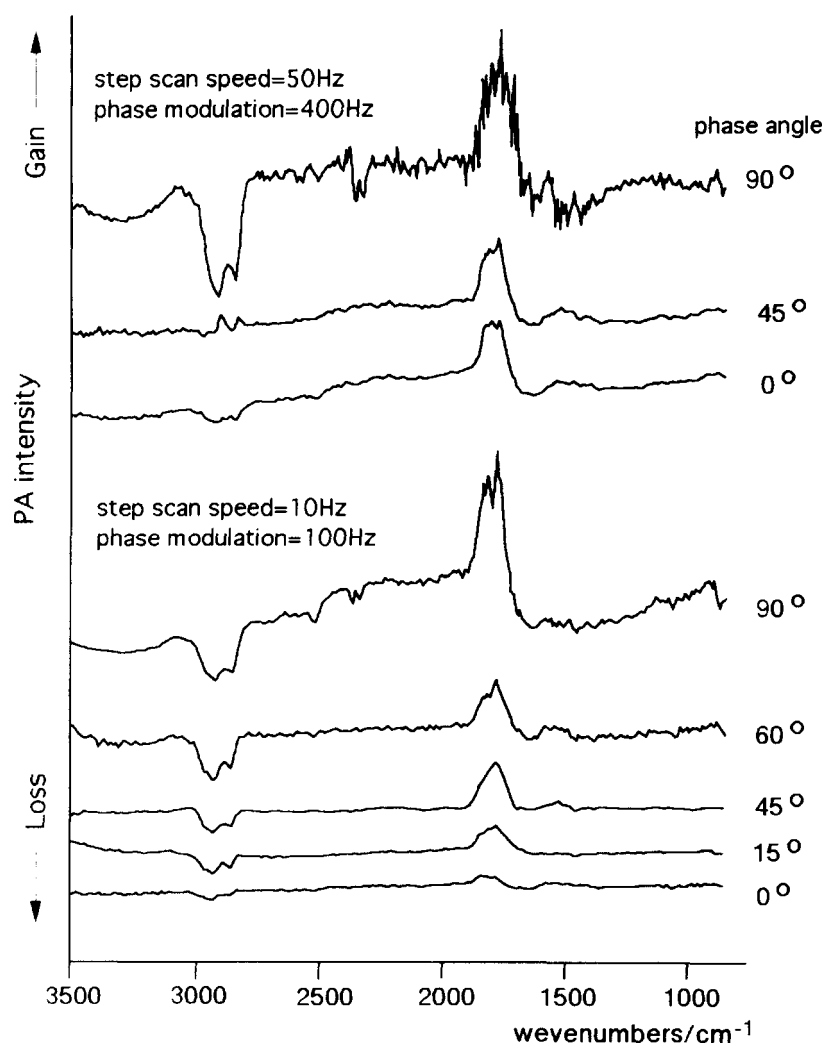


Fig. 2 Depth profiling FT-IR/PA spectra of oxidized Taiheiyo coal.

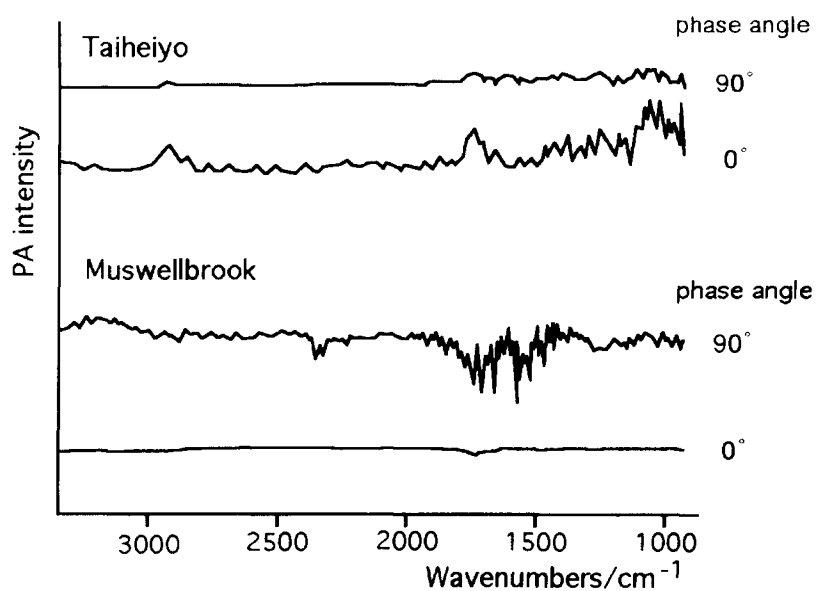


Fig. 3 Depth profiling FT-IR/PA spectra of gasification chars obtained from HYCOL gasifier.

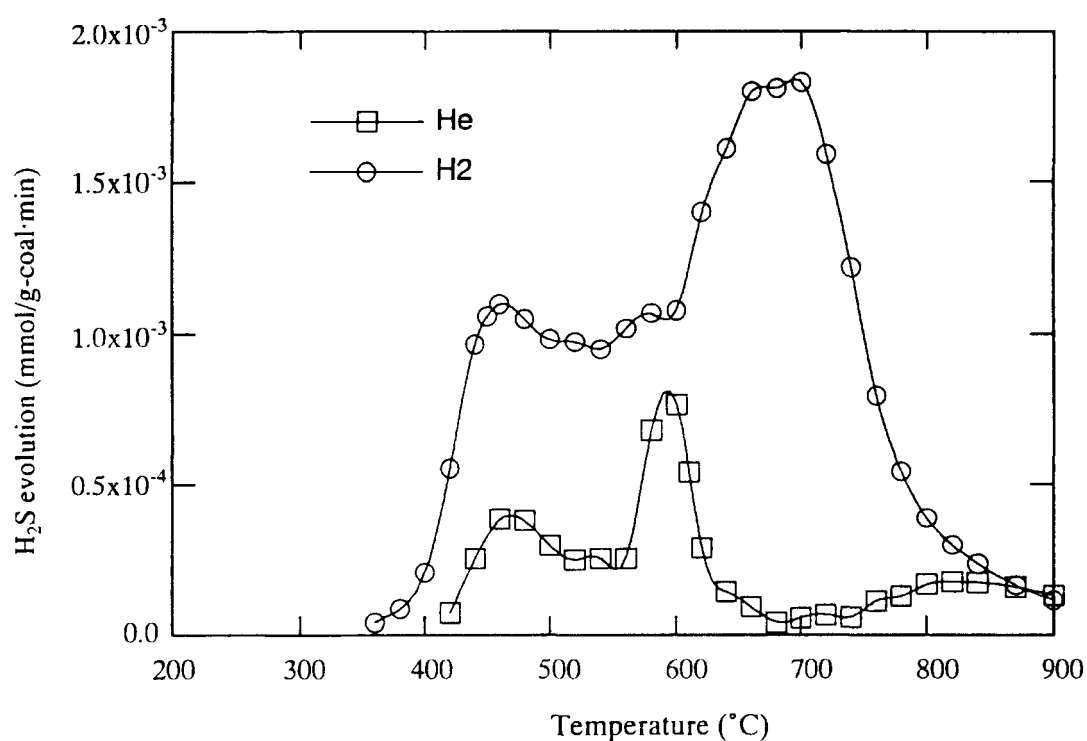


Fig. 4 The effect of atmosphere for H_2S production from Datong coal.

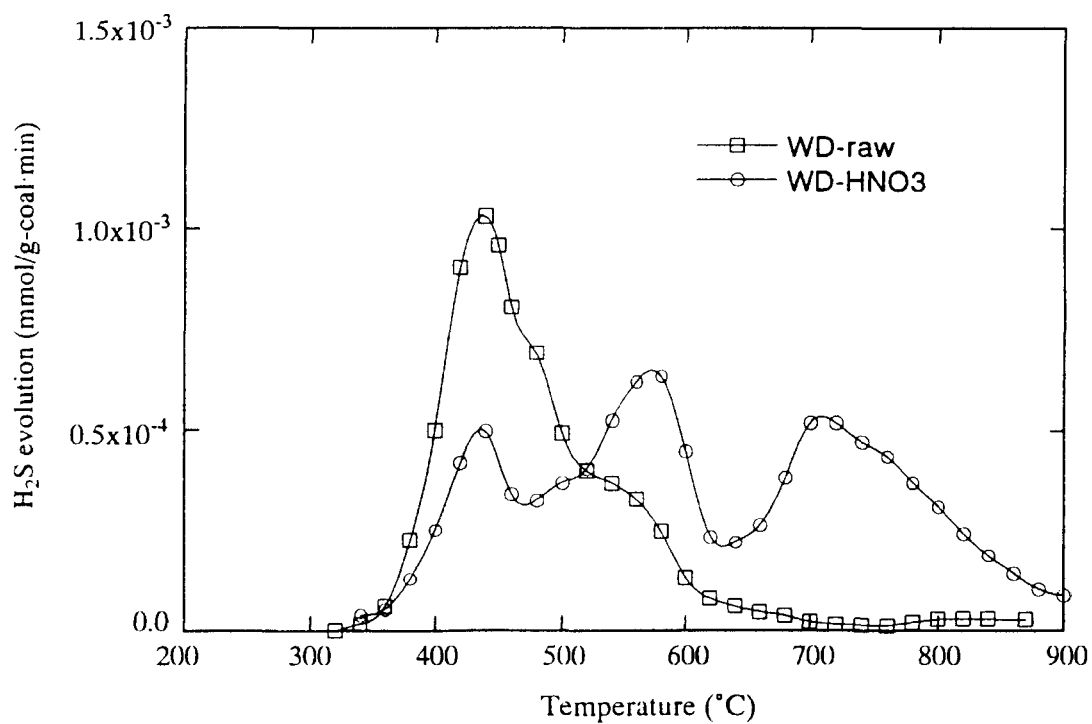


Fig. 5 The effect of HNO_3 treatment for H_2S production from Wandoan coal.

3. DEVELOPMENT OF BITUMINOUS COAL LIQUEFACTION TECHNOLOGY

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

(2) Supporting Research for the Pilot Plant

① Research Using the 1t/d Process Supporting Unit (PSU)

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

(b) Evaluation of Advanced Materials for Coal Liquefaction Plants

② Study on Hydrogenation Catalyst for Recycled Solvent

③ Development of Slurry Letdown Valves

④ Study on the Synthetic Iron Sulfide Catalyst

⑤ Coal Selection Studies for Chinese Coal Liquefaction

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

New Energy and Industrial Technology
Development Organization (NEDO)

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 (1994)

Following the 1993 plan, equipment and materials for the bituminous coal liquefaction pilot plant with a capacity of 150 t/day will be procured, and the the construction work, including installation, piping work, electrical and instrumentation work, and painting and insulation work will be conducted. At the same time, the basic operation plan will be reviewed, and the preparations for the start-up and operation of the pilot plant will be conducted. And studies and technical survey related to coal liquefaction will be performed.

(1) Study on research program

- Reviewing the basic operation plan, including the number of runs
- Reflecting the results of research and development conducted on coal liquefaction, especially the operation of the process supporting unit (PSU), in the pilot plant operation plan
- Planning to obtain operation data on equipment to be developed

(2) Construction of pilot plant

- Applying to governmental procedures in connection with the construction
- Conducting detailed desing work
- Procuring equipment and materials, and conducting construction work

(3) Operation preparation

- Determing the operation personnel plan, and establishing the operation organization
- Planning and providing operation training, and drawing up operation manuals
- Determing the kinds, quantities, and procurement plans of the coal, solvent, and catalysts required for the start-up and operation of the pilot plant
- Planning the subcontractors' jobs related to the operation, such as analyses of samples
- Planning methods for disposing of liquefied residues and oil from the pilot plant operation

(4) Study and technical survey

- Study on improving the performance of the liquefied catalyst
- Drawing up a data analysis system for liquefaction reactor
- Feasibility study of the liquefaction plant

Summary (1984-1994)

1. Up to FY 1993

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 started in FY 1985. The detailed design of the pilot plant was completed in FY 1986. 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 started. And survey and soil test of the site of a 150 t/d pilot plant were conducted. Preparatory work on application to governmental procedures for construction was begun in FY 1989.

In FY 1991, the detailed design for the auxiliary facilities was completed. Applications to governmental procedures for construction were submitted. The site preparation was made. And a part of temporary construction and civil work was conducted. Materials for liquefaction reactors were arranged.

In FY 1992, towers and vessels, heat exchangers, miscellaneous equipment, materials for steel structures, and piping materials were procured. Work for temporary facilities was conducted. Civil work for the facilities was conducted, and oil retaining walls were built.

In FY 1993, 174 sets of equipment, materials for steel structures and piping were procured. The civil work for the facilities was completed. Construction of the facilities, such as architectural work, steel structure work, installation of equipment, piping work, electrical and instrumentation work, and painting and insulation work, was begun.

2. For FY 1994

(1) Study on the research program

- (a) In order to make the existing basic operation plan (nine runs) efficient, a new basic operation plan (seven runs) was developed, setting a new target for higher achievement, focusing on certain specialized studies rather than a wide range of studies, and reflecting the operation results of the PSU.
- (b) The results of research and development on coal liquefaction, including that of PSU, were compiled. Some of these results were reflected in the pilot plant operation plan.
- (c) Based on the basic operation plan, a list of items for the requisite operation data on the equipment to be developed were assembled. And preparations for making a coal liquefaction technical package were begun.

(2) Construction of pilot plant

The process outline of the pilot plant under construction are shown on Table-1. Construction work on fifteen facilities was conducted, while the pilot plant comprised a total of 22 facilities. In total, 67% of the overall construction work, including design, equipment procurement, and construction, was completed.

(a) Application to governmental procedures

In connection with the partially revised facility plan, the applications of changes in the approval of high-pressure gas production under High-Pressure Gas Control Laws and in installing a hazardous material plant under Fire Service Laws were made to government offices. Completion inspections of two sets of boilers and two sets of pressure vessels were made by government officials to ensure that they satisfied Industrial Safety & Health Laws. We applied to governmental procedures for approval of the construction plan under Electricity Enterprises Act.

(b) Detailed design

The detailed design work for a operating data processing system was conducted.

(c) Equipment procurement

The equipment and materials procured in FY 1994 are shown in Table-2. We procured 27 sets of towers and vessels, 2 sets of heat exchangers, 6 sets of rotating machineries and 9 sets of others. Among them are included a coal pulverizer, a slurry preheating furnace, a solvent hydrogenation preheating furnace, slurry heat exchangers and various equipment for hydrogen production. We also procured electric equipment, instruments and materials, as well as piping materials which comprised 410 tons of piping, pipe fittings and valves.

(d) Construction

160 sets of equipment procured up to this year were installed. This year's construction focused on piping work. All of the main piping work was completed except for that of six facilities. Electrical and instrumentation work were conducted. Painting work for pipes and some equipment, insulation work for pipes, and insulation and fire-resistant jacketing work for equipment were also conducted. Some of piping racks and passages were constructed.

Table-1 Outline of 150 t/d Bituminous Coal Liquefaction Pilot Plant
(Typical Process Conditions of NEDOL Process)

Liquefaction Process		Solvent Hydrogenation process	
Temperature	450 °C	Temperature	320 °C
Pressure	170 kg/cm ² G	Pressure	100 kg/cm ² G
Catalyst	Fine Particles of Iron Compound	Catalyst	Ni-Mo-Al ₂ O ₃
Additional Quantity of Catalyst	3 wt% (daf coal basis)	LHSV	1 hr ⁻¹
Slurry Concentration	40 wt% (dry coal basis)	Gas Solvent Ratio	500 Nm ³ /t
Residence Time	60 min.	H ₂ Concentration in Recycle Gas	90 vol%
Gas Slurry Ratio	700 Nm ³ /t		
H ₂ Concentration in Recycle Gas	85 vol%		

Table-2 Equipment and Materials Procured

• Equipment	
Towers & Vessels	27 sets
Heat Exchangers	2 sets
Rotating Machineries	26 sets
Others	9 sets
Total	64 sets
• Steel Structure	20 tons
• Piping	410 tons
• Electric Equipment, Instruments and Materials	

(3) Operation preparation

(a) Operational personnel

The operation organization and personnel plan were devised based on the basic operation plan. At the same time, key operation personnel were assigned.

(b) Operation training

Operation training was planned and provided for the key operation personnel, including training in PSU. Preparation of operation manuals was started.

(c) Materials

Kinds and quantities of raw and subsidiary materials, such as coal, solvent, coal oven gas and catalysts, as well as chemicals and utilities were determined, and their procurement plans were examined.

(d) Subcontractors' jobs

Sample analysis was planned. The plan and organization for maintenance were examined. Subcontracting maintenance and other plant-related jobs were planned.

(e) Product disposal

The internal disposal plan for the drainages and the liquefied oil, as well as the external disposal plan for sludge, waste catalyst, waste slurry, and waste amine were examined. The plan for disposing of the liquefied residue at a cement plant was also examined.

(4) Study and technical survey

(a) Study on improving the performance of the liquefied catalyst

To establish the natural pyrite catalyst pulverization system for the pilot plant, the continuous pulverization test was conducted on three kinds of pulverizers that could be applied to the pilot plant, i.e., a dry-system roller mill, a wet-system bead mill, and a wet-system ball mill. The pulverization capacity and operative stability of each machine, and the liquefaction performance of the pulverized catalyst were evaluated. And it was decided to use a two-stage integrated pulverization system for the pilot plant, consisting of a wet-system ball mill and a wet-system bead mill aligned in series.

(b) Drawing up a data analysis system for liquefaction reactor

The data obtained by a bench scale unit (BSU) were used to examine and

analyze the initial reaction process, reaction rate in the heterogeneous phase, flow patterns in reactors, as well as for the heat analysis and the formation heat analysis in an attempt to improve the simulator's function. The data from PSU were used to evaluate the simulation results for making prototype simulation software applicable to the pilot plant.

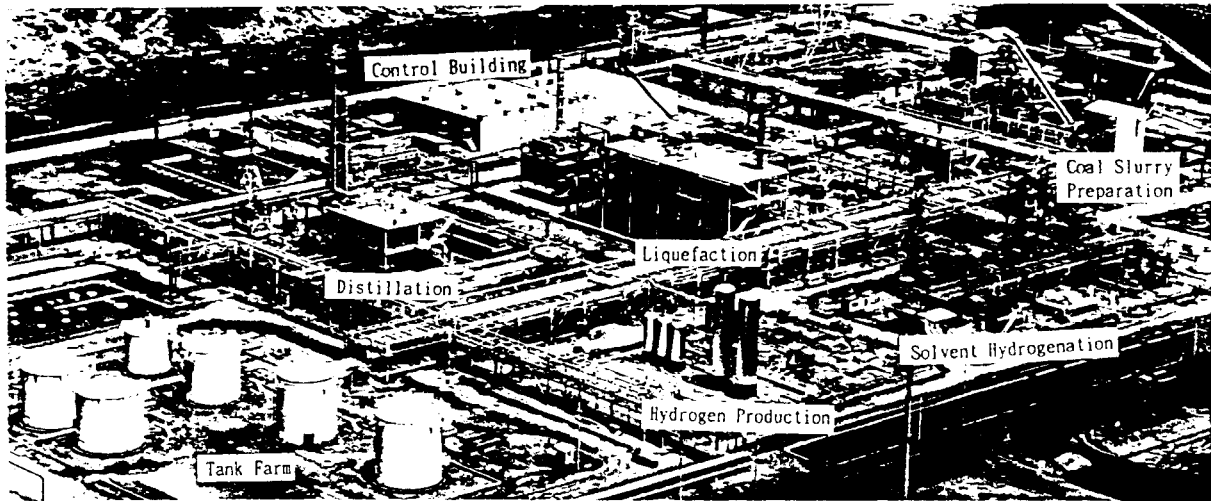
(c) Feasibility study of the coal liquefaction plant

Field surveys in China were carried out at the two seaside locations selected for the coal liquefaction plant. Construction costs and total material balance were estimated based on the surveys, and the discounted cash flow method was used to calculate the liquefied oil cost. The sensitivity and feasibility analyses for commercial plants in China were made, and the result showed that improving the catalyst and concentrating the slurry are essential for reducing the liquefied oil cost.

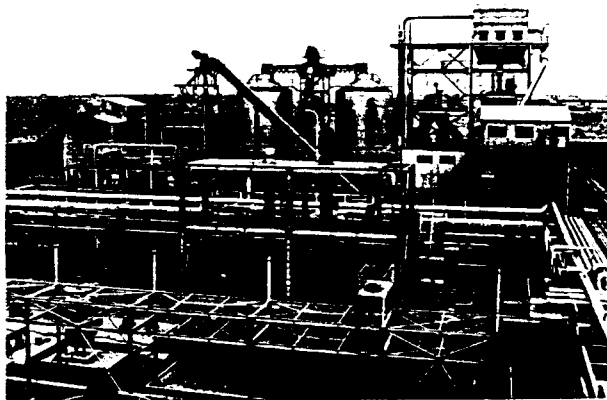
Future Tasks

- (1) Completing the remaining work, such as electrical and instrumentation work, to build the pilot plant
- (2) making preparations for start-up and operation, operating the pilot plant for studies, demonstrating the performance of the NEDOL process, and obtaining data for assembling the coal liquefaction technical package for future large plants

View of the 150 t/d Bituminous Coal Liquefaction Pilot Plant
as of March 1995



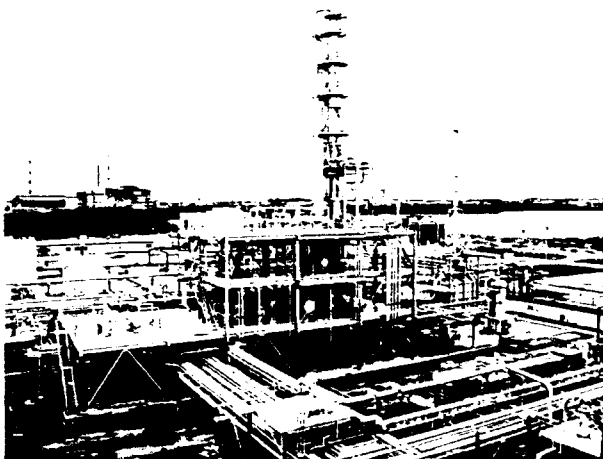
Coal Slurry Preparation



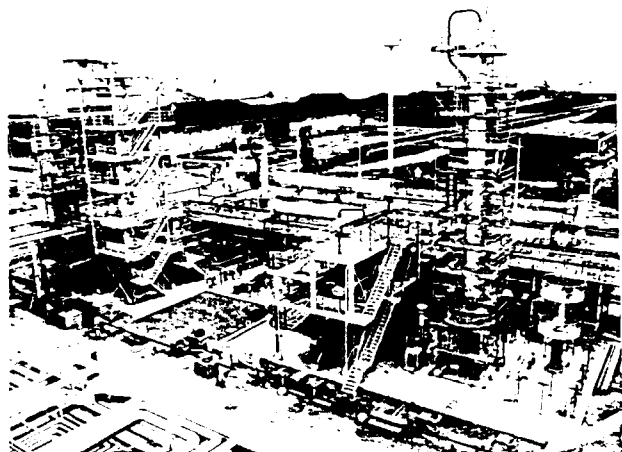
Liquefaction



Distillation



Solvent Hydrogenation



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

Dr. Shigeru Ueda

Director General of Technology Development Department, CCTC

New Energy and Industrial Technology

Development Organization (NEDO)

Objectives

In order to support the coal liquefaction research for the pilot plant(PP), the NEDOL Process 1t/d PSU shall be operated to check 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) Installation of the measurement unit of residence time distribution of coal liquid in the coal liquefaction reactor using Neutron Attenuation Tracer Technique (NAT)
- (b) Installation of the coal liquid sampling unit for the coal liquefaction reactor
- (c) Installation of the measurement unit of differential pressure in the coal liquefaction reactor
- (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 investigate the behavior of fluids in the coal liquefaction reactor
- (d) Research program to establish the support for PP

(3) Research Work

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

Attenuation Tracer Technique (NAT) was installed.

- (b) The coal liquid sampling unit for the coal liquefaction reactor was installed.
- (c) The measurement unit of differential pressure in the coal liquefaction reactor was installed.
- (d) Overhaul for governmental security inspections, periodic self inspections and repair of equipment after each operation were implemented.

(2) Planning of Research Program

- (a) Detailed research program for the operations (Run0601, Run0602 and oil operation) in FY 1994 was made.
- (b) Long-term program for operation research and equipment modifications was reviewed.
- (c) Manuals for operating procedure were reviewed and prepared.

(3) Research Work

The PSU was operated for a total of 100 days which consisted of 50 days/Run $\times$ 2Runs (Run0601, Run0602) with Tanito Harum coal. Effect of coal liquefaction catalyst on the yields and properties of products was investigated. The various kinds of problems which occurred during operation were solved, and the results were confirmed.

- (a) Effect of the natural pyrite catalyst on the yields and properties of products

Run0601 was carried out to research the effect of the natural pyrite catalyst on the yields and properties of products with Tanito Harum coal. Reaction conditions of Run0601 which were basic operating conditions, 465°C conditions and 465°C Max conditions and same as those of Run0502(with Tanito Harum coal and wet method synthetic iron sulfide) are shown in Table 1.

- ① The effect of the natural pyrite catalyst on product yields is shown in Figure 1,2. There was no significant difference in oil, gaseous and water yields between the wet method synthetic iron sulfide and the natural pyrite. With both catalysts, the oil yield was about 52 wt%(daf coal basis) at basic operating conditions, and about 59 wt%(daf coal basis), equivalent to 4.4 bbl/t-daf coal, at 465 °C Max conditions.

- ② Between the use of natural pyrite and wet method synthetic iron sulfide, there was no significant difference in plant operabilities, such as differential pressure of preheater, removal of deposited solids from coal liquefaction reactors, softening point of residue and discharging residue from vacuum distillation tower.
- (b) Effect of dry method synthetic iron sulfide catalyst on the yields and properties of products
- Run0602 was carried out to research the effect of the dry method synthetic iron sulfide catalyst on the yields and properties of products with Tanito Harum coal. Reaction conditions of Run0602 which were same as those of Run0502 and Run0601 are also shown in Table 1.
- ① The effect of the dry method synthetic iron sulfide catalyst on product yields is shown in Figure 1,2. The oil yield at basic operating conditions was 54.6 wt%(daf coal basis), and was higher than those at the use of dry method synthetic iron sulfide catalyst and natural pyrite. On the other hand, the residue and gaseous yield were lower than those at the use of the other catalysts. At 465°CMax conditions, the oil yield was 61.8 wt%(daf coal basis), equivalent to 4.6 bbl/t-daf coal.
 - ② Among the use of dry method synthetic iron sulfide, natural pyrite and wet method synthetic iron sulfide, there was no significant difference in plant operabilities, such as differential pressure of preheater, removal of deposited solids from coal liquefaction reactors, softening point of residue and discharging residue from vacuum distillation tower.
- (c) Study of hydrogenation properties of improved catalyst
- Improved catalyst(CH0401) was used 50days at Run0602. The properties of hydrogenation product were compared with those in case of Ketjenfine catalyst(153 S).
- ① It was evaluated that the life of the improved catalyst is longer than that of Ketjenfine catalyst.
 - ② There was no significant difference in catalyst temperature at reaction and fraction of aromatic carbon (fa) of solvent

between the improved catalyst and Ketjenfine catalyst.

(d) Study of behavior of fluids in coal liquefaction reactor

In order to investigate behavior of fluids in the coal liquefaction reactor, the coal liquid sampling unit, the measurement unit using Neutron Attenuation Tracer Technique (NAT) and the measurement unit of differential pressure were used. As a result, it was confirmed that these means are applicable to PP.

① Coal liquid in coal liquefaction reactor was sampled by the coal liquid sampling unit under high-temperature and high-pressure conditions, and its properties were analyzed. As an example of the properties, specific gravity of the coal liquid sample is shown in Figure 3. It was confirmed that the behavior of reaction in the reactor was able to grasp.

② Gas hold-up was able to obtain from the measurement of differential pressure of fluid in the coal liquefaction reactor. Comparison with gas hold-up is shown in Figure 4. It was found that gas hold-up at PSU was similar to that of EDS.

③ Residence time distribution of coal liquid in the coal liquefaction reactor was obtained by Neutron Attenuation Tracer Technique (NAT). Mean residence time for coal liquefaction reactor is shown in table 2. Under slurry conditions, range of mean residence time through three coal liquefaction reactors was 92~147 minutes.

(4) Environmental Impact Study

Analysis of waste water and an acclimation test for activated sludge was 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 coal slurry properties

(b) The study of behavior of fluid in the reactor

- (c) The study of deposited solid in coal liquefaction reactors
- (d) The study of particle size distribution of coal liquefaction catalyst
- (e) Evaluation test of dry method synthetic iron sulfide

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 1994

Operating condition	basic	465°C	465°CMax
Coal	Indonesian coal (Tanito Harum coal)		
Liquefaction catalyst	Natural pyrite (Run0601) Dry method synthetic iron sulfide (Run0602)		
Reaction Temperature (°C)	450	465	→
Reaction Pressure (kg/cm ² G)	170	→	190
G/L (Nℓ/kg)	700	→	900
Amount of catalyst addition (wt%)	3	→	4
fa of recycle solvent	0.5	→	→

Table-2 Mean residence time for coal liquefaction reactors by NAT

	Operating condition					Mean residence time(min)	
	Feed (Kg/hr)	Temperature (°C)	Pressure (Kg/cm ² G)	G/L (Nℓ/kg)	Catalyst (Wt%)	1 reactor DC201	3 reactors DC201~203
Hot oil	106.0	385	170	700	—	26.6	68.3
Slurry	108.8	450	170	700	3.0	26.8	91.5
	108.3	465	170	700	3.0	50.7	118.0
	108.5	465	190	900	4.0	50.8	146.7

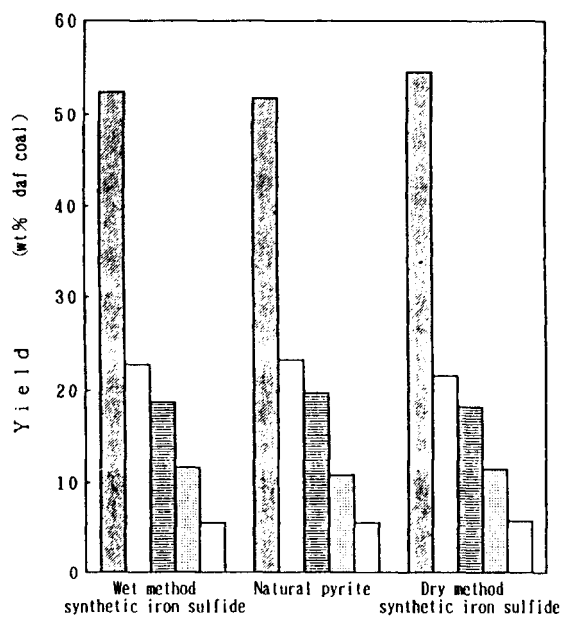


Fig-1 Effect of catalyst type on product yields

Coal Tanito Harum coal (Run0502~0602)
 Operating condition basic
 Reaction temperature 450 °C
 Reaction pressure 1.70 kg/cm²G
 Amount of catalyst 3 wt% dry coal addition
 G/L 7.00 Nl/kg
 fa of recycle solvent 0.5

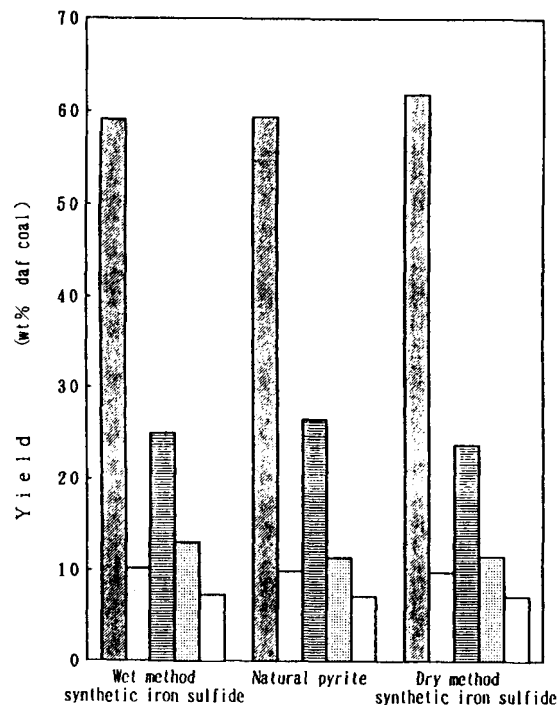


Fig-2 Effect of catalyst type on product yields

Coal Tanito Harum coal (Run0502~0602)
 Operating condition 465°CMax
 Reaction temperature 465 °C
 Reaction pressure 1.90 kg/cm²G
 Amount of catalyst 4 wt% dry coal addition
 G/L 9.00 Nl/kg
 fa of recycle solvent 0.5

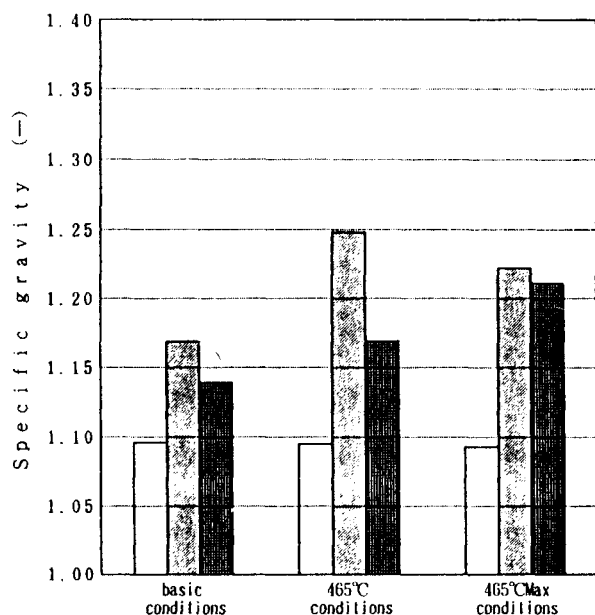


Fig-3 Specific gravity of the coal liquid sample

□ Feed slurry
 ▨ Reactor (Lower nozzle)
 ▩ Reactor (Upper nozzle)

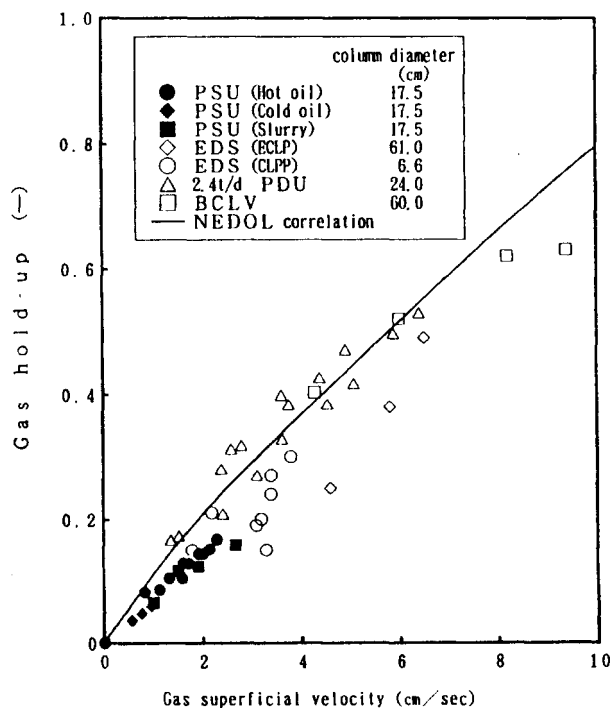


Fig-4 Relation between gas velocity and gas hold-up

Evaluation of Advanced Materials for Coal Liquefaction Plants

Dr. Shigeru Ueda

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

Objective

Purpose of this research and development program is to improve reliability of equipment for coal liquefaction plant and to reduce cost of equipment through the development of reliable and economical materials. New types of materials, including organic, inorganic, metallic and composite materials, shall be examined to evaluate the applicability as the materials of the equipment which is subject to erosion and corrosion through laboratory tests, and in-plant tests to be held in the process support unit (PSU) and the pilot plant (PP).

Work Program

1. Technical survey

Survey for evaluation methods of new materials and availability to equipment was conducted and the results were reflected to the laboratory and in-plant tests in the PSU.

2. Laboratory tests

(1) Erosion/corrosion tests

Erosion/corrosion tests of metallic and surface treated materials were conducted to evaluate erosion /corrosion characteristics using high temperature-pressure autoclave.

(2) Corrosion test using mock-up vessels

Corrosion test of coating alumina using mock-up vessels were conducted to evaluate durability against the thermal history and corrosion. Applicability of nondestructive inspection methods was confirmed.

3. In-plant tests

(1) Metallic material

Samples of the high strength 3Cr-1Mo were exposed to the circumstance of the liquefaction reactors to evaluate hydrogen resistance characteristics.

(2) US-Japan material exchange program

On the basis of the US-Japan collaborative research agreement regarding coal liquefaction materials, both specimens shipped from the USA and same specimens as shipped to the USA were exposed to the circumstance of the liquefaction reactors at the PSU to evaluate sulfide corrosion characteristics.

Summary (1987- 1994)

1. Up to FY 1993

New materials have been selected through technical survey and tested to evaluate applicability as materials for coal liquefaction plant equipment in laboratories.

Experiments for metallic and surface treated materials conducted in the laboratories were hydrogen resistance test, hydrogen permeation test, sulfide corrosion test and erosion/corrosion test. Through the tests, materials to be installed in the PSU plant were selected and exposed to the circumstance of the reactors for evaluating applicability as the materials of coal liquefaction plants. In addition to metallic and surface treated materials, organic materials have been evaluated for coal liquefaction plant through oil resistance test, steam diffusion test and stress relaxation test.

Materials concluded being applicable in laboratory tests have been exposed to the circumstance of the liquefaction reactors and atmospheric distillation towers in the PSU.

Through the above tests there has been hopeful about the advantage of composite materials, that is, Cr-Mo metals in the outer part of the reactor in the aspect of hydrogen resistance combined with stainless steels, Fe-Al metals and Al_2O_3 coats in the inner part of it in the aspect of sulfide corrosion resistance.

2. For FY 1994

(1) Technical survey

Technical survey had been conducted to study corrosion resistance of advanced materials for coal liquefaction plant in the USA.

(2) Laboratory tests

a) Erosion/corrosion tests

Erosion/corrosion tests were conducted using an autoclave apparatus in the conditions of 400°C, 200 kg/cm²G, 500 rpm, 60 days and 10 wt% of 100 μ m SiO₂. Test specimens are 5 kinds of metals(SS400, 2.25Cr-1Mo, 3Cr-1Mo, SUS316 and SUS347) and 5 surface treated 2.25Cr-1Mo steels(coated with stellite6B, WC(TS-10713), CoNiCrAlY, NiCrAlY and Al₂O₃). The test results are summarized as follows;

-SS400, 2.25Cr-1Mo and 3Cr-1Mo

Slight corrosion was observed in the surface inspection and sulfide or oxide of iron was observed in EPMA examination. Erosion/corrosion rate of these specimens after the tests was about 0.1-0.3mm a year.

-Al₂O₃ coating

The Al₂O₃ layer was entirely lost in handling after exposure and under coated Ni-Cr layer was partially sulfurized.

-SUS316, SUS347, stellite6B, WC(TS-10713), CoNiCrAlY and NiCrAlY

Any traces of erosion and corrosion were not observed in each specimen in the surface inspection. Erosion/corrosion rate of these specimen after the tests was less than 0.1mm a year. It implies that these materials are effective to prevent erosion and corrosion.

b) Corrosion test using mock-up vessels

Corrosion tests of alumina coating was conducted using mock-up vessels, which were autoclaves coated by alumina in the inner wall. The autoclaves were heated up and cooled down, repeatedly. One heat cycle consists of heat-up (5°C/min), liquefaction exposure in the conditions of 450 °C , 170kg/cm²G, 400 rpm, 60min, 24 g coal,36 g solvent and 0.72 g catalyst, and cool down to room temperature by forced air quenching by two hours. The test results are summarized as follows;

-As cracks were observed in the alumina layer of the bottom of No.1 testing vessel after 11th heat cycle test, the further was canceled. A part of the alumina layer has peeled off in 1mm³ occurred at the bottom of No.2 testing vessel after 11th heat cycle test, and this area was spread to about a third of the bottom after 20th heat cycle test. However, the test was continued 36th times.

-Besides of the cracks in alumina layer, corrosion resistance of alumina and underlying Ni-Cr was confirmed in the tests. This resistance comes from self-stuffing phenomena of the iron sulfide in alumina layer.

-It was concluded that defective in the layer was detected by means of nondestructive inspection.

-Deterioration of the sprayed layer was detectable as the result of nondestructive inspection after the test, for example the degree of the back echo in ultrasonic inspection was decreased at the deteriorated part.

(3) In-plant tests

a) Metallic material

High strength 3Cr-1Mo steel was exposed to the circumstance of coal liquefaction reactor in the PSU RUN 0502 - RUN 0602 (450 - 465 °C of reaction temperature, 170 - 190 kg/cm²G of reaction pressure, 150 days of total duration) to evaluate hydrogen resistance characteristics.

The specimens were the heat affected zone treated at the condition of 1200 °C -0.5 hrs. and 690 °C -17 hrs. These specimens were coated with alumina for preventing sulfide corrosion and were cylindrically shaped with a length of 60 mm and outer diameter of 30 mm.

These specimens are to be analyzed after exposure tests scheduled in 1995.

b) US-Japan material exchange program

Six kinds of specimens(2.25Cr-1Mo, 3Cr-1.5Mo, 9Cr-1Mo, FAS, FAL and FA180) prepared by U.S.A. side and three kinds of specimens(Al diffusion coating 1, Al diffusion coating 2 and chromizing) prepared by Japanese side were installed and exposed to the circumstance of the PSU reactors during the 50 day-operation of RUN 0602 (reaction temperature:450 - 465 °C, reaction pressure :170 - 190 kg/cm²G).

Each sample was cylindrically shaped with length of 50 mm and outer diameter of 25 mm and nine specimens, one of each kind, were assembled on a rod made by SUS 316 coated with alumina. Two rods were prepared for 18 specimens of 9 kinds.

These specimens are to be analyzed after exposure tests scheduled in 1995.

Future Tasks

All planned laboratory tests have been finished and to achieve the objective, the following items are listed as the future tasks.

- (1) Evaluation of hydrogen resistance characteristics of metallic materials exposed to the reactor circumstance for a long time.
- (2) Implementation on the exposure test of the specimens shipped from the USA.
- (3) Measurement of the deterioration of the reactor material in the PSU.

Study on Hydrogenation Catalyst for Recycled Solvent

New Energy and Industrial Technology
Development Organization (NEDO)

Objectives

1. For a hydrogenation catalyst;
 - (1) To improve the hydrogenation performance.
 - (2) To evaluate the industrial applicability of the improved catalyst.
2. For a n-paraffin hydrocracking catalyst;
 - (1) To improve the hydrocracking performance.
 - (2) To investigate the process application of the improved catalyst.

Work Program

1. Evaluation of the industrial applicability of a hydrogenation catalyst.
 - (1) Evaluation of the industrial applicability of the developed catalyst for Tanito Harum coal recycled solvent.

A 2,400 hrs hydrotreating test of the catalyst is done using Tanito Harum coal recycled solvent in order to confirm the catalyst life.
 - (2) Analysis of Tanito Harum coal recycled solvent and the hydrotreated oils.

Properties of Tanito Harum coal recycled solvent and the hydrotreated oils are analyzed by various methods in order to study the reactivity of the solvent.

2. Final evaluation of the developed catalysts

All results on newly developed hydrogenation and n-paraffin hydrocracking catalysts are synthetically reported from points of view of the preparation and the application.

Summary (1981-1994)

1. Up to 1993 FY
 - (1) Development of a hydrogenation catalyst for the recycled solvent.

A suitable commercial catalyst, KF-153S, does not have a sufficient stability for the hydrogenation of Illinois No.6 coal recycled solvent. As a result of the improvements, a new catalyst that has a better stability than KF-153S have been developed up to 1991. In 1992, the catalyst was prepared on a 100 l scale for loading in the 1 t/d PSU. There were no problems in the catalyst preparation and the catalytic performance. Therefore, it was showed that the industrial production of the catalyst is possible. In a reactivity test of last year, it was found that the catalyst prepared on a 100 l scale have the applicability to Tanito Harum coal recycled solvent.

(2) Development of a n-paraffin hydrocracking catalyst

As a countermeasure to the accumulation of C₂₂⁺ n-paraffin in Wandan coal recycled solvent, a catalyst incorporated with a high-silica pentasil type zeolite was newly developed. Consequently, the catalyst attained a higher conversion of C₂₂⁺ n-paraffin than the target conversion of 15 %. Furthermore, it has been found that a partial pre-hydrotreatment promoted the hydrocracking conversion. In 1993, the catalyst was prepared on a 100 l scale in order to confirm the industrial production of the catalyst. There were no problems in the catalyst preparation and the catalytic performance.

2. For 1994 FY

(1) Evaluation of the industrial applicability of a hydrogenation catalyst

(a) Evaluation of the industrial applicability of a developed catalyst to Tanito Harum coal recycled solvent.

The changes of aromaticity (fa) and nitrogen content of hydrotreated oil on the long-run test are shown in Fig.-1. The catalyst activity maintained in stable during ca. 2,500 hr.

Catalyst life was simulated based on this test result as shown in Fig.-2. The life of the developed catalyst (CH-0401) was estimated ca. 4,300 hr, that was improved comparing with conventional commercial catalyst (KF-153S).

(b) Analysis of Tanito Harum coal recycled solvent and the hydrotreated oils.

Properties of Tanito Harum coal recycled solvent and the hydrotreated oils were analyzed by various methods in order to study the reactivity of the solvent (Fig.-3, -4, Table-1). It was consequently showed that hydrogenation of aromatic ring and hydrocracking proceed with increasing of reaction temperature.

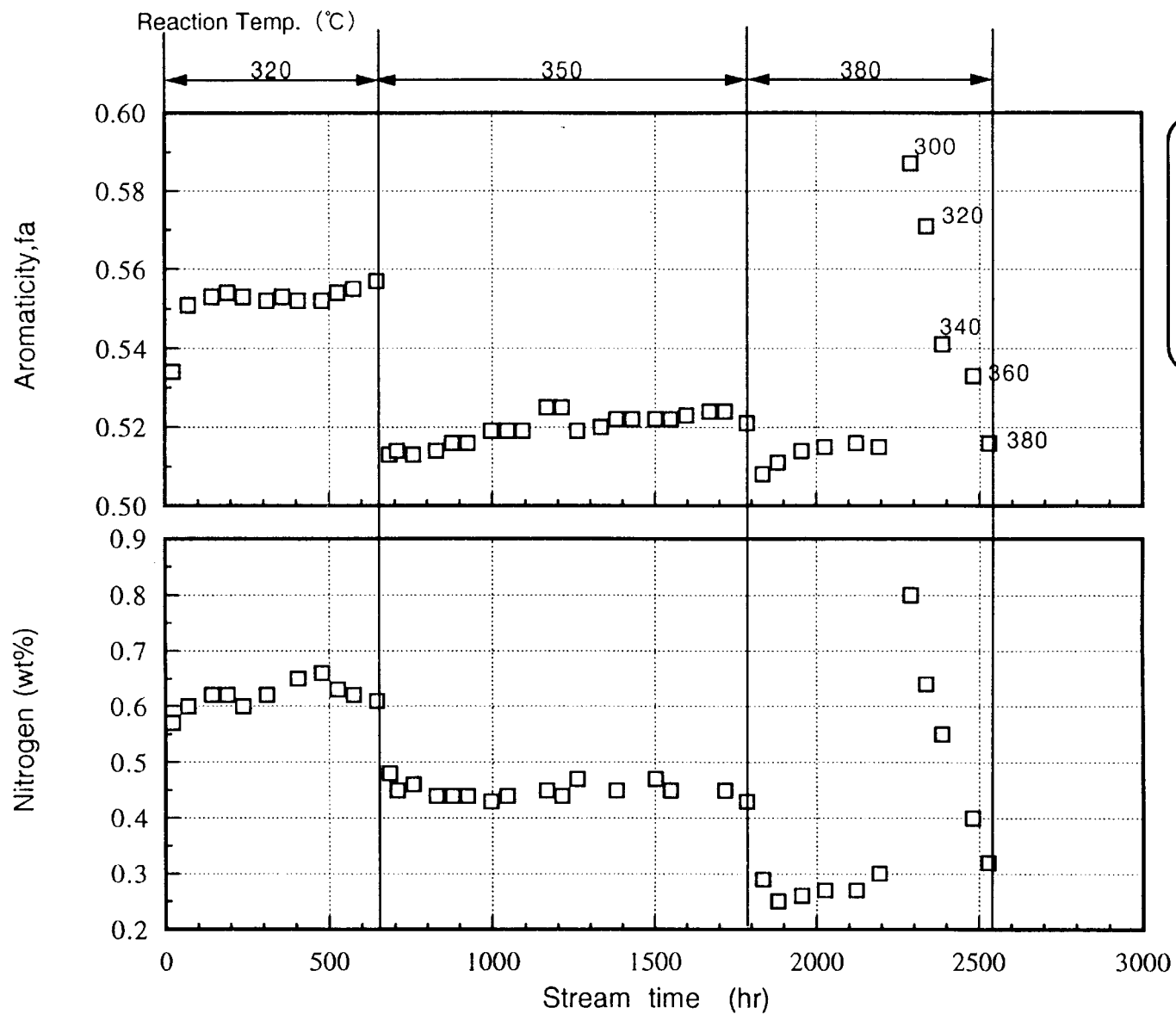
(2) Final evaluation of the developed catalysts

All results on newly developed hydrogenation and n-paraffin hydrocracking catalysts were synthetically reported from points of view of the preparation and the application.

Future task

As the supporting research for the 150 t/d Pilot Plant, the following studies are necessary.

1. Application studies of the developed hydrogenation catalyst in 1t/d PSU
(A stability test using Tanito Harum coal recycled solvent and application to various grades' coals)



Reaction condition

Feedstock : Tanito Harum coal
recycle solvent

Catalyst : CH-04-01

Pressure : 100 kg/cm²G

LHSV : 1 hr⁻¹

H₂/Oil ratio: 1000 NI/1

Fig.-1 Change of fa and nitrogen content of hydrotreated oil on long-run test

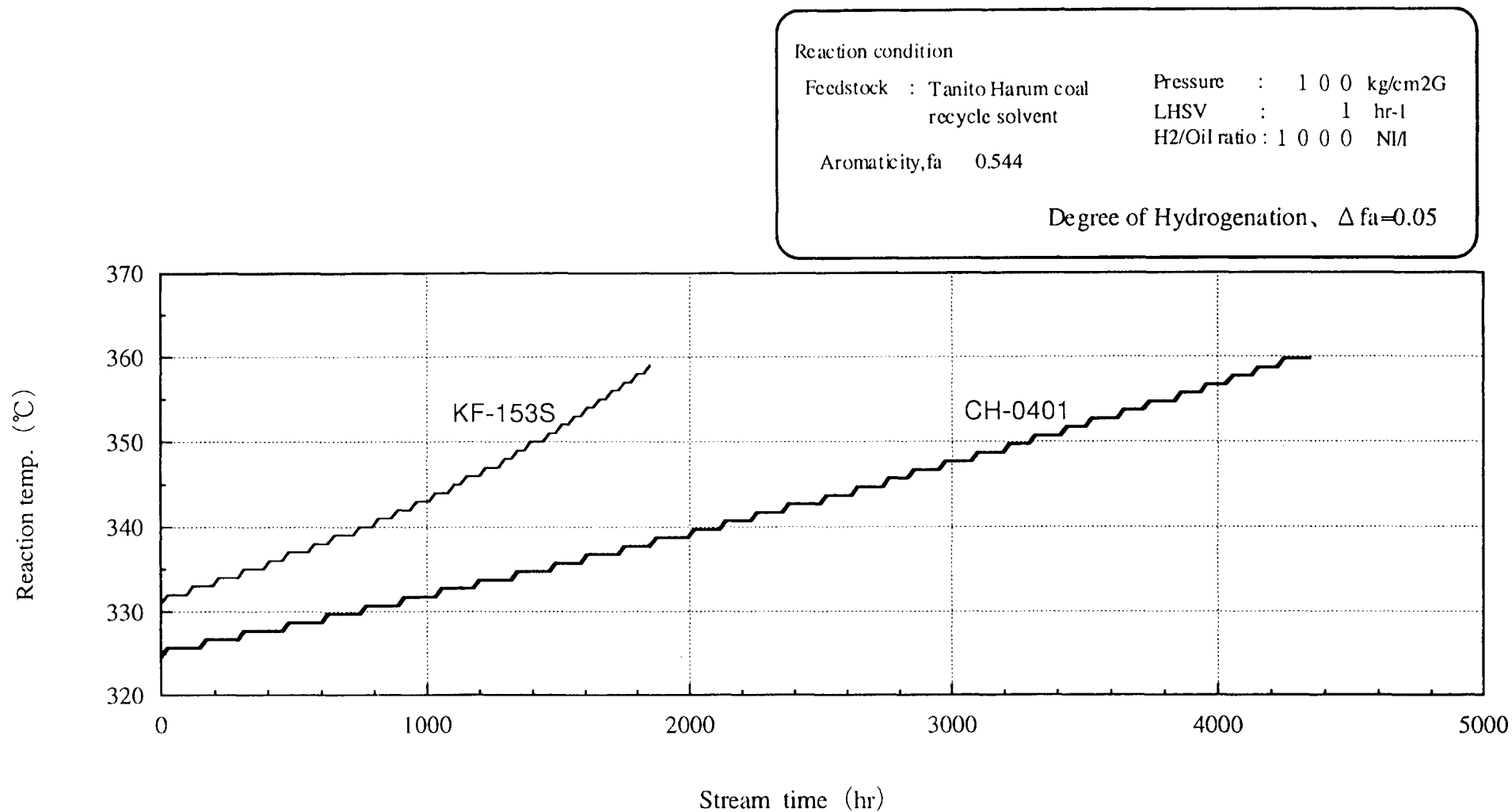


Fig.-2 Comparison of estimated temp.-time curve

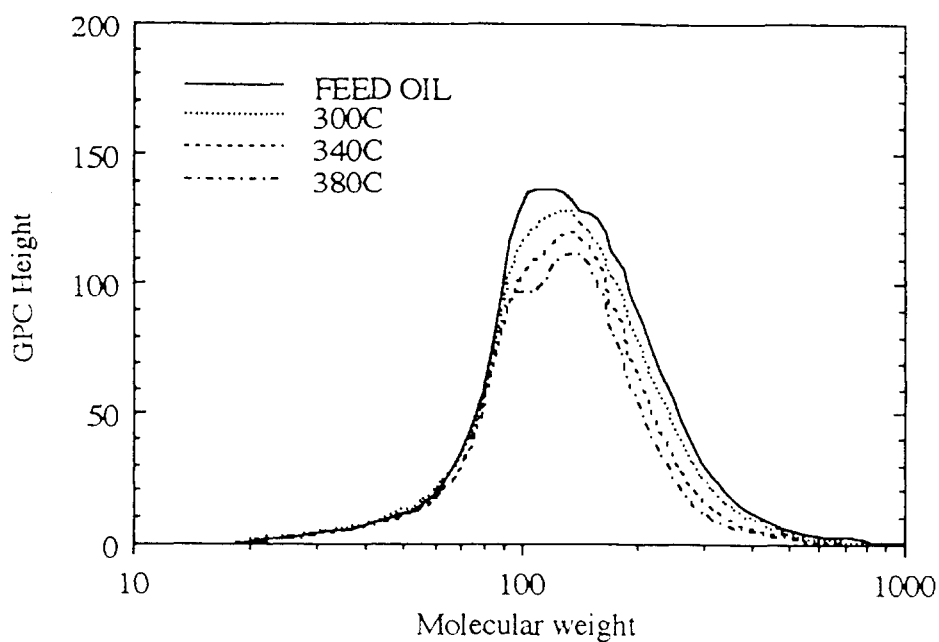


Fig.-3 Molecular weight distribution of Tanito Harum coal recycled solvent and the hydrotreated oils

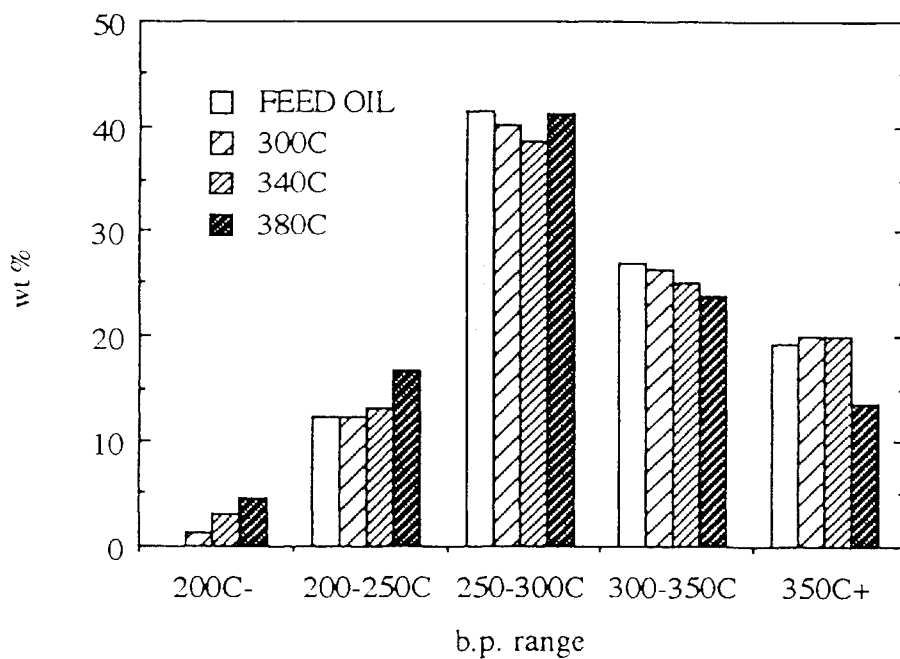


Fig.-4 Boiling range distribution of Tanito Harum coal recycled solvent and the hydrotreated oils

Table-1 Hydrocarbon in Tanito Harum coal recycled solvent and the hydrotreated oils

Samples	Feed oil	Experiment 2	Experiment 1	Experiment 5
Temp. (°C)	—	300	340	380
H ₂ consumption (Nl/l)	—	55	120	170
Hydrocarbon	content (wt%)			
Aromatics	43.50	38.34	27.87	27.48
Hydrogenated aromatics	25.83	31.08	35.11	36.54
Naphthene	0.21	0.47	2.54	4.33
n-Paraffin	12.91	12.34	13.60	12.22

* Feed oil : Tanito Harum coal recycled solvent (PSU Run0502B)

Development of Slurry Letdown Valves

Shigeru Ueda

Clean Coal Technology Center

New Energy and Industrial Technology Development Organization(NEDO)

Objectives

The goal of this program is to develop slurry letdown valves and slurry flow meters for the slurry service of commercial coal liquefaction plants. The program includes erosion tests in laboratories and field tests in the Process Supporting Unit (PSU).

Work Program

1. Experiment in laboratories

In order to study design factors of large scale slurry letdown valves, circulation erosion tests have been implemented using various plugs with different diameters, shapes, materials and also under various fluid and flow conditions. The fluid included a slurry of hot-oil with coal liquid residue from the PSU. And influence of a fluid pulsation on the accuracy of the flow measurement for a slurry flow meter, both venturi type and orifice type, were evaluated.

2. Field tests in the PSU

In the PSU plant, field tests were carried out on the letdown valve, and the slurry flow meter of venturi type to evaluate their performance and to assess their integrity.

Summary (1987-1994)

1. Up to FY 1993

Several kinds of slurry erosion tests and solid impingement test have been conducted to select the materials having good resistance to erosion among advanced materials such as cemented carbides, ceramics and coating materials. From those materials, ultra-fine particle cemented carbide with Ti(C,N) coating, B₄C and synthesized diamond have been selected as the candidate materials for the letdown valves. And the circulation erosion

tests for ultra-fine particle cemented carbide with Ti(C,N) coating, and synthesized diamond were implemented by using a model letdown valve under various flow conditions. Furthermore, the slurry flow meter of venturi type was tested to see the influence of erosion and fluid pulsation on the measurement.

Field tests of a slurry letdown valve, a venturi type slurry flow meter and a block valve have been carried out in the PSU. It was shown that the letdown valve could be operated for 1000 hrs continuously. And the slurry flow meter and the block valve were also operated with no trouble.

2. For FY 1994

(1) Experiment in laboratories

(a) Circulation erosion test

Circulation erosion tests has been carried out to study a relation between geometries or materials of plugs and seat-rings and life expectancy of letdown valves, and to investigate an influence of flow range or pressure on life expectancy of the valves. In the tests, the following conditions were applied.

flow rate : 300 liters/hr
fluid : hot-oil
temperature : 150 °C
solid : liquefaction residue from Tanito Harum coal, fine-crushed pyrite or mixture of above two, each of which ratio to fluid is 1 wt%
pressure : 3 MPa
plugs : SKD11, a sort of stainless steels

Figure 1,2 and 3 show the test results. From these results, it was shown that the difference of life of valves between in cases of residue slurry and pyrite slurry was not noticeable and it was also shown that the difference of life of valves between in cases of hot-oil fluid and non hot-oil fluid was not noticeable, either. Data from circulation erosion tests are reflected in setting field test conditions and determining design factors of large scale letdown valves.

(b) Fluid pulsation test on a slurry flow meter of venturi type

In order to investigate an influence of a fluid pulsation on the accuracy of the flow measurement, fluid pulsation tests on slurry flow

meters of both venturi type and orifice type were conducted. Figure 4 and 5 show results of these tests. It was shown that the venturi type had high response, while the orifice type did not show so high response.

(2) Field test in the PSU

Field tests on the letdown valves and the slurry flow meter were carried out at the PSU plant. Possibility of practical use of the letdown valve and the slurry flow meter were confirmed.

One of the results on the letdown valve is shown in Figure 6. Plug and orifice used in the letdown valve are made of ultra-fine particle cemented carbide with $Ti(C,N)$ coating and seat-ring is made of synthesized diamond. It is shown that the life of the valve has been getting longer year by year.

Further Tasks

The field tests will be continued to demonstrate the performance of the letdown valve and the slurry flow meter. And also the circulation erosion tests will be conducted to accumulate technical data regarding materials and geometry of these equipments and to determine design factors of large scale letdown valves.

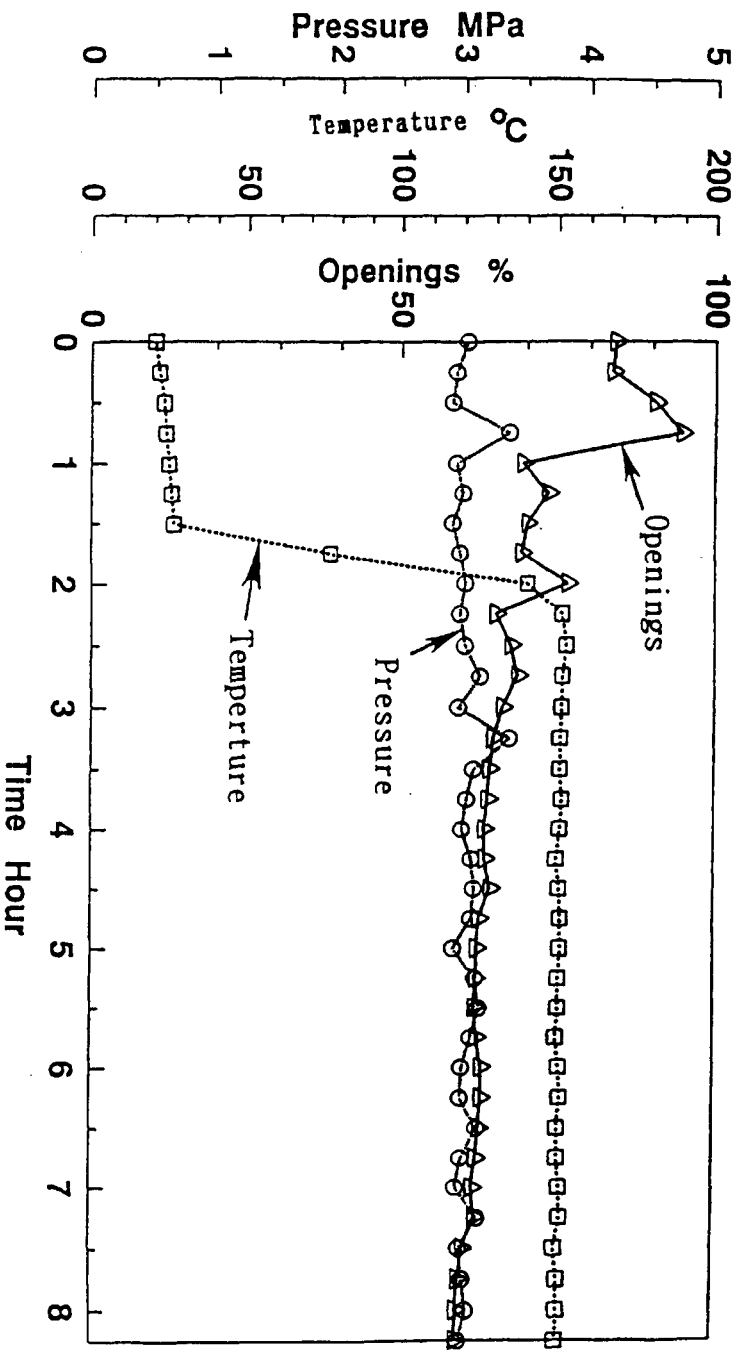


Fig. 1 Results of circulation erosion test
in case of fine crushed pyrite

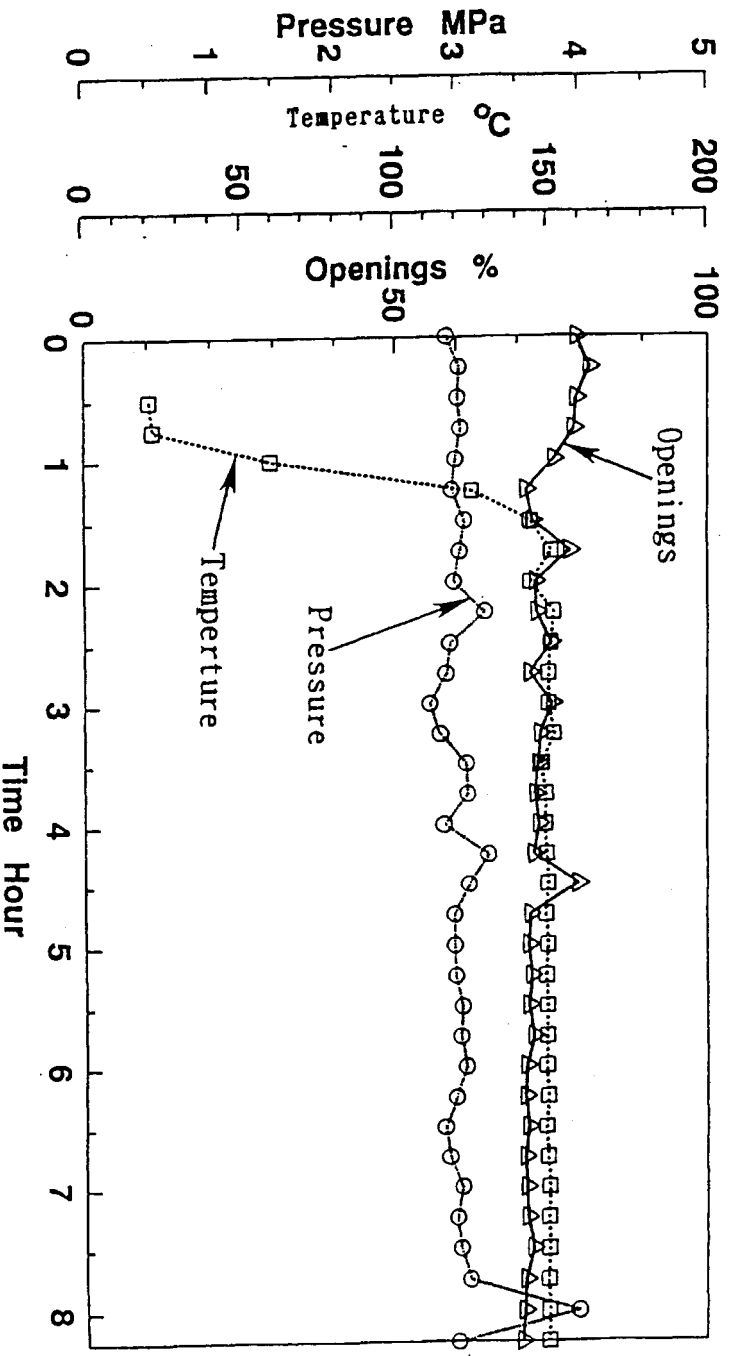


Fig. 2 Results of circulation erosion test
in case of residue from Tanito harum

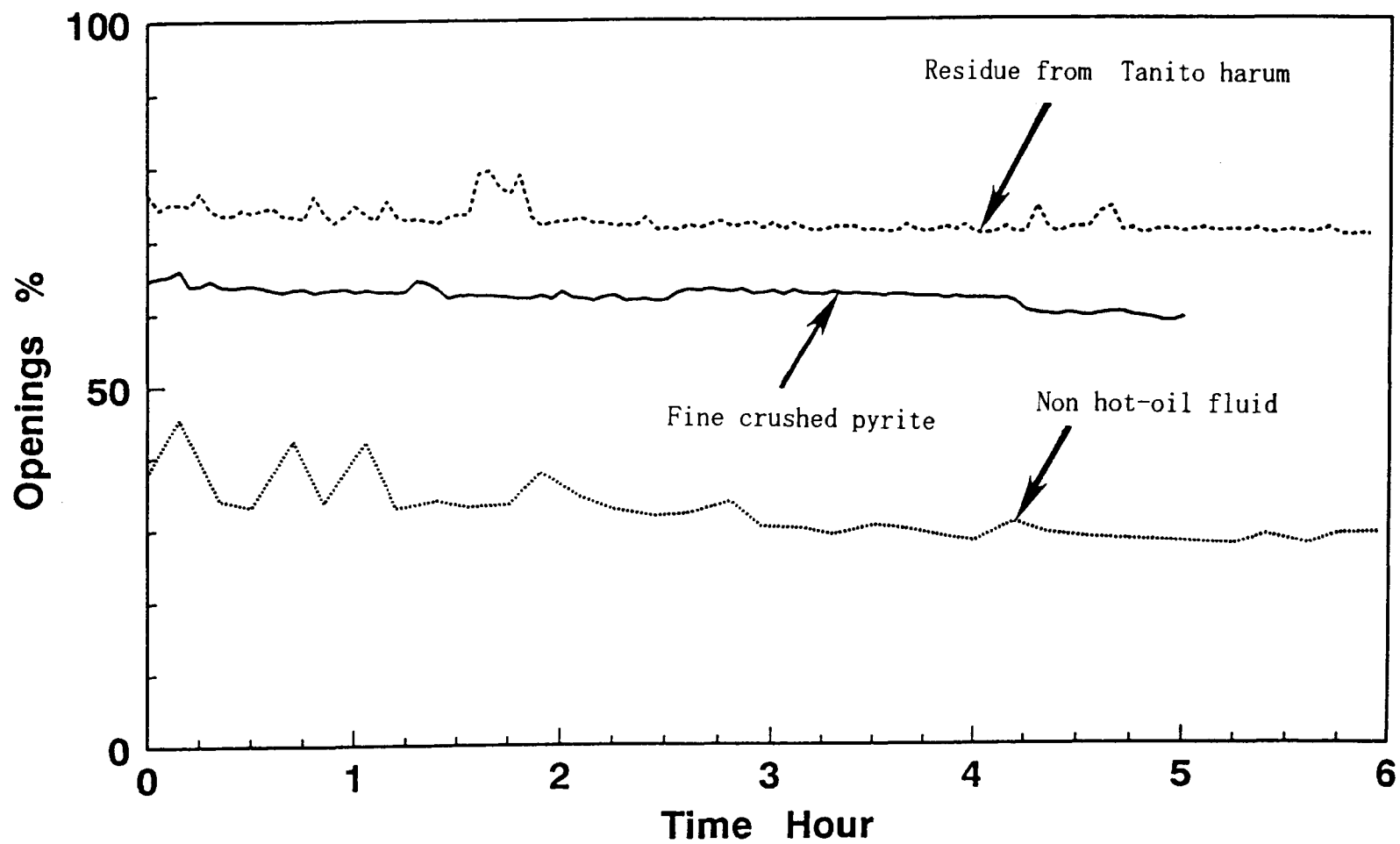


Fig.3 Results of circulation erosion test
in case of hot-oil and non hot-oil fluid

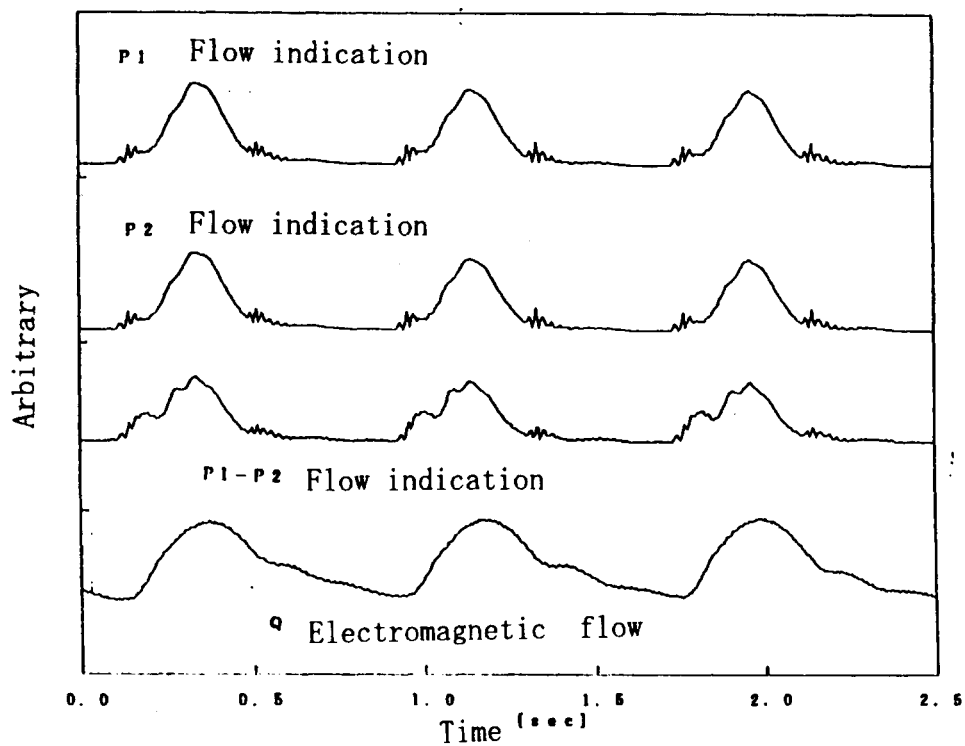


Fig.4 Results of fluid pulsation tests
in case of a venturi type of slurry flow meter

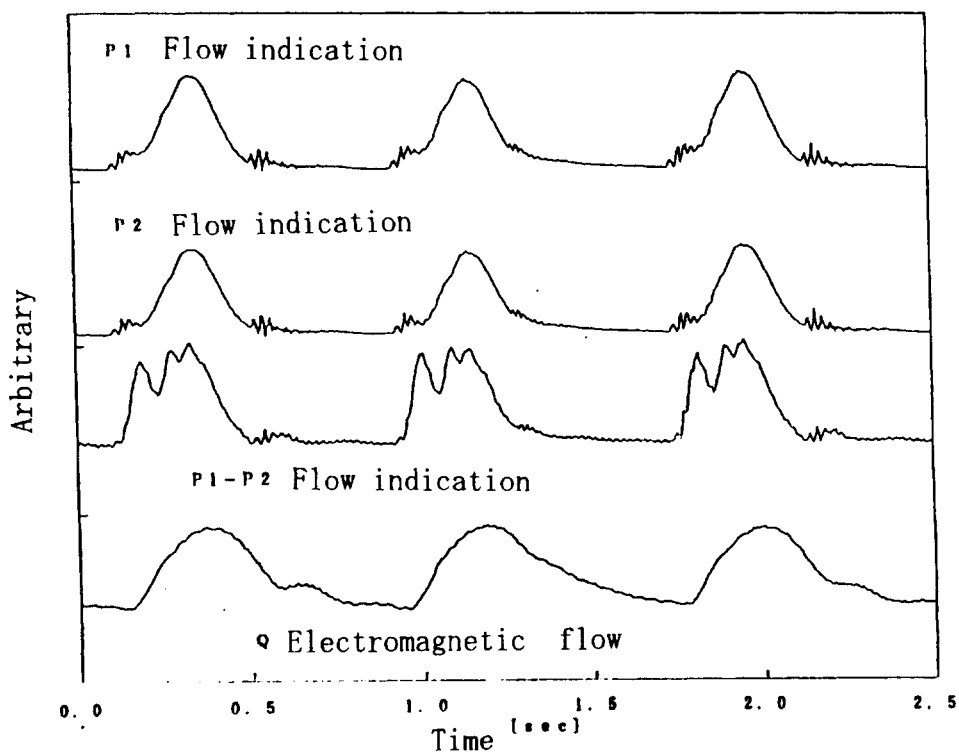
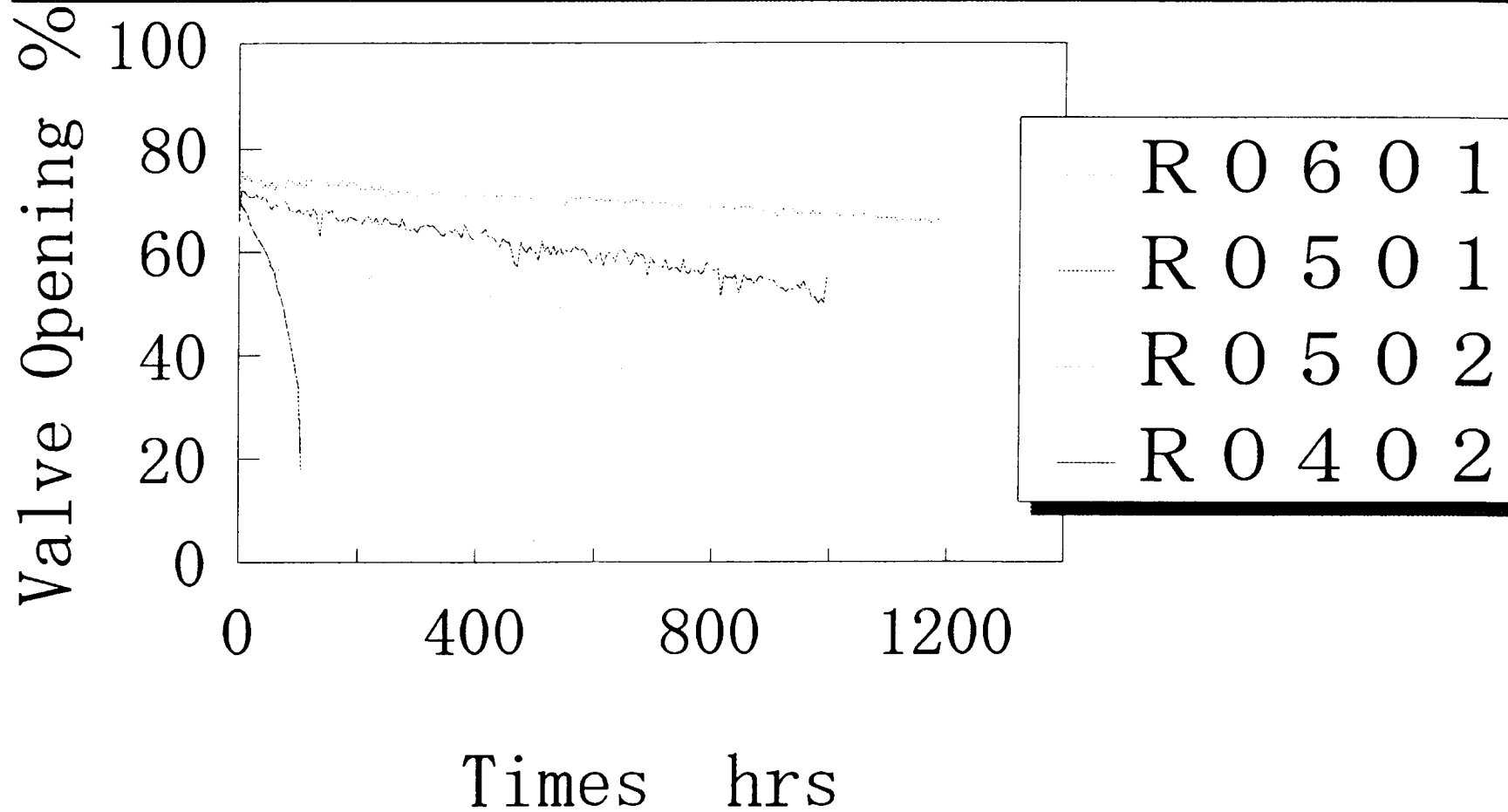


Fig.5 Results of fluid pulsation tests
in case of a orifice type of slurry flow meter

Fig. 6

Results of Field Tests



Study on the Synthetic Iron Sulfide Catalyst

Dr. Shigeru Ueda

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

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 in the research work on the NEDOL Pilot Plant with the capacity of 150 t/d, by developing a catalyst production method based on the dry process.
3. To supply the synthetic iron sulfide catalyst based on the dry process to PSU which will contribute to the research work.

Work Program

1. Catalyst Supply
To produce the synthetic iron sulfide catalyst to supply for PSU etc. using the small scale apparatus (10 kg/hr).
2. Modification and Maintenance
To install unreacted sulfur incinerator before the waste gas cooler in order to get longer continuous operation.
To inspect and repair the apparatus.
3. Coal Liquefaction Activity Test
To evaluate liquefaction activity of the synthetic iron sulfide catalyst, using autoclave.
4. Technical Evaluation
To evaluate engineering data obtained by the small scale apparatus operation and to conduct technical evaluation of the catalyst production method based on the dry process.
5. Detailed Work Program for the FY 1994.
6. Governmental Authorization for the modification and operation of the apparatus.

Summary (1991-1994)

1. Up to FY 1993

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, using 1000 ml autoclave.

2. For FY 1994

(1) Operations for catalyst supply

After modification work based on the result of the Test Runs in FY 1993, Run-9401 was conducted from 27th October to 6th November in 1994 in order to establish continuous operation and to supply the catalyst for PSU.

In order to obtain FeS_2 content higher than 90 wt%, following operating conditions were selected based on the result of the Test Runs in FY 1993.

- reaction temperature : 480 °C
- S/Fe molar ratio for reaction : more than 3.1
- gas linear velocity : 0.20 m/sec

The catalyst of total weight 2,030 kg was produced in 8 days operation at production rate of 11 kg/hr and 1,986 kg of these was used for Run-0602 of PSU.

Weighted average FeS_2 content of catalyst recovered from reactor over-flow and cyclone was 92 wt% higher than target of 90 wt%.

Analysis of the product is shown in Table-1.

Catalyst particles from over-flow and cyclone were broken to pieces of submicron size by five minutes ultra-sonic vibration in alcohol solution before particle size measurement.

The rate of operation was 96 % much higher than that of Run-9303. Reasons of operation interruption were powder plugging in the feed system and piping corrosion in the waste gas cooler.

Two days operations at production rate of 12 kg/hr and 13 kg/hr were conducted to check production capability of the apparatus. However, stability of the

feed system get somewhat worse and weighted average FeS_2 content was lowered to 91 wt% in the both case. To prevent catalyst particle sedimentation in PSU, the catalyst were blended and crushed by using a wet mill. Average particle size of crushed catalyst was 1.0 micron.

(2) Modification and Maintenance

In order to eliminate sulfur deposition in the waste gas cooler, a sulfur incinerator was installed, and the electric precipitator was modified to improve isolation.

(3) Coal liquefaction activity test

Before Run-0602 of PSU operation in FY 1994, coal liquefaction test for the Run-9401 product catalyst was made using 1000 ml autoclave. The result is shown in Table-2.

Oil yield of 68.3 wt% was the same as that of Run-9303 catalyst. Pulverized catalyst by ultra-sonic treatment for five minutes showed small improvement in oil yield. This suggests that the catalyst would be broken into submicron size under the condition of coal liquefaction reaction. Electron microscope observation shows that the product catalyst (secondary particle) consists of many submicrone size primary particles. Oil yield in case of 2 wt% catalyst addition was 67.0 wt% but that of 1 wt% addition was lowered to 60.8 wt%.

(4) Technical evaluation (a part of the work)

Main engineering data obtained by the operation in FY 1993 and FY 1994 are:

(a) Basic process

By using iron sulfate and sulfur as feedstock, process to produce FeS_2 with content of higher than 90 wt% were established. Oil yield obtained by PSU liquefaction operation using this product catalyst is 2~3 % higher than that of iron sulfide catalyst by the wet process.

(b) Operation conditions

Controlability of fluidized bed reactor temperature were confirmed. Desirable reaction temperature is 480~500 °C. Data as to relation between gas linear velocity and disperse quantity of fine products from fluidized bed were obtained.

(c) The reactor design

The reactor design able to form stable fluidized bed were confirmed. But it is necessary to install wall

heaters because of large heat capacity of castable insulation in this case of small reactor.

(d) Recovery of the product catalyst
Data on recovery of the catalyst particle from reactor overflow, cyclone and electrostatic precipitator were obtained.

(e) Incineration of unreacted sulfur
Incinerator to burn unreacted sulfur performed as designed. In addition, contents of technical evaluation work were studied.
In the future, the technical evaluation report on the synthetic iron sulfide catalyst by the dry process will be made including study for further development work on the production method.

(5) Work Program

Detailed work program for the FY 1994 was made.

(6) Governmental Authorization

Governmental authorization for the modification of the apparatus was made.

Future Tasks

In order to make more stable operations, modification of the small scale apparatus will be done ahead of operation to supply catalyst for PSU etc.

The technical evaluation work will be made succeedingly.

- Study of operability of the apparatus.
- Evaluation of coal liquefaction performance of the synthetic iron sulfide catalyst.
- Study for development work for the catalyst production method based on the dry process.

Table-1 Analysis of Synthetic Iron Sulfide Catalyst

		Overflow	Cyclone	Sum.	Analytical method
Product Quantity (kg)		1,117	869	1,986	
Composition (wt%)	FeS ₂	95 ~ 99	80 ~ 90	92	XRF
	Fe _{1-x} S	1 ~ 2	4 ~ 8	3	
	Fe ₃ O ₄	0 ~ 1	0 ~ 3	1	
	FeSO ₄	0 ~ 2	5 ~ 11	4	
Particle Size Distribution (?m)					Laser Refraction
D ₅₀		122 ~ 164	32 ~ 71	106	
D' ₅₀		0.22~0.42	0.22~0.77	0.49	

D' ₅₀ : Average particle size after 5 min. of ultrasonic vibration

Table-2 Coal Liquefaction Activity Test

Sample	(1) Run 9401	(2) →	(3) →	(4) →	Ref. Run 9303	Ref. by Wet Process
FeS ₂ Content (wt%)	94	→	→	→	93	85
D ₅₀ (?m)	116	→	→	→	124	8.1
D' ₅₀ (?m)	0.41	→	→	→	0.5	4.1
Ultrasonic Vibration	○	×	○	○	○	×
Catalyst Addition(wt%)	3	3	2	1	3	3
Yield (wt% daf coal)						
H ₂	5.6	5.0	5.1	4.5	4.8	4.5
H.C. Gas	10.1	9.1	8.9	10.3	11.5	11.0
In-org Gas	5.3	5.2	5.1	4.8	5.9	5.5
Oil	68.3	67.3	67.0	60.8	67.5	63.5
H ₂ O	8.1	8.6	8.6	7.9	6.1	7.2
n-hexane insoluble	10.9	11.2	12.0	13.9	11.0	11.6
Residue	2.9	3.6	3.5	6.8	2.8	5.7
Sp. gr. Oil (25°C)	1.0078	1.0082	1.0085	1.0154	1.0078	1.0140

Note: Oil=(Coal+H₂)-(Gas+H₂O+n-Hexane insoluble+Residue)

Coal selection studies for Chinese coal liquefaction
New Energy and Industrial Technology
Development Organization (NEDO)

Objectives

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

Work program

Liquefaction test of Chinese coals is done by using a small-sized continuous bench scale unit(BSU), installed at Central Coal Mining Research Institute (CCMRI) of China, and autoclave test and other basic studies are promoted

Summary(1980-1994)

1. Up To FY1993

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.

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, Meihoukou 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.

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. 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 baselines 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.

Concerning the up-grading of coal-derived oil, a specialist was dispatched to China, and the technical information was exchanged mutually.

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 derived from Hailaerh coal 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 recognised 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 analyses of Shengli lignite cases showed the superior conversion rate and yield of production oil. hydrogen consumption and asphalt yield are recognized to be small.

Also, the analyses 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 using 3 wt% FeS₂ catalyst and five cases of once-through operation using (3 wt% Fe₂O₃ + 0.8 wt% S) catalyst and one case of solvent circulation operation for Long kou coal were executed. and also, another each five cases of similar NEDOL mode operation using 3 wt% FeS₂ catalyst 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

2. For FY1994

Four 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 Helong Jing Yilan coal were executed. and also, another each two cases of similar NEDOL mode operation using the same condition of the above 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.

Future tasks

To collect data by conducting liquefaction tests of Chinese coals using the BSU.

To support the research of NEDOL/PP(150T/D) operation by conducting similar NEDOL mode operation using hydrogenated solvent.

To search for naturally existing mineral catalyst conducting its analysis and performance test.

To investigate separation method of ash and inert materials in coal.

4. BASIC RESEARCH FOR COAL LIQUEFACTION PROCESS DEVELOPMENT

(1) Refining Technology and Product Utilization

- ① Study on Upgrading Process Development Unit
- ② Development of Valuation on Coal Liquefaction Process Study on Upgrading Technology of Coal-derived Distillates
- ③ Development of New Catalysts for Upgrading Coal Derived Distillates
- ④ The Development of Technology for the Separation and the Utilization of Heteroatomic Compounds from Coal-derived Liquids
- ⑤ Study of Toxicological and Environmental Effects of Coal-derived Liquids

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

- ① Improvement Research of Coal Liquefaction Process
- ② Research on Novel Concepts for Coal Liquefaction Technology development
 - (a) Advanced Technology for Coal Liquefaction
 - (b) A Reduction of Catalyst Amount in Coal Liquefaction System
 - (c) Coal Liquefaction under Advanced Conditions
- ③ Survey and Information Exchange with Overseas Organization
 - (a) Applicability Study of Coal Liquefaction Technology
 - (b) Preliminary Survey on the Mongolian Coal

Study on upgrading process development unit
Sigeru Ueda
Director General
Clean Coal Technology Center (CCTC)
New Energy and Industrial Technology Development
Organization (NEDO)

Objectives

Liquefaction of coal is a technique for converting coal into liquid fuel. The liquefaction process produces a relatively clean energy source and has advanced the utilization of coal. In order to maintain stable domestic energy supplies and promote international technical cooperation, it is vitally important for Japan to develop coal liquefaction techniques and engage in technical R&D related to the practical use of these techniques, as part of an overall strategy for maintaining a steady supply of fuel oil.

Studies on the applications of liquefied coal products and the associated refining techniques are part of an overall program to develop liquefaction techniques. In terms of quality, liquefied coal oil is unable to compete with petroleum products on the Japanese market due to a variety of drawbacks: it contains sulfur, nitrogen, oxygen, hetero atoms, as well as polycyclic aromatic compounds and gummy matter. Its color is poor and it can deteriorate during storage.

Research into the applications and the refining of liquefied coal oil products is vital to eliminating the problems associated with the introduction of liquefied coal oil into the existing petroleum products distribution system.

Basic studies have already indicated that methods such as hydrogenation refining have the potential to address quality-related problems associated with liquefied coal oil products. Such research is now in the demonstration stage, which means that the quality of upgraded coal oils can now be improved by commercial equipment. To achieve this end, samples of upgraded coal oil are required so that their commercial applicability can be assessed. Upgrading research on a pilot scale is required to collect the necessary engineering data.

Our R&D objectives are as follows:

- 1 Demonstration of liquefied coal oil refining and reforming technology
 - Sample production of practical performance evaluation
 - Collection of engineering data
 - Demonstration of continuously stable operation
- 2 Demonstration of practical use of liquefied coal oil products
 - Practical performance test by engine test etc.
 - Recognition of users and automobile manufacturers
- 3 Demonstration of satisfying environmental regulations
 - Automobile exhaust gas regulation
 - Products quality improvement (aromatic compounds reduction etc.)

Work program

The objectives of our R&D program during the current fiscal year are to revise the basic design of upgrading plants and conduct detailed design and long-term storage tests on liquefied coal oil samples.

1. Plant design

- 1) Revise basic design of the PDU (Process Development Unit)
 - process design
 - layout design
 - data sheets (detailed specifications and skeleton drawings for each piece of equipment etc.)
 - 2) Conduct detailed design of each process of the PDU
 - foundation design
 - equipment design
 - instrument design
 - electrical facilities design
 - others (documents, drawings etc.)
 - 3) Preparatory work for government permission
2. Long-term storage tests on liquefied coal-derived oil samples
Continue the previous year's tests

Summary (1991-1994)

Basic research on the upgrading process of liquefied coal oil since the fiscal year in 1983 has indicated that methods such as hydrogenation refining have the potential to address the problems associated with product quality. Based on the results of this research, we conducted further research into the PDU plant in the fiscal year in 1991 to investigate the applications of liquefied coal oil products and refining technology.

1. Up to 1993

1) Fiscal 1991

- Basic design of the pilot plant
Based on basic specifications of the plant, we compiled basic flow and operation procedure and determined the basic requirements for the design and the construction of the plant, including the overall layout of facilities, a utilities plan and the relevant laws and regulations.
- Detailed design
Based on the basic design, we drew up the basic specifications and design for the foundation, equipment, piping, instrumentation and electrical and other installations.
- Long-term storage tests
We proposed test methods and other details concerning the long-term storage of liquefied coal-derived oil. We stored the samples then analyzed the initial conditions under storage.

2) Fiscal 1992

- Detailed design
We established basic specifications for the instrumentation systems and DCS, as an emergency instrumentation systems.
- Long-term storage tests
We investigated the chronological changes in the samples stored in nitrogen-sealed tanks. Except for a slight increase in sludge, deterioration in liquefied coal oil stored for a period of one year was negligible.

- Examinations and tests

We examined the treatment of wastewater discharged in the liquefied coal oil upgrading process. Our results showed that combustion, adsorption and electrolysis were all suitable methods for wastewater treatment containing phenol compounds at the PDU plant.

We also examined corrosion of equipment materials by document investigation and complied with material specifications for major equipment.

3) Fiscal 1993

- Plant design

We established basic specifications for the control function related to the software design installed in the instrumentation system and designed graphic panels for the CRT and engineering data analysis systems.

- Long-term storage tests

We reduced the items to be checked for stability to eight evaluation points such as density, bromine number, viscosity, color, gum, total acid value, sludge and SS (suspended solid). We tested these points periodically and evaluated their stability.

- Examinations and tests

We imagined three cases of upgrading process configuration and estimated construction and operation costs for each case. According to this result we selected a process configuration applied to the PDU plant and established the basis of the future research plan. We also experimented with three methods of wastewater such as combustion, active carbon adsorption and electrolysis methods and selected the combustion method as the optimum facility for the PDU plant.

2. For fiscal 1994

1) Revision of PDU basic design (refer to figure one)

We decided on the PDU process configuration which was a Distillation, NO.1 Hydrotreating, NO.2 Hydrotreating, Catalytic reforming, Hydrogen manufacturing, with Off-site and Utilities units. We revised the basic design of each process based on the change of the specified feed coal and the effective use of each unit. We revised the three units of NO.1 Hydrotreating, NO.2 Hydrotreating and Catalytic reforming to enable a change in the flow between these units each time a naphtha feed and a diesel oil feed would be used commonly.

2) Revision of detailed design

Based on the new specifications from the revised basic design, we conducted detailed design of the foundation, equipment, piping, instrumentation and electrical facilities.

3) Long-term storage tests on liquefied coal oil samples were continued from the previous year's test.

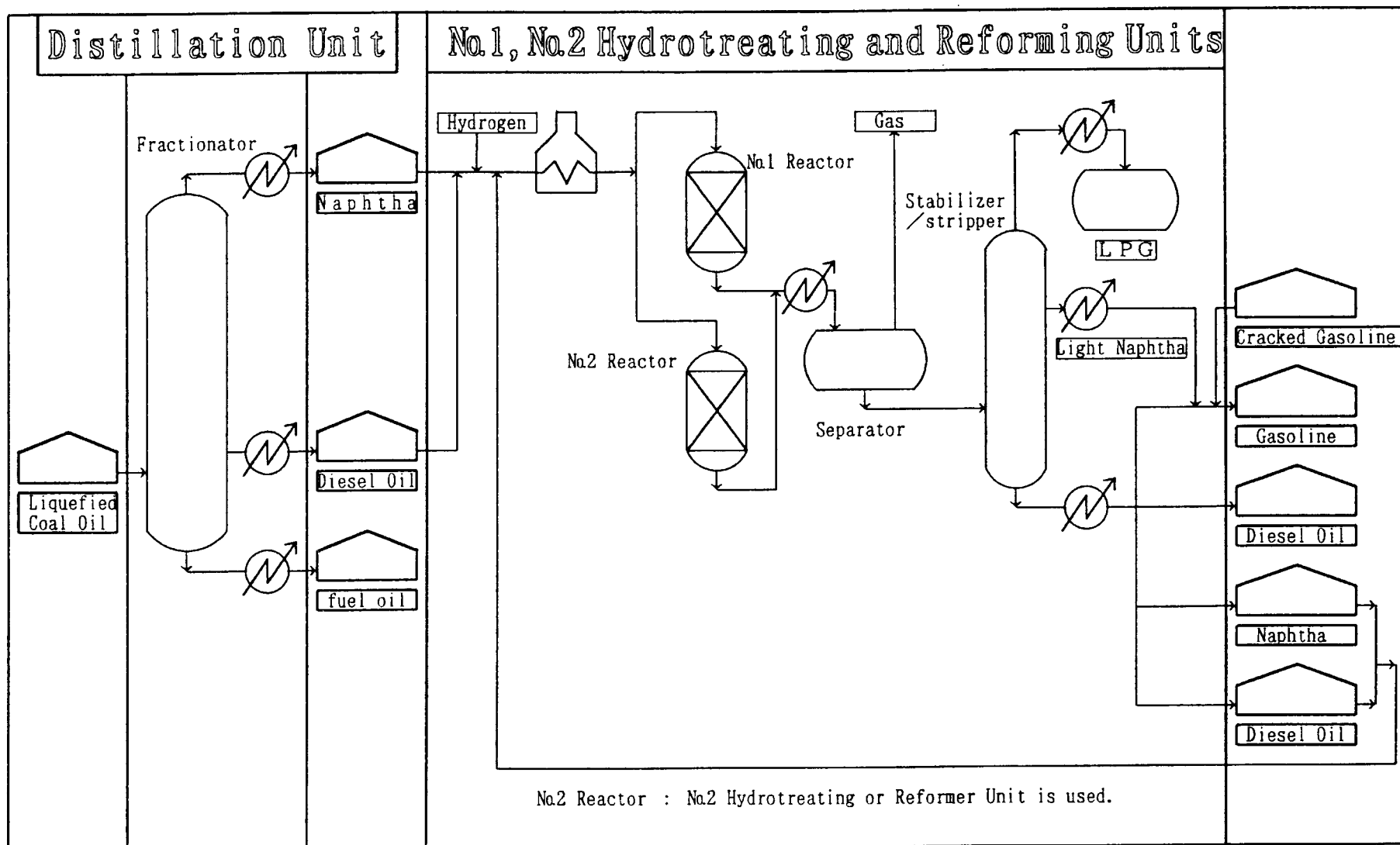
Future tasks

Regarding the construction of the plant, the necessary procedure for government permission is required and detailed drawings of each piece of equipment are finally decided with equipment manufacturers.

Long-term storage tests on liquefied coal-derived oil samples started in 1991 are ongoing.

Figure 1

Liquefied Coal Oil Upgrading Process Flow Sheet (PDU)



DEVELOPMENT OF VALUATION ON COAL LIQUEFACTION PROCESS
STUDY ON UPGRADING TECHNOLOGY OF COAL-DERIVED DISTILLATES

Shigeru Ueda

Director General

Clean Coal Technology Center (CCTC),

New Energy and Industrial Technology Development Organization (NEDO)

Objectives

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

Work Program

(1)Hydrotreating of coal-derived naphtha and middle distillate

Coal-derived liquid was derived from Indonesian coal with 1t/d Process Support Unit (PSU) of NEDOL process.

(a)Study of naphtha fraction

Optimum hydrotreating conditions to remove nitrogen content of less than 1ppm

(b)Study of middle distillate

-Determining heterocyclic compounds and hydrocarbons in middle distillate

-Evaluating hydrodenitrogenation performance

-Influence of hydrogen partial pressure on hydrogenation and hydrocracking of aromatic compounds

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

(a)Study on upgrading technology

The hydrotreating experiment on the second catalyst bed using a Tanitoharum coal-derived liquids was carried out at a micro-reactor.

(b)Development of utilization technology

Accelerated storage stability tests were performed for coal-derived liquids.

Summary (1983-1994)

1. Up to FY 1993

(1)Upgrading of coal-derived naphtha

Upgrading study from 1983 to 1987 as Phase 1 was conducted by construction of micro and bench scale reactors, screening commercially available HDS and reforming catalysts, and preparation of fuels and evaluation of end-use performance (combustion test in engine and heater). At the end of phase 1 study, feasibility study for introducing coal-derived liquid into Japanese fuel market, and co-refining of coal liquid with petroleum resulted in the most acceptable case in several configurations examined in the study.

From FY 1989 as phase 2 study, Hydrotreating to remove nitrogen- and oxygen-containing compounds, which is one of the important subject to produce petroleum alternative fuels, had been examined to reduce severity of operating conditions and hydrogen consumption. The investigations had been focused on clarifying the effect of coal liquid properties on the hydrodenitrogenation (HDN) in neat treating and co-refining.

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

The study of hydrotreatment was carried out for kerosene and gas

oil fractions derived from liquefied Wandoan, Illinois, Wyoming Battleriver coal and Yallourn brown coal, and raffinate oils prepared by extracting with methanol/water or alkali. Also the improvement of color, Cetane number, low temperature fluidability, and thermal stability of hydrotreated coal liquid and combustibility in gas turbine and diesel engine.

(3)Hydrocracking of middle distillates

In 1989, Wandoan gas oil and brown coal middle distillate were hydrocracked.

In 1990, the life tests of the first section hydrotreating catalyst which had been used for the hydrocracking experiments since 1987 were carried out with brown coal middle distillate.

In 1991, the life tests of the second section hydrocracking catalyst which had been used for those experiments since 1987 were carried out with the hydrotreated brown coal-derived middle distillate obtained by the life test of the hydrotreating catalyst in 1990.

In 1992, the performance of the hydrocracking catalyst developed by NEDO for the middle distillate of coal liquid was evaluated to compare with that of the commercial hydrocracking catalyst which had been used for the hydrocracking experiments since 1987.

2. For to FY 1994

(1)Hydrotreating of coal-derived naphtha and middle distillate.

Coal-derived liquid was derived from Indonesian coal with 1 t/d Process Support Unit (PSU) of NEDOL process.

(a)Study of naphtha fraction

Table 1-1 shows the properties of feed stock and hydrotreated coal-derived naphtha. Indonesian coal-derived naphtha contains higher nitrogen content than any other naphtha derived from NEDOL process. Therefore hydrotreating conditions to remove nitrogen content to less than 1 ppm were also the severest conditions in the past as shown in Table 1-1.

(b)Study of middle distillate

Table 1-2 shows the composition of Indonesian coal middle distillate comparing petroleum straight-run gas oil fraction. Comparing petroleum gas oil, n-paraffin and sulfur contents are low, and cyclic hydrocarbons and nitrogen content are high in coal middle distillate. Aniline, indole, quinoline and carbazole type nitrogen compounds are contained. Particularly, total nitrogen content was extremely high in Indonesian middle distillate as corresponding naphtha fraction.

Fig. 1-1 shows the gas chromatograph of nitrogen compounds of feed stock and hydrotreated middle distillate. Most of nitrogen compounds in hydrotreated middle distillate were aniline type nitrogen compounds. This indicates that nitrogen compounds were removed via hydrotreated intermediates of alkyl aniline to give ammonia.

Table 1-3 shows the influence of hydrogen pressure on hydrogenation and hydrocracking of Indonesian middle distillate. Although hydrogenation was improved with increasing hydrogen pressure, and hydrocracking hardly took place even if the hydrogen pressure reached up to 150kg/cm². Therefore Cetane numbers of coal middle distillate could not be improved to the specification of diesel fuel, when hydrotreatments are carried out with single stage using alumina based hydrotreating catalyst. Consequently we concluded that two stage hydrotreatment were necessary to improve Cetane number

of middle distillate.

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

(a) Study on upgrading technology

1) Hydrotreatment on the first catalyst bed

We studied the effect of hydrotreating conditions on the first catalyst bed on denitrogenation and deoxygenation reactions using a commercial catalyst for kerosene and gas oil fractions derived from liquefied Tanitoharum coal. The results showed that the liquefied Tanitoharum coal has twice nitrogen content compared with the liquefied Wyoming, Illinois, and Wandoan coal (Table 2-1). Hetero compounds were not easier to remove under mild hydrotreating condition nearly equal to that of indirect desulfurization in petroleum refinery, for example, denitrogenation rate was 50~73%, deoxygenation rate 75~93%. Under more severe hydrotreating condition than that of indirect desulfurization, almost of nitrogen compounds were removed, but oxygen compounds were not easier to remove.

The study of the activities of the new Ni-W catalyst (UGC-424) developed by NEDO and commercial Ni-Mo catalysts (H01 and H02) was also performed for the mixture of kerosene and gas oil fractions derived from the liquefied Tanitoharum coal. The results showed that the activity of Ni-W catalyst was most highest among the three catalysts (Fig. 2-1).

2) Hydrotreatment on the second catalyst bed

The hydrotreating experiment on the second catalyst bed was performed using the mixture of petroleum gas oil and the refined Tanitoharum coal oil, which was the mixture of kerosene and gas oil fractions refined with Ni-W catalyst on the first catalyst bed. The results showed that the maximum content of coal-derived liquid to petroleum to meet JIS standard was about 30 volume percent.

3) Evaluation of newly developed catalyst

The 1,400 hours test of the new Ni-W catalyst developed by NEDO last year for hydrotreating of coal-derived kerosene and gas oil fractions was performed. The Denitrogenation and Deoxygenation activities of new catalyst were equal to those of commercial Ni-Mo catalyst. These activities were less than those of new catalyst developed the year before last.

(b) Development of utilization technology.

Hydrotreating experiments of the mixture of kerosene and gas oil fractions derived from Tanitoharum coal oil were carried out in order to clarify the relationship between depth of hydrotreating and sludge formation. The sludge formation of refined oils was measured by the accelerated storage stability test (ASTM 4625-86). It was clear that the deep refined oil showed less sludge and sludge formation was decreased, as the hydrotreating depth higher and remarkably controlled by mild hydrotreating (denitrogenation rate: about 40%) (Fig. 2-2).

Future Tasks

(1) Upgrading of coal-derived naphtha

Optimum conditions and process configuration for hydrodenitrogenation will be studied to construct costly less hydrotreating process. Hydrotreated sample will be prepared to produce 2nd stage feed stocks, nitrogen content of less than 5ppm. Screening of catalysts for 2nd stage will also be carried out.

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

The evaluation of catalyst life on the first catalyst bed in two

step hydrotreating method will be carried out. And feed oil used to hydrotreating tests on the second catalyst bed will be prepared. The research of catalyst on the second catalyst bed and the study of co-processing conditions will be also carried out.

Table 1-1 Properties of feed stock and hydrotreated naphtha fractions derived Indonesian coal

		Feed	Hydrotreated
Process Data			
Temp., °C			319.8
Press., kg/cm ²			80.0
LHSV, 1/hr			0.485
WHSV, 1/hr			0.457
H ₂ /OIL, Nm ³ /kl			722.0
Gas Yield, wt%			9.24
H ₂ , wt%			7.60
C ₁ , wt%			0.00
C ₂ , wt%			0.11
C ₃ , wt%			0.40
C ₄ , wt%			0.30
C ₅ , wt%			0.83
H ₂ S, wt%			0.00
Product Yield, wt%			94.18
M/B, %			95.4
Analysis Data			
Sp. Gr., 15/4°C		0.7789	0.7668
Analysis	C, wt%	83.9	-
	H, wt%	13.4	-
	N, ppm	3410	1
	S, ppm	560	1
	O, wt%	2.2	0.2
Composition	Sat., vol%	84.5	95.0
	Ole., vol%	5.4	0.0
	Ar., vol%	10.1	5.0
Distillation, °C			
	IBP	30	55
	5%	59	75
	10%	73	82
	20%	86	91
	30%	101	102
	40%	114	115
	50%	132	127
	60%	144	138
	70%	157	152
	80%	168	161
	90%	174	172
	95%	179	177
	97%	182	180
	EP	201	188

Table 1-2 Properties of petroleum gas oil and Indonesian coal middle distillate

		Petroleum SR-LGO	Coal-derived Middle Distillate
Hydrocarbon Analysis			
n-Paraffins	wt%	40.0	11.3
Mono-cyclic	wt%	2.7	7.3
Indenes	wt%	1.1	2.7
Naphthalenes	wt%	4.7	27.4
Biphenyls	wt%	0.0	0.7
Phenathrenes	wt%	0.0	1.0
Sulfur Analysis			
Total S, S-ppm		8300	200
DBT	S-ppm	266	3
4-MDBT	S-ppm	357	3
MDBT	S-ppm	273	0
MDBT	S-ppm	179	0
4,6-DMDBT	S-ppm	166	1
DMDBT	S-ppm	330	0
DMDBT	S-ppm	249	0
Nitrogen Analysis			
Total N, N-ppm		81	7700
Aniline	N-ppm	-	22
Indole	N-ppm	-	831
Anilines & Indoles	N-ppm	-	-
Quinoline	N-ppm	-	181
H-Quinoline	N-ppm	-	337
Carbazole	N-ppm	-	138
Carbazoles	N-ppm	-	138

Table 1-3 Influence of hydrogen pressure on hydrogenation and hydrocracking of coal-derived middle distillate

Type of Compounds	Feed	P=50k	P=80k	P=100k	P=120k	P=150k
C ₁₁ -C ₂₁ -Paraffins	11.2	11.5	11.2	10.7	11.1	10.7
-C ₄ -Cyclohexanes	0.0	8.9	10.5	11.6	12.1	12.6
-C ₃ -Benzenes	0.2	2.1	1.3	0.6	0.5	0.3
-C ₃ -Phenols	7.1	0.0	0.0	0.0	0.0	0.0
1-Rings	7.3	11.0	11.8	12.2	12.6	12.9
-C ₂ -8H-Indenes	0.0	2.4	3.6	4.0	4.1	4.0
-C ₂ -Indanes	2.7	2.5	1.1	0.7	0.6	0.4
Indenes	2.7	4.9	4.7	4.7	4.7	4.4
-C ₄ -Decalines	0.0	8.0	19.2	21.0	25.7	26.2
-C ₄ -Tetralines	15.2	21.0	8.8	5.8	2.4	1.8
-C ₄ -Naphthalenes	12.3	0.0	0.0	0.0	0.0	0.0
2-Rings	27.5	29.0	28.0	26.8	28.1	28.0
14H-Phenanthrene	0.0	1.2	1.3	1.3	1.5	1.4
8H-Phenanthrene	0.0	0.3	0.1	0.1	0.0	0.0
4H-Phenanthrene	0.3	0.4	0.1	0.0	0.0	0.0
Phenanthrene	0.7	0.1	0.0	0.0	0.0	0.0
3-Rings	1.0	2.0	1.5	1.4	1.5	1.4

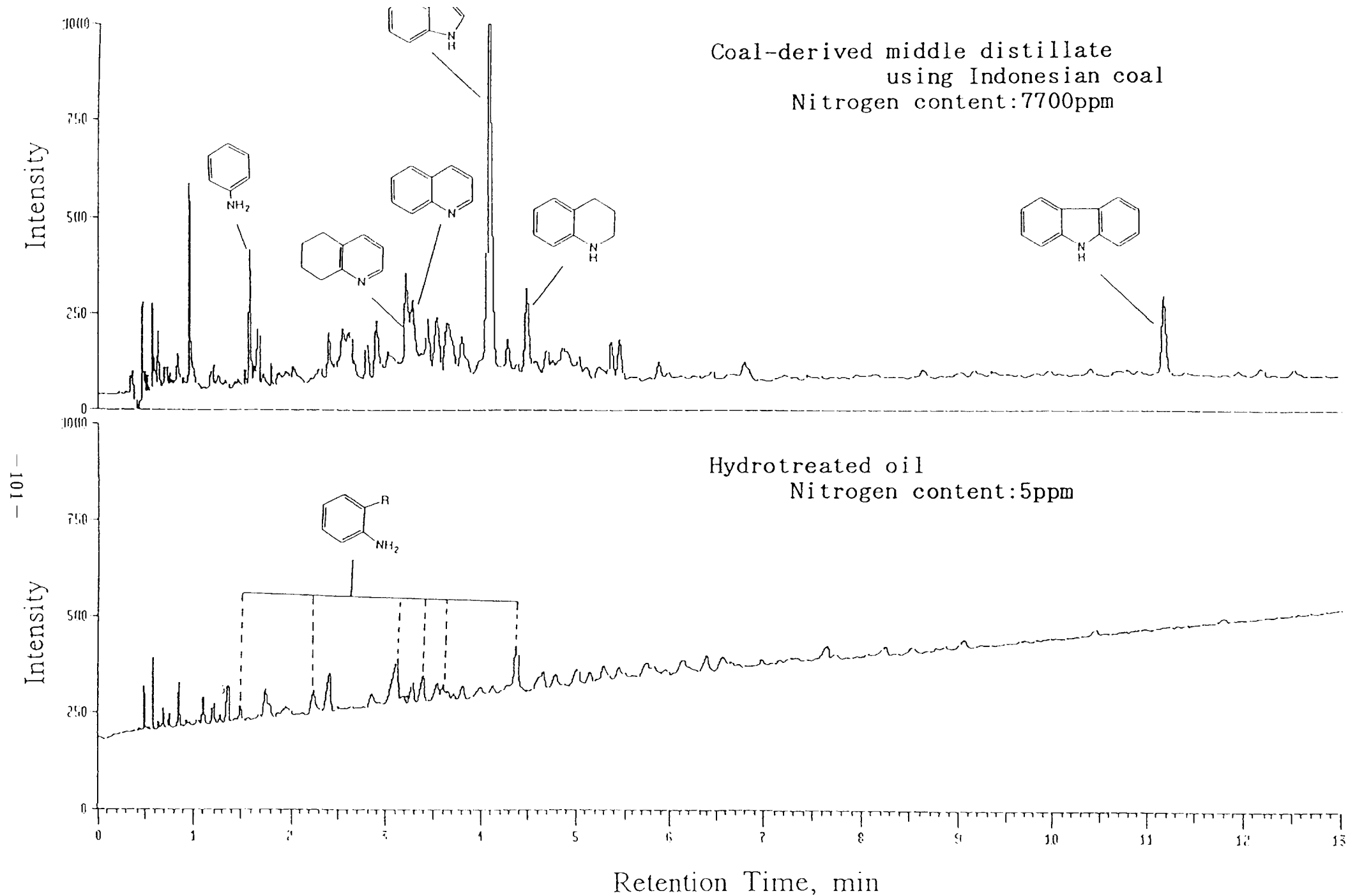


Fig. 1-1 Nitrogen compounds in feed stock and hydrotreated

Table 2-1 Propertice of Tanitoharum coal-derived liquids

	Kerosene	Diesel	Mixture of Kerosene and Diesel
Specific Gravity (15/4°C)	0.9377	0.9780	0.9542
Elementary Analysis			
C (wt%)	86.5	88.7	87.4
H (wt%)	10.4	9.7	10.1
N (wt ppm)	8,100	6,500	7,500
S (wt%)	0.01	0.01	0.01
O (wt%)	3.0	1.3	2.0

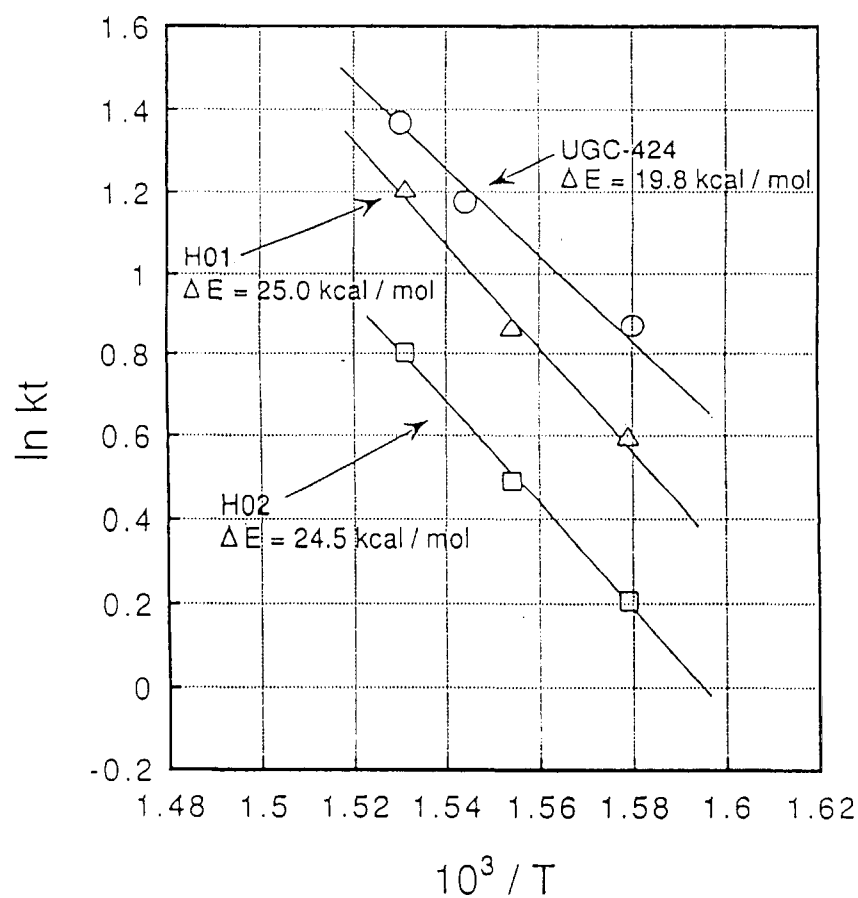


Fig.2-1 Relationship between denitrogenation reaction rate and reaction temperature

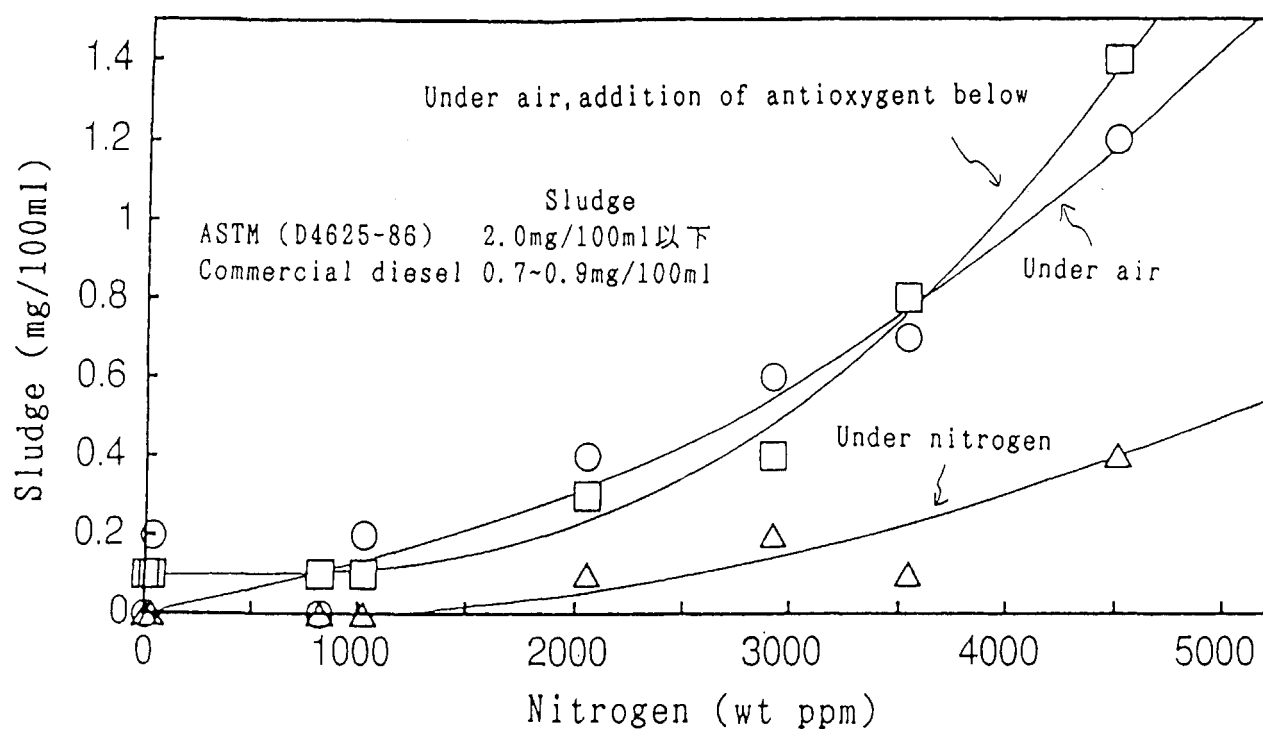


Fig.2-2 Relationship between sludge formation and nitrogen concentration in hydrotreated oil at an accelerated storage stability test

Development of New Catalysts for Upgrading Coal Derived Distillates

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New Energy and Industrial Technology
Development Organization (NEDO)

Objectives

We develop new catalysts suitable for refining coal derived distillates (naphtha, kerosene and gas oil fractions) which are produced from the coal liquefaction process now under research in Japan.

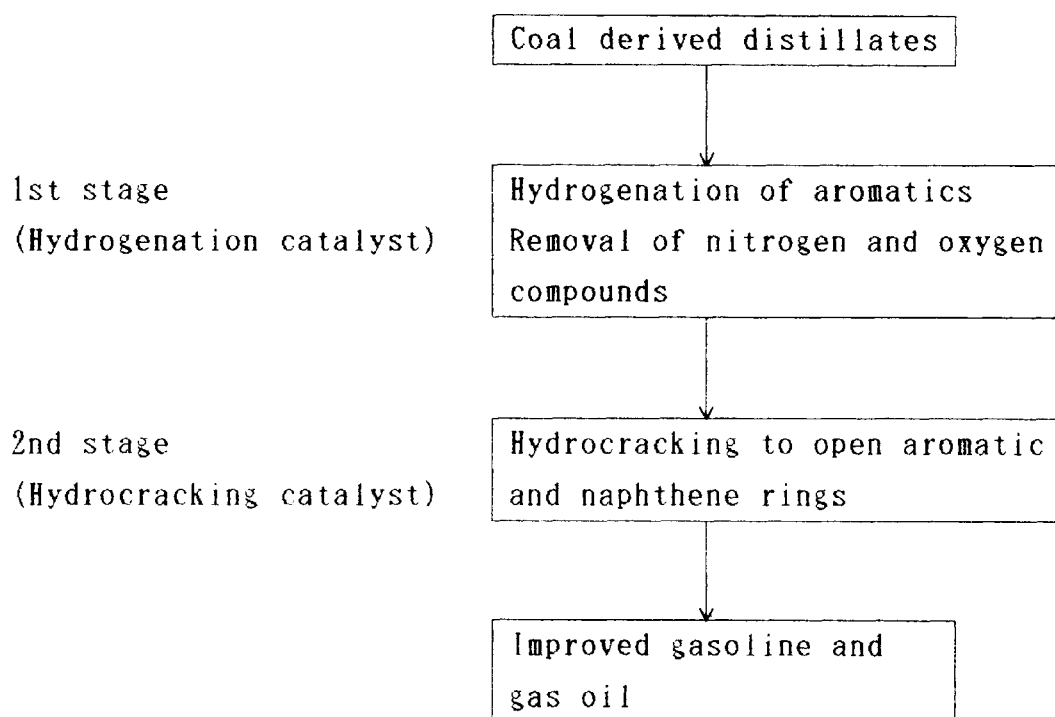
Work Program

1. Study for practical use of developed catalysts

We study large scale production test of developed catalyst and the effects of operating conditions in a upgrading process development unit (PDU) on the performances of the developed catalysts.

2. Development of new catalysts for upgrading of coal derived distillates

As coal derived distillates contain much nitrogen, oxygen compounds and aromatic hydrocarbons, it is difficult to make upgrading with conventional catalysts. In this study, two kinds of catalysts having different functions are developed, and an upgrading of coal derived distillates is conducted with two stage reactions. Hydrogenation catalyst in the first reactor is given the roles of denitrogenation, deoxygenation and hydorgenation functions, and hydorcracking catalyst in the second reactor is given the opening function of naphthene and aromatic rings shown as follows.



Summary

(1988–1993)

At first, we installed flow type micro-reactors for screening of commercial catalysts. Through the test, we selected most suitable catalyst as the standard catalyst for comparison with developed catalysts.

The preliminary evaluation of developed catalysts are made by batch type autoclave reactor by using model compound. Then selected catalysts are evaluated by flow type by using model compounds or coal derived distillates. A short term life test is also conducted by the flow type reactor. The best catalyst evaluated by flow type reactor is provided to the Research Association for Petroleum Alternatives Development (RAPAD) for long term life test and other catalyst performance tests.

Regarding hydrogenation catalyst, we studied the effects of active metals or carrier's characteristics on the performances of catalysts. As a result, we find the catalyst which consist of specified alumina carrier impregnated with nickel-tungsten exhibited most superior performances.

However, the coagulation of tungsten and a decrease of nickel on spent catalyst inner

surface were observed by Electron Spectroscopy for Chemical Analysis (ESCA) and EXAFS. Therefore, we are continuing the development of hydrogenation catalyst to obtain more stable deposition of tungsten.

Regarding hydrocracking catalyst, we learned that Y-zeolite mixed with alumina showed superior cracking activity and the catalyst also shows equivalent activity to the catalyst evaluated by RAPAD in a previous study. But there is a problem that the activity decreases by the deposition of carbon on the catalyst, therefore, we are continuing to develop new zeolites having high activity.

(for 1994)

1. Study for practical use of developed catalyst

- (1) Study for large scale preparation of developed catalyst

To obtain the conditions of commercial scale production, hydrogenation catalyst obtained by laboratory was made by large scale production units. At 500hrs on stream, the results revealed that the activity of the catalysts produced by large scale unit showed 20% lower denitrogenation and 10% lower hydrogenation activities in comparison with those prepared in the laboratory. We will continue to study for improvement of preparation procedures.

- (2) Study on the effects of operating conditions on catalyst performances and life

Multiple stage reactors (4 stages) were installed and tested for obtaining detailed operating conditions, and we evaluated the effects of operating conditions using this units. The operability of those units were good and satisfactory.

2. Development of new catalysts for upgrading of coal derived distillates

- (1) Hydrogenation catalyst

For improving catalyst life, we prepared nickel rich catalyst. This catalyst showed 5% higher activity than that of the catalyst which was evaluated by RAPAD in January, 1993. Therefore, we submitted them to RAPAD for performance evaluation in October, 1994. We evaluated 16 grades of catalysts changing active metals level and nickel-tungsten ratio for further improvement of catalyst performance. In the next, we carry out short term life test of 500hrs for prepared catalyst, and investigate quantity of active metals and impregnation methods in future.

For catalyst carrier, we are studying on the effects of second components such as zirconium. Regarding nickel–tungsten catalyst we are studying on the relation between the sulfiding conditions of the catalyst and catalyst life. From the study that the catalyst life is possible to prolong by using high temperature presulfiding (400– 480 °C) method.

(2) Hydrocracking catalyst

For modifying zeolite which is a component of hydrocracking catalyst, we synthesized two grade of Na–Y zeolites with different $\text{SiO}_2 / \text{Al}_2\text{O}_3$ molar ratio and we prepared four grades of different sodium contained H–Y zeolites respectively by conventional cation exchange method. For these cation exchanged H–Y zeolites cracking activities were investigated by autoclave tests using model compound. The results showed that H–Y zeolite having high $\text{SiO}_2 / \text{Al}_2\text{O}_3$ and low residual sodium has high cracking activity.

Future Tasks

1. Study for large scale production of developed catalyst

For supplying developed catalysts to the PDU operation, catalyst production procedures should be optimized. So that, we will investigate large scale preparation procedures of the catalysts and check the performances of them by using bench scale and multiple reactors.

2. Development of new catalyst for upgrading of coal derived distillates

By characterizing spent catalysts with ESCA and others, we will clarify the causes of deactivation and study how to improve the characteristics by using these results. In particular, regarding hydrogenating catalyst we concentrate to study on catalyst carrier. Regarding hydrocracking catalyst we concentrate to study on Zeolite.

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

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Objectives

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

This research will contribute to the coal liquefaction process in the following ways;

- (1) Decrease the cost of upgrading coal-derived liquids.
- (2) Improve the cost performance of the coal liquefaction process by utilizing heteroatomic compounds.

Work program

The program of this research is as follows;

- (1) Detailed investigation of the possibility and problems of applying the following separation techniques to the heteroatomic compounds in coal-derived liquids.
 - (a) Frozen distillation
 - (b) Extraction (hot water, acid/base or organic solvent)
 - (c) Supercritical gas extraction
 - (d) High pressure crystallization
 - (e) Crystallization
 - (f) Adsorption
- (2) Experimental confirmation of the applicability of some of these separation techniques to the heteroatomic compounds in coal-derived liquids (naphtha and middle distillate) by using existing apparatus.
- (3) Confirmation of detailed performance of the most applicable process selected based on the above laboratory experiments and storage of engineering data by using bench-scale testing apparatus which would be manufactured for the program.
- (4) Investigation of utilization of the heteroatomic compounds separated from coal-derived liquids.

Summary (1987-1994)

1. Up to FY 1993

(1) Investigation of industrial separation techniques

Investigation was performed in the field of separation techniques which could be applicable industrially. The results were used for the design of small-scale extraction units.

(2) Study of the composition of coal-derived liquids

Compositional analysis of naphtha and middle distillate of various coals showed that heteroatomic compounds were mainly acidic and consisted of alkyl-substituted phenols in an amount of 15-30%

(3) Investigation of the utilization of separated heteroatomic compounds

As for phenolic compounds several new applications such as raw material for novel resins and for additives of motor fuel were considered, however it did not seem to be easy to develop new applications owing not only to economical reason, but also to environmental problems.

(4) Separation and purification of heteroatomic compounds (Preliminary experiments)

Based on the investigation of separation techniques, the following experimental studies were carried out in which solvent extraction, alkali/acid extraction, hot water extraction and supercritical gas extraction were studied as separation technique, and high pressure crystallization, adsorption and precision distillation were studied as purification technique.

(a) Alkali/acid extraction

The optimum conditions were studied for alkali extraction of acidic fraction with aqueous sodium hydroxide. It was found that the optimum alkali concentration was found to be 10% and the preferable oil/solvent ratio was 1. Extraction temperature was found not to influence the extractability significantly.

Continuous extraction unit was manufactured, and extraction tests of naphtha and middle distillate of several kinds of coal-derived liquids were performed. Per cent extraction of acidic fraction from naphtha and from middle distillate was almost 100% and 90%, respectively. Lower extractability of middle distillate would be caused by material transport resistance in oil layer, so it was suggested that extraction efficiency was strongly influenced by the mixing method.

From the results on investigation of sludge formation mechanism, it was speculated that the source of sludge was heavier compounds in coal-derived liquids which was dissolved in the liquids due to the existence of phenolic compounds, and they would precipitate when phenolic compounds moved to water layer by extraction. Contact with oxygen in air was also considered to be a factor. Some countermeasures were investigated and tried experimentally. As a result, pre-distillation before extraction was found to be effective for preventing sludge formation. For example, around 1500ppm of sludge was formed without pre-distillation, whereas the amount of sludge was negligible if pre-distillation was carried out.

Per cent extraction of nitrogen compounds with 15-30% sulfuric acid (aq.) was found to be about 60% (as nitrogen content) from naphtha and middle distillate fraction. Based on the data in batchwise experiment continuous extraction unit was manufactured same as alkali extraction.

(b) Solvent extraction

Comparative studies between sequential extraction with methanol and water, and extraction with water/methanol mixture, showed that the former gave a higher extractability and ten times as high extraction rate as the latter.

Based on the data obtained from batch experiment, a continuous extraction unit (1l/h scale) was manufactured, and extraction tests of phenolic compounds from various coal-derived naphtha were carried out. The results showed that extractability strongly depended on methanol/oil ratio and amount of added water. High extractability was obtained with larger methanol/oil ratio, however considering economical factor, the optimum ratio was estimated to be 0.5-2. And preferable amount of added water was also estimated to be around 1.

In case of naphtha fraction of Wandoan coal-derived liquid, per cent extraction of phenols and nitrogen compounds was 90% and 70%, respectively. And small amount of methanol (ca. 5%) was entrained into the raffinate.

(c) Hot water extraction

Extraction experiments with Battle River, brown and Wandoan coal-derived liquids showed that the extractability was influenced by the amount of water, extraction temperature and phenolic concentration. Hot water extraction is thought to be not applicable to rough separation of heteroatomic compounds for the following reasons;

- 1) Separation of oil and water was difficult because of the unclear interface.
- 2) Extractability increased as the amount of water increased or as the extraction temperature lowered, however extraction selectivity decreased contrarily.

(d) Supercritical extraction

Experimental data so far has indicated that this method was not so effective owing to low selectivity to heteroatomic compounds.

(e) High pressure crystallization

Fundamental technique could be established for the separation and purification of *p*-cresol and *p*-ethylphenol. More than 98% purity of *p*-cresol and *p*-ethylphenol could be recovered by this method combined with distillation and urea-adduct separation. Application for the separation of nitrogen compounds such as quinoline and isoquinoline was also investigated, consequently 98.6% purity of isoquinoline was recovered from raw material in which concentration of isoquinoline was 69.7%.

These results demonstrated that applicability of high pressure crystallization to the solid solution system was found to be higher than frozen crystallization.

(f) Adsorption

- 1) Breakthrough behavior of K-substituted X-type zeolite or Y-type zeolite was studied on the concentration of *p*-ethylphenol from *m*- and *p*-ethylphenol, using a continuous adsorption unit. The concentration up to the composition applicable to high pressure crystallization was demonstrated to be possible, by choosing the conditions in which adsorption selectivity was low but not influenced by water content.

2) Urea-adduct method was studied as a concentrating method for *p*-cresol from cresol isomers. As a results, this method is thought to be a possible pretreatment of high pressure crystallization, but the operable conditions were limited.

(g) Precision distillation

Phenolic compounds recovered by methanol/water extraction and alkali extraction from Wandoan coal-derived light naphtha were distilled for the separation of phenol and *o*-cresol.

Although the purity of them almost satisfied JIS standard, further purification seemed to be required in order to become comparable to commercial reagents.

(5) Evaluation of rough separation

(a) Evaluation of raffinate

Hydrotreating(upgrading) experiments of raffinates obtained from methanol/water extraction, alkali extraction and alkali/acid extraction were performed. Hydrogen consumption was lowered to 1/3 for naphtha and 1/3-1/2 for light oil for each raffinate. Nitrogen content was lowered to about half by extracting naphtha fraction with methanol/water extraction or alkali/acid extraction, and also by extracting light oil fraction with alkali/acid extraction.

(b) Evaluation of rough separation process

Performance of upgrading

(naphtha fraction) H_2 consumption: alkali/acid extraction=alkali extraction<solvent extraction

H/C of raffinate: alkali/acid extraction>alkali extraction>solvent extraction

N,O in raffinate: alkali/acid extraction<alkali extraction=solvent extraction

(light oil fraction) H_2 consumption: alkali extraction<alkali/acid extraction<solvent extraction

H/C of raffinate: alkali/acid extraction=alkali extraction>solvent extraction

N,O in raffinate: alkali/acid extraction<solvent extraction<alkali extraction

Simplicity of process solvent extraction>alkali extraction>alkali/acid extraction

Construction and utility costs of 50,000BPD scale commercial plant were estimated based on material balance obtained from the continuous extraction tests of naphtha fraction. Comparative study of solvent extraction and alkali extraction showed that the latter process was economically advantageous owing to the superior quality of recovered phenols in spite of its higher operating cost. As a result alkali extraction was selected as the most preferable rough separation process.

2. For FY 1994

(1) Fundamental study for the improvement of reliability and economic conditions of alkali/acid extraction process.

(a) Neutralization of phenolate with CO_2

Phenols are recovered by neutralization with CO_2 containing gas in the tar industry. Behavior of phenolate obtained from coal-derived liquids at the neutralization process and its optimum

conditions were investigated by continuous flow apparatus which was manufactured for the purpose. The apparatus has reaction column ($40\phi * 1000L$), and CO_2 containing gas can be introduced from the bottom of the column. Typical operation conditions were that CO_2 concentration was 20vol% (in N_2), flow rate was 2l/min and column temperature was $40^\circ C$. Figure 1 shows correlation between pKa of phenolic compounds and the rate of neutralization of corresponding phenolate. It shows phenolates derived from more acidic phenols were harder to neutralize. So it can be speculated that phenolates obtained from the extraction of heavier fraction could be neutralized easily. Results on neutralization test showed that conversion of phenolate increased on the straight line approximately until 90%, but then the rate reached the limit at around 95%.

In case of the test of phenolate from coal-derived liquids, the same phenomenon was observed. Mechanism of the phenomenon was studied minutely and it was found that the solubility of phenolate in the water layer decreased owing to the increment of $NaCO_3$ concentration, and the phenolate moved to the oil (phenol) layer where reaction with CO_2 was very difficult, consequently neutralization stopped.

To avoid reaching the limit and complete the reaction, xylenes was added in the middle of the process. The result is shown in Fig.2. When xylenes were added, conversion increased linearly to around 100%. This method was proved to be very useful technique for the neutralization process.

(b) Study of the behavior of heteroatomic compounds in the extraction process.

In the solvent extraction separated phase was observed under specific naphtha/methanol ratio. If a particular associated state of heteroatomic compounds exist, extractability might be affected. So, extractability was examined under different conditions of water addition as follows,i)after separating two layers, add water to each layer,ii)add water to the mixture of the layers. As a result, both per cent extraction and selectivity were nearly equal between the two conditions. The result showed there was no difference in the associated state of heteroatomic compounds between the two, and the latter condition was considered to be preferable practically.

(c) Optimization of extraction conditions

Extraction tests have been performed for naphtha, kerosene and atmospheric gas oil separately. However, taking the efficiency of extraction into account, it was considered to be preferable that single fraction in which useful phenolic compounds were condensed was the feedstock of extraction. Through the compositional analysis of coal-derived liquids and distillation test, boiling point of preferable feedstock was estimated to be $150-250^\circ C$. Hereafter extraction test was performed using this phenolic compounds condensed (PHC) fraction.

(d) Evaluation of raffinate in upgrading process.

Hydrotreating test of PHC fraction of Tanito Harum coal-derived liquids with and without alkali extraction was carried out under following conditions, pressure:100atm, LHSV:1h⁻¹, G/L:1000, themperature:350 $^\circ C$ and 380 $^\circ C$. The results are shown in Table1. Higher HDS and

HDN activities were obtained when feed oil was treated with alkali solution before reaction. Furthermore gaschromatography analysis of product oil showed that the amount of benzene and cyclohexane was drastically decreased by alkali extraction of feed oil, owing to the absence of phenol which was the precursor of them. Decrease of benzene must be preferable from the environmental point of view.

(2) Chemical properties and environmental adaptability of the raffinate.

(a) Hydrotreating behavior of the extract (heteroatomic compounds)

Literature search was carried out concerning hydrotreatment of phenolic compounds. According to literature, selectivity of phenolic compounds to corresponding cyclohexanol derivatives increased with reaction temperature, and it was speculated that hydrogenation of aromatic rings occurred firstly followed by removal of oxygen atom at higher temperature.

Hydrotreatment of phenolic compounds was carried out with NiMo/Al₂O₃ at 350°C and 380°C. When phenol with 1-methylnaphthalene was used as raw material, almost all of phenol converted to benzene and cyclohexane (benzene ≪ cyclohexane), however, when phenol with Wandoan coal-derived kerosene was used, plenty amount of phenol remained in product oil. Considering these results, extraction seemed to be more preferable process for the removal of phenolic compounds than hydrotreatment.

(b) Benzene formation in the process of upgrading

In hydrotreatment of phenol the ratio of cyclohexane and benzene formation was ca.10:1, and the formation of cyclohexane decreased with reaction temperature.

(c) Environmental adaptability in combustion of the raffinate

Literature search was carried out for last 20 years. More than 200 literature were found to be related with aromatic hydrocarbons in exhaust gas. There were a fewer literature about gasoline than expected. As for the relation between aromatic compounds and properties of exhaust gas a lot of studies were carried out from the view point of total amount of aromatic compounds and analysis of them in exhaust gas.

(d) Separation and utilization of nitrogen compounds in coal-derived liquids

Literature search was performed concerning characterization, separation and utilization of nitrogen compounds. Most of related literature was concerned with characterization, and it was found that there were very few literature about novel separation and utilization techniques. As for utilization, an application to the reformer of asphalt seemed to be attractive, which could improve water-resistance and repeatability of asphalt.

Future task

(1) Fundamental study of the elemental process such as decomposition of phenolate and recovery of alkali must be continued to establish total technology for the selected process. And extraction test of PHC fractions will be carried on to optimize the conditions.

- (2) Optimization of rough separation process, such as the combination of alkali extraction and solvent extraction, will be investigated from the view point of economics and the effect on upgrading.
- (3) Properties about environmental safety of the raffinate will be investigated by means of studying the behavior of it in upgrading process, especially about benzene formation.
- (4) Novel separation techniques will be searched to improve rough separation process continuously. As for a separation technique with surfactant, preliminary study will be performed.

Collaboration with other research organization

Collaboration is continuing with National Institute for Resources and Environment, Agency of Industrial Science and Technology.

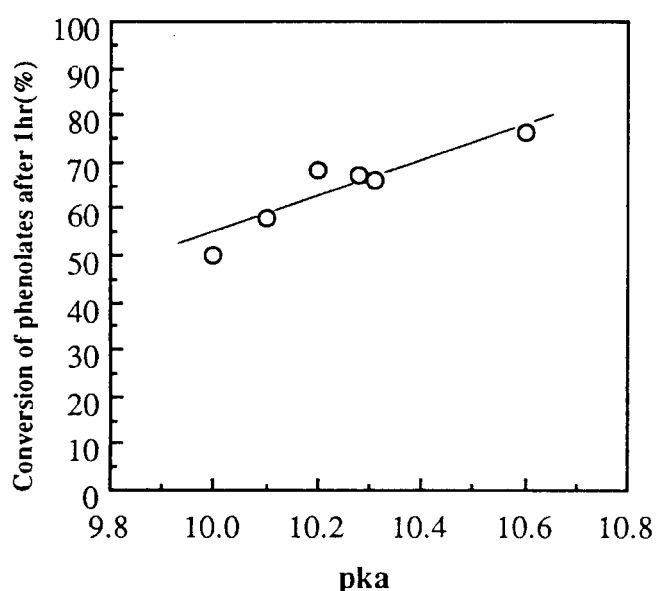


Fig1. Correlation between pKa and neutralization rate of phenolates.

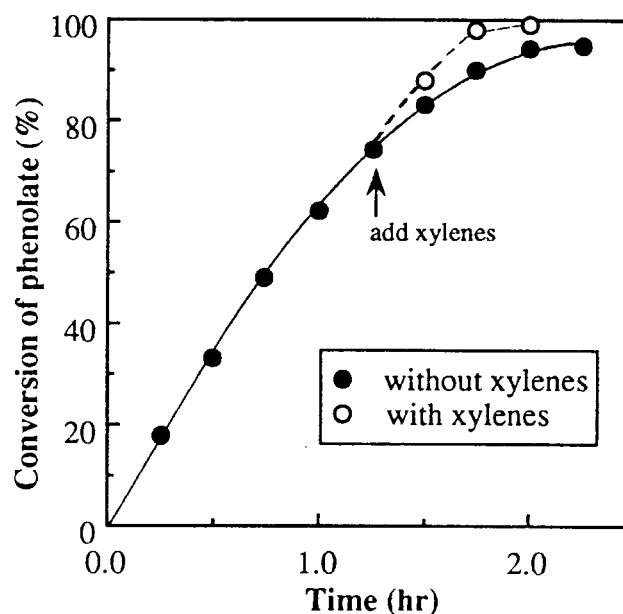


Fig 2. Effect of xylenes addition on the neutralization of phenolate.

Table 1. Effect of alkali extraction on the hydrotreatment of Tanito Harum coal-derived liquids.

Reaction temperature (°C)	Elemental analysis of liquid products(wt%)					Hydrocarbons in outlet gas (vol%)			
	C	H	N	S (ppm)	O (dif.)	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀
without alkali extraction									
(feed oil)	85.1	10.3	0.54	570	4.0	-	-	-	-
350	87.4	11.6	0.13	120	0.9	0.03	0.03	0.03	0.01
380	87.3	11.8	0.08	7	0.8	0.07	0.04	0.04	0.01
with alkali extraction									
(feed oil)	87.5	11.1	0.53	450	0.8	-	-	-	-
350	88.0	11.7	0.12	5	0.2	0.02	0.02	0.02	<0.01
380	87.9	12.0	0.06	3	0.04	0.04	0.03	0.03	<0.01

Study of Toxicological and Environmental Effects of
Coal-derived Liquids

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New Energy and Industrial Technology Development Organization (NEDO)

Objectives

A series of toxicological and environmental safety studies on coal-derived liquids to be developed in Japan has been conducted using laboratory animals, and basic data have been compiled. They aim at ensuring the health of workers in coal liquefaction plants, and also establishing public acceptance for the liquid's distribution and safety from leakage. 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. An analytical study and a survey of foreign information are added in order to support the evaluation.

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

Work Program

During this fiscal year, the studies were conducted on medium and heavy liquids derived from the integrated operations in the brown

coal liquefaction pilot plant, and for the naphtha fraction of crude oil derived from the bituminous coal-liquefied oil.

Summary (1983-1994)

1. Up to FY 1993

To study the safety of brown coal-derived oils, in 1987 some preliminary data were obtained from the liquefied liquids of the first hydrogenation process during the early stage of operation of the Australian pilot plant. In 1988 a variety of tests were conducted using the total fraction (the representative average oil of products) of the liquids derived from the integrated test operations in the brown coal liquefaction pilot plant in order to understand the safety of the liquefied 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 was compiled for the total fraction as well as for the fractions of the oils derived from the integrated operations in the brown coal liquefaction pilot plant. As a result, a comprehensive picture of the safety of the liquefied oils derived from the brown coal liquefaction pilot plants was obtained. Further, a variety of tests for the safety of the liquids derived from the bituminous coal PSU have been started.

2. For 1994

(1) Physical-chemical properties

"Tests of Physical-Chemical Properties" of OECD/MPD were conducted in accordance with the required guidelines, using the naphtha fraction 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.

Naphtha from bituminous coal

- Dissociation constant No dissociation
- Partition coefficient 3.86 (24°C)

(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 naphtha fraction of crude oil derived from the bituminous coal liquefied oil. As a result, the single oral dose toxicity was extremely low, and the 50% lethal dose (LD_{50}) is estimated to be more than 2,000 mg/kg for both male and female rats.

Naphtha from bituminous coal: $LD_{50} > 2,000$ mg/kg

(3) 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 naphtha fraction of crude oil derived from the bituminous coal liquefied oil. As a result, the no-observed-effect level (NOEL) of the naphtha fraction of crude oil derived from the bituminous coal liquefied oil was judged to be 6 mg/kg based on clinical signs, body weight changes, food consumption, hematology, clinical biochemistry, urinalysis, organ weights, and autoptic findings of the animals.

(4) Mutagenicity (Chromosomes)

"The Chromosomal Aberration Tests in Cultured Mammalian Cells" of the Chemical Substances Control Law and Industrial Safety and Hygiene Law were performed using CHL/IU cells for both existence and non-existence of metabolic activation in accordance with the required guidelines, using the medium and heavy liquids derived from the integrated operations in the brown coal liquefaction pilot plant, and the naphtha fraction of crude oil derived from the bituminous coal liquefied oil. As a result, the following results were obtained:

Medium liquid	: positive (+)
Heavy liquid	: positive (+)
Naphtha from bituminous coal	: negative (-)

(5) Bioaccumulation

"Bioaccumulation Tests" of the Chemical Substances Control Law were performed using carp in accordance with the required guidelines, using the naphtha fraction of crude oil derived from the bituminous coal liquefied oil. As a result, the range of bioaccumulation factor of five peak components on the gas chromatogram was as follows:

Naphtha: high exposure level ($0.5\mu\text{g/ml}$): 309 to 3,956 times
low exposure level ($0.05\mu\text{g/ml}$): 297 to 3,264 times

Future tasks

We conducted a series of environmental safety evaluation studies on the total fraction and the individual upgraded fractions of the liquids derived from the integrated operations in the brown coal liquefaction pilot plant from 1989 to 1993.

As a result, the reduction of polycyclic aromatic hydrocarbons and phenols which are regarded as toxic substances were confirmed, and the inhibition of toxicity development was found in the tests of eye irritation, chromosomal aberration (bacteria and chromosomes), and fish toxicity. Thus, the effects of upgrading were remarkable.

Further, we will conduct the environmental safety assessment tests on the individual fractions of the liquids derived from bituminous coal from this fiscal year on, selecting test items from the Industrial Safety and Hygiene Law, the Chemical Substances

Control Law and the MPD of the OECD, and compiling environmental safety data. When these assessment tests are completed, the environmental safety of the liquids derived from bituminous coal will be judged comprehensively.

IMPROVEMENT RESEARCH OF COAL LIQUEFACTION PROCESS

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OBJECTIVES

For the substantial improvement on reliability, economics and environmental acceptance of coal liquefaction process:

- (1) To solve the common technical problems of coal liquefaction process by using continuous reaction facility.
- (2) To contribute the improvement of the existing technical package.

WORK PROGRAM

- (1) Improvement of properties of coal

Prior to hydro-liquefaction, thermal treatment of coal in solvent is effective to suppress the scale formation caused by alkaline earth metals in the reaction system. This treatment improves coal properties, concentrates the coal slurry and makes easier to recover CO₂ in high level. They are important factors to improve the thermal efficiency and harmonization with global environment for coal liquefaction process.

- (2) Optimization of reaction conditions

As key technologies of liquefaction reaction, the research for higher activity catalysts, higher performance solvents and development of their effective application methods are conducted by combination with CLB and gas recycle to increase the distillate yield and improve the quality of products.

SUMMARY

1. Up to FY 1993

The Brown Coal Liquefaction project which was started in 1981 carried out the design, construction and operation of 50 t/d pilot plant. All these works were completed successfully in 1990. Since that time, the conceptual design of a demonstration plant and follow up experimental study were carried out. Finally, all the results were compiled as the project report which consisted of 10 volumes, totally 10,000 pages, and all the programs were completed in 1993.

In 1991, a special advisory committee was set up under "Industrial Technology council" to evaluate the results of pilot plant operation, and 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 problem is expected to become more serious in 21 century.

Considering such circumstance, environmental compatible coal conversion complex was advocated by the Promotion Headquarters of the "New Sunshine" Program, Agency of Industrial Science and Technology, Minister of International Trade and Industry.

This project started in 1994 succeeded by the results of the preliminary study in 1993 to improve the reliability and economics of coal liquefaction technology harmonizing to global environment.

2. For 1994

(1) Improvement of properties of Coal

① Pretreatment of coal

Coal was pretreated in solvent to suppress the scale formation of metal compound. Coal was thermally treated in 1-methyl naphthalene or tetralin as model solvent, and the decomposing behavior of oxygen functional group and effects of treating condition on liquefaction reactivity were studied.

- Carboxyl group started to decompose remarkably near 250 °C, and about 90% of the group in brown coal decomposed to CO₂ at 400°C.
- Carboxylate in coal, which was considered as the precursor of scale formed in a hydro-liquefaction system, decomposed to carbonate as increasing in temperature of pretreatment. Higher temperature over 400 °C was required to decompose more than 50% of carboxylate.
- Introducing hydrogen donor solvent like tetralin or solvent from the secondary hydrogenation prevented the pretreating coal from decreasing the liquefaction reactivity. Further more, treated coal with liquefaction catalyst in hydrogen atmosphere tended to show higher reactivity than non treated coal.

② Pretreatment of coal and mechanism of scale formation

To investigate the scale formation behavior in reactor system, adhesion of carbonate on a test piece which was attached to an agitator in the

autoclave was studied.

- Analysis results of scale on the test piece by XRD and SEM-EDX or Auger spectroscopy showed that it contained Fe_{1-x}S , $\text{CaMg}(\text{CO}_3)_2$ and Na.
- The amount of scale deposition on the test piece was analyzed by ICP, and less deposition was confirmed in case of pyrite catalyst and the effect of pretreatment of coal in solvent was also observed. These results were good consistent with the data in BSU, then the evaluation method with small size autoclave was considered as a useful method to study the scale formation phenomena in a liquefaction reaction system.
- From results of FT-IR and XRD, Ca in ion exchanged coal existed as carboxylate and converted to carbonate at higher than 400°C.

(2) Optimization for liquefaction condition

① Improvement of solvent

To obtain light distillate with higher yield, combination effects of boiling point range of the recycling solvent on liquefaction were studied.

- As the boiling point sifted to higher side, higher yield of light fraction was obtained.
- Distillate yield, especially solvent fraction, decreased according to recycling higher boiling point solvent, but CLB recycle improved the solvent yield and light fraction also increased significantly.
- In continuous BSU experiments using the solvent whose boiling point was 300 to 420°C, distillate yield increased and almost all of the distillate consisted of light fraction whose boiling point was lower than 300°C under combination of CLB and gas recycle.
- These results suggested that recycle of high boiling point solvent can constitute the coal liquefaction process enable to get high yield of distillate over 60% which consists of light fraction under 300°C.

② Liquefaction Activities of Newly Developed Catalysts

To increase the distillate yield and reduce an amount of catalyst, reaction performance of pulverized catalysts was evaluated. The catalysts examined were γ -iron oxyhydroxide and pyrite which were pulverized to various size from 0.4 to 0.7 μm in solvents.

- There were no significant differences on distillate yield neither in pulverized size nor boiling point range of solvent.
- γ -iron oxyhydroxide was easily converted to pyrrhotite at 200°C in 10 minutes, and it was found that the catalyst having smaller crystal lattice size gave higher liquefaction activity.
- In liquefaction experiments with 5 liters autoclave, 1 wt % of γ -iron

oxyhydroxide catalyst showed similar distillate yield to 2wt % of pyrite (0.4μ) and 3 wt % of pyrite(2μ) catalyst.

- Liquefaction performance was evaluated also in 0.1t/d continuous BSU, and γ - iron oxyhydroxide showed higher oil yield than pyrite. High oil yield over 60wt% on mafc was attained under the condition dosing 3wt % of γ - iron oxyhydroxide as Fe and combining with CLB and gas recycle. As far as amount of scale formation in whole reactor system, no significant differences between iron oxyhydroxide and pyrite were observed, however higher portion of scale was accumulated in the first reactor in the case of iron oxyhydroxide.
- The second metal such as Mo, W, Co or Ni was added to iron-based catalyst to improve its catalytic activity, then the Mo added catalyst showed best result.

③Improvement of brown coal properties

Effects of particle size and moisture content of brown coal on liquefaction were investigated, and following results were obtained.

- There were no apparent differences in liquefaction performance between raw coal particle size examined, which were under $75\mu\text{m}$, 75 to $500\mu\text{m}$, 0.5 to 1mm and 1 to 3mm .
- When moisture content in coal decreased from 17 to 1.7 wt% on mafc, the distillate yield decreased, and the selectivity of naphtha was slightly increased, then it was suggested that dewatering degree of coal before liquefaction reaction should be determined on economical point of view.
- Effects of particle size of brown coal and kinds of solvent on slurry viscosity were examined, then no significant differences by particle size were observed among $75\mu\text{m}$ under, 75 to $500\mu\text{m}$, 0.5 to 1mm .
- Differences between measured viscosity and the estimated value by the existing method were remarkable when solvent of higher boiling point was used. Modification of estimation equation is required.

④Improvement of Reaction Condition

To increase distillate yield, effects of gas flow rate and the condition of CLB recycle were investigated.

- Effects of gas flow was investigated in BSU. Distillate yield increased with increase of gas flow rate up to $7\text{Nm}^3/\text{kg-mafc}$ without CLB recycle and further increase was expected according to higher gas flow rate. From the experiments changing feed rate of coal slurry and gas flow rate, the effect of gas flow rate could be unified as dimension of gas to slurry ratio independent of gas flow rate itself.

- The effect of CLB recycle on increase of distillate yield was restrained with gas recycle comparing to without gas recycle.
- Increase of gas flow rate was very effective to extend the residence time of liquid phase in reactors resulting in hydrogenation of CLB, namely increasing the fraction of hexane soluble.

FUTURE TASKS

(1) Improvement of properties of Coal

- ① Improvement of solvent and operating condition could minimize the deterioration of the liquefaction reactivity of coal during pretreatment in solvent. Further experimental study on solvent quality and effect of catalyst to the pretreatment will be executed for the improvement of reactivity of coal.
- ② To establish a convenient method for the evaluation of scale formation, the method using autoclave will be continued and the results will be compared with the results of BSU.

(2) Optimization of liquefaction condition

- ① High distillate yield which consisted of mainly light fraction was attained by improvement of recycling solvent and operating condition. For further improvement on reaction condition, effect of amount of catalyst, best mixing of light fraction and heavy fraction for recycle solvent will be investigated, where an effect of introducing hydrogenated solvent will be also studied.
- ② It has been confirmed that γ -iron oxyhydroxide has higher liquefaction activity than pyrite. Operation condition to minimize the amount of catalyst and the activity and scaling behavior in longer operation will be examined. And The effect of gas and/or CLB recycling route on liquefaction performance and operability will be also studied.

Advanced Technology for Coal Liquefaction

Dr. Shigeru UEDA

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

Objective

Research and development of basic and innovational technologies to improve economics and efficiencies of coal liquefaction process and to construct a basis of the development for the advanced and environmentally friendly coal liquefaction technology based on new concepts with a progress of liquefaction technology, advancing to the technical package of coal liquefaction.

Work Program

(1) Fundamental research on highly dispersed catalyst with high activity

Preparation of highly dispersed catalyst made up of ultra fine particles.

Analysis and activity test for coal liquefaction with prepared catalyst.

(2) Basic study on the possibility of complete coal liquefaction process

Study of reaction conditions in the initial stage during coal liquefaction, in relation to the yield pattern of between oil and gases without residue, to minimize economical costs of the coal liquefaction process.

Analysis of coal structure and liquefaction products for the investigation of the most suitable reaction conditions, especially to reduce the cost of hydrogen for the coal liquefaction process.

Summary (1981– 1994)

1. Up to FY 1993

The Brown Coal Liquefaction project which was started in 1981 had completed the design, construction and operation of 50 t/d pilot plant successfully in 1990. Since that time, the conceptual design of a demonstration plant and follow up experimental study have been carried out. Finally, all the results compiled as the project report which consisted of 10 volumes, totally 10,000 pages, then all the programs were completed in 1993.

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On the other hand, the energy resources problems of fossil fuels, including coal, is entering to a new phase, as it impacts upon the matter of safeguarding the global environment. Consequently, a harmonious balance between energy resources and environmental problem is expected to become more serious in 21 century. Considering such circumstance, environmental compatible coal conversion complex was advocated by Promotion Headquarters of the "New Sunshine" Program, Agency of Industrial Science and Technology, Minister of International Trade and Industry.

This project started in 1994 backed up by the results of the preliminary study in 1993 to improve the reliability, economics of coal liquefaction technology harmonizing to global environment.

2. For FY 1994

(1) Fundamental research on highly dispersed catalyst with high activity

(a) Preparation of highly dispersed catalyst by microemulsion method

- Highly dispersed iron hydroxide emulsion was obtained by mixing two microemulsions containing respectively an aqueous solution of ammonium iron(III) sulfate and an aqueous solution of ammonia, which were solubilized separately in cyclohexane uniformly by addition of nonionic surfactant, (polyoxyethylene nonylphenyl ether), before the mixing. It was found that produced micelle had diameter between 20 and 50 nm from the observation through HR-TEM, and the produced particles were regarded as amorphous by XRD. Liquefaction activity test of iron loaded on the coal surface by using these emulsions was carried out. It was recognized to increase in both coal conversion and HS yield compared to the test without a catalyst.

(2) Basic study on the possibility of complete coal liquefaction process

(a) Study on the conditions for the initial stage during coal liquefaction

- It was found that both THFI conversion and HS yield were increased by using tetralin as a hydrogen donor solvent above 400°C, at which temperature, thermal decomposition of coal occurs sprightly. The change in atomic ratio of Hydrogen to Carbon (H/C) of THFI obtained from liquefaction products indicated that hydrogen transfer from solvent to coal occurred from about 300°C.

- It was also found that the pretreatment of coal at appropriate temperature for 30 minutes with both catalyst and hydrogen donor solvent contributed to improve the yield pattern of coal liquefaction at 450°C, indicating the increase in both coal conversion and HS yield with decrease in gas yield. The effect of pretreatment was greater at 350°C than 300°C.

THFI after coal liquefaction had a high value of H/C. It was appeared that hydrogen was transferred to coal more effectively during preheating stage. Hydrogen activated on the catalyst could play a important role for hydrogen transfer to coal during the pretreatment, because this effect was not found in the case without catalyst or hydrogen in gas phase.

(b) Relationship between liquefaction condition and yield pattern

- The effects of transferable hydrogen and catalyst on the yields of product were investigated by changing the mixing ratio of between tetralin and 1-methylnaphthalene (1-MN) as a liquefaction solvent. It was found that yield of solvent fraction was increased by addition of a catalyst, while the yield of Naphtha fraction was increased by transferable hydrogen in solvent. Finally, the yield of distillates was increased with a decrease in the yield of hydrocarbon gas by using of both a catalyst and a hydrogen donor solvent such as tetralin.
- From the analysis in structure of liquefaction products, it was found that the fa of asphaltenes decreased with the amount of transferable hydrogen, while by the addition of a catalyst, both of average ring number of unit structure and average molecular weight were decreased. Also, structure parameters of the liquefaction products by ¹H-NMR suggested that the formation of hydrocarbon gases was suppressed by existing of both catalyst and hydrogen donor solvent during coal liquefaction.

(3) Analytical study of structural change in coal

- By the thermal treatment of coal at 150–350°C, a remarkable change in physical structure of coal was observed. The surface area of treated coal became larger with the increase in micropores by the treatment with the tetralin–mixed solvent.
- The heat of adsorption of tert-butylpyridine per unit area decreased gradually by thermal treatment with the tetralin–mixed solvent. This is thought to due to the decrease in oxygen containing functional groups, which act as a adsorption site, with the increase in treating temperature. On the other hands, in the case of the thermal treatment with pure 1-MN, the heat of adsorption maximized around 300°C. It was considered that thermal decompositions of coal resulted in different structural

changes, when the treating solvent has less hydrogen donability to coal under the thermal treatment conditions.

- From the results of TG–MS measurement, it was showed that oxygen containing gases (CO_2 , H_2O , CO) started to get out of coal at around 200°C and hydrocarbon gases broke out remarkably from the temperature of about 350°C .
- High temperature ESR spectrum were measured in situ, increasing temperature up to 500°C under 10kg/cm^2 of the pressure in N_2 . It was revealed that the radical concentration in Yallourn coal increased rapidly from 350°C with 1–MN as a solvent, and the heating with DHA as a hydrogen donor solvent minimized the radical concentration in $200\text{--}350^\circ\text{C}$ region in which thermal decomposition of coal had not been activated sufficiently. These results suggested that the transferable hydrogen from DHA stabilized the radical fragments produced by thermal decomposition of coal.

Future Tasks

(1) Fundamental research on highly dispersed catalyst with high activity

Improvement of preparation method for a highly dispersed catalyst by microemulsion method and so on.

(2) Basic study on the possibility of complete coal liquefaction process

Improvement of reaction conditions in the initial stage during liquefaction of coal, in relation to the yield pattern of between oil and gases without residue to minimize economical costs of the coal liquefaction process by investigation of effects of the heating rate, amount of the transferable hydrogen in solvent, and catalyst through the analysis in coal structure and liquefaction products, including the pretreatment of coal.

A REDUCTION OF CATALYST AMOUNT IN COAL LIQUEFACTION SYSTEM

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and Industrial Development Organization (NEDO)

Objectives

The objectives of this study is, in order to improve the performance and efficiency of the NEDOL process, to investigate how the level of elemental technologies may be raised. As one approach, attention is paid to the highly dispersed iron catalysts searching the possibility of the reduction of catalyst amount through preparation of Fe-loaded coals and liquefaction tests.

Work program

Investigations were made into the selection of the preparation method of Fe-loaded coal so far studied, and further research was made into the practical preparation conditions to apply this technology to a liquefaction plant and construct the system.

Summary(1978-1994)

1. Up to FY1993

This research started in 1978 for the development of direct coal hydroliquefaction technology. The BSU (0.1 t/d continuous Bench Scale Unit) had been successfully operated since 1980.

In 1985 the BSU was modified to the NEDOL process. After the retrofit, in order to obtain basic data for screening the candidate coals for the NEDOL pilot plant, liquefaction experiments were carried out by using Synthetic Iron Sulfide catalyst (SIS) in twelve coals. Among them, Wandoan coal was presented for stationary operation for about 510 hours. In 1991, the results and findings from NEDOL BSU research were compiled ; the liquefaction of high concentration coal slurry was one of the promising technologies resulting from this research. Here, to improve reactivity of coal and increase the economic efficiency of the liquefaction process, our attention was turned to highly dispersed iron catalysts.

We have prepared three catalysts loaded on coal as dispersed catalyst or catalyst precursor as shown in Table 1. All the catalysts showed a higher activity than direct introduction of SIS catalyst. Among them, AWIP exhibited the highest activity.

One of the attractive features of the catalyst-loading approach is 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 in the reaction system. At the mix rate of 5-10 wt% and mean catalyst content of 0.6 wt% (as Fe+S), the oil yield was 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 is compared by the oil yield at the same catalyst amount, the ranking was AWIP > AIP, CIS > SIS.

In a mix-liquefaction of Wandoan coal, along with the increase of slurry concentration (40,45,50 wt%), the catalyst activity was nearly maintained in the case of AWIP.

2. For FY1994

This year we concentrated our efforts on research how the AWIP preparation conditions affect the liquefaction characteristics in a mix-liquefaction.

(1) Selection of catalyst preparation method

Although all the catalysts (CIS, AIP and AWIP) so far studied have almost the same catalytic activity at 1/4-1/5 weight of SIS, AWIP has the potential in a practical use from the following reasons;

(a) When compared the preparation materials required for three catalysts, on the premise that activities are not different largely between the three at the same catalyst weight, though raw material of iron is the same, the cost expensive surfactant and sodium sulfide is needed for CIS preparation. In the case of AIP and AWIP, surfactant is unnecessary and relatively inexpensive sulfur source such as solid sulfur is added at slurry preparation. And because the difference is the alkalis only, AWIP using ammonia contained process wastewater is cost effective.

(b) Inherent nature of CIS preparation conditions required - restricted coal and iron concentration at preparation - prevents the preparation system from small-sizing.

(c) Catalytic activity is in the order AWIP > AIP, CIS

(d) AWIP is applicable to wide range of coal rank.

(e) Usage of process wastewater from PSU (1t/d Process Support Unit) is confirmed in addition to those from BSU.

(2) AWIP preparation conditions and characteristics in mix-liquefaction

(a) As the starting material, ferrous (Fe²⁺) sulfate is superior than

ferric (Fe^{3+}) sulfate in handling at preparation and catalytic activity of AWIP. Liquefaction performance is shown in figure 1.

(b) Relation between AWIP preparation conditions such as reagents ratio, coal concentration and amount of Fe loaded on coal was made clear. Moisture in AWIP coal after vacuum filtration increased as the amount of Fe loaded increased. Enlargement of particle size of coal to be Fe-loaded made the moisture content of AWIP lower at higher loading of Fe but there was only a small effect at the lower loading of Fe around 5 wt% or less. As shown in figure 2, the oil yield (containing product water) decreased slightly as particle diameter of raw coal to be Fe-loaded increased. In the mix-liquefaction tests, particle diameter of Fe-unloaded coal was 100 mesh minus (mean dia. $50\mu\text{m}$).

(c) In the mix-liquefaction tests using wet-AWIP at average catalyst weight set constant (0.6 wt% as Fe+S), oil yield decreased slightly at AWIP mix ratio of 10 wt% or less in a batch reaction system. But in a continuous micro-reactor system, oil yield and oil property were equal to those from reference conditions of SIS 3 wt%. Further study will be needed as to whether the drying of AWIP is necessary or not.

(d) Figure 3 compares the oil yield between three coals in batch mix-liquefaction tests. The order was Wandoan > Tanito Harum > Black Thunder.

(e) AWIP showed a good performance in a mix-liquefaction of high concentration coal slurry. Results of batch tests are shown in figure 4-1. Figure 4-2 summarized the liquefaction test results of dispersed Fe catalysts loaded on Black Thunder coal using continuous micro-reactor system.

(3) Catalytic activity of AWIP

(a) Figure 5 shows the relationship between oil yield and AWIP mix ratio at average catalyst amount of 0.6-0.64 wt%. In this figure, mix ratio zero corresponding to a direct introduction of separated-AWIP catalyst gave the lowest oil yield. The phenomenon is one of the evidences which refer to the effect of Fe-loading on coal particles.

(b) Transformation of catalyst component of AWIP into pyrrhotite after sulfurization or activation was confirmed.

(c) Separated-AWIP and AWIP-on-Carbon black were sulfurized in the temperature range of 280-320 °C. By XRD analyses of activated samples, it was predicted that the catalytic activity was higher when activated at lower temperature.

Liquefaction tests were conducted using a continuous micro reactor system equipped with the activation reactor. Two AWIP coal samples were prepared, wet-AWIP and dry-AWIP. Activation temperatures were set at 280 °C and 320 °C, and liquefaction temperature was 450 °C. Figure 6 compares the effects of activation temperature and moisture in AWIP on oil yields. As predicted from the activation test results, oil yields were higher at activation temperature of 280 °C than at 320 °C for both samples, and of which wet-AWIP gave slightly higher oil yield.

(d) From a difference in the reduction temperature in TPR-S analysis, AWIP will have a higher activity than SIS.

(4) AWIP preparation and mix-liquefaction system

The system was constructed on the basis of the results so far obtained, as shown in figure 7. Using the process wastewater and ferrous sulfate, catalyst component (Fe) is loaded on a fraction (X) of the feed coal (100). This fraction is then mixed with the remainder of the feed coal (100-X) and sulfur in the slurry preparation.

It was estimated that the materials cost, especially that of ferrous sulfate in the catalyst preparation cost was large, so the introduction of ferrous sulfate manufacturing process will be necessary to secure the stable supply and cost reduction.

Future Tasks

Related to the AWIP mix-liquefaction, the relation between catalyst activation conditions and liquefaction characteristics will be studied especially from a view point of the effect of moisture in AWIP coal on the liquefaction performance.

It is also planned to start investigations into AWIP preparation conditions in a flow system.

Table 1 Dispersed Iron Catalysts

Symbol	Catalyst/precursor formation	Sulfur
CIS	$\text{FeSO}_4 + \text{Na}_2\text{S} \rightarrow \text{FeS} + \text{Na}_2\text{SO}_4$ Coal + FeS $\xrightarrow{1)}$ FeS on Coal	-
AIP	$\text{FeSO}_4 + \text{Coal} + \text{Ammonia} \xrightarrow{1)}$ Iron hydroxide on Coal	added at liquefac- tion
AWIP	$\text{FeSO}_4 + \text{Coal} + \text{Process Wastewater} \xrightarrow{2)}$ Iron hydroxide on Coal	added at liquefac- tion

1) Filtration + Drying, 2) Filtration + (Drying)

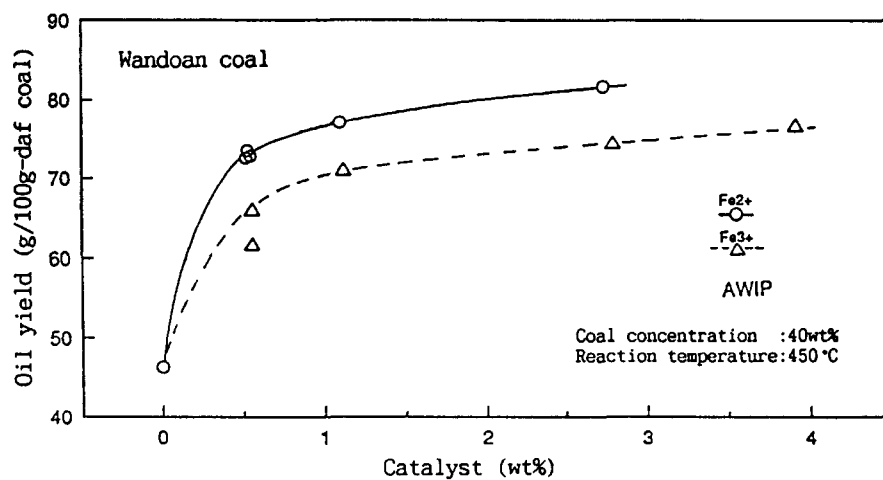


Fig.1 Oil yield vs. amount of catalyst
(Comparison between Fe²⁺ and Fe³⁺ as

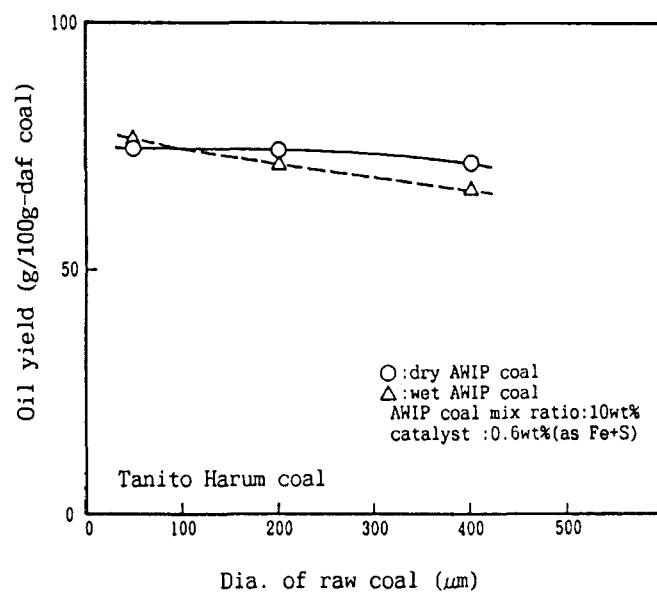


Fig.2 Oil yield vs. diameter of raw coal
to be Fe-loaded

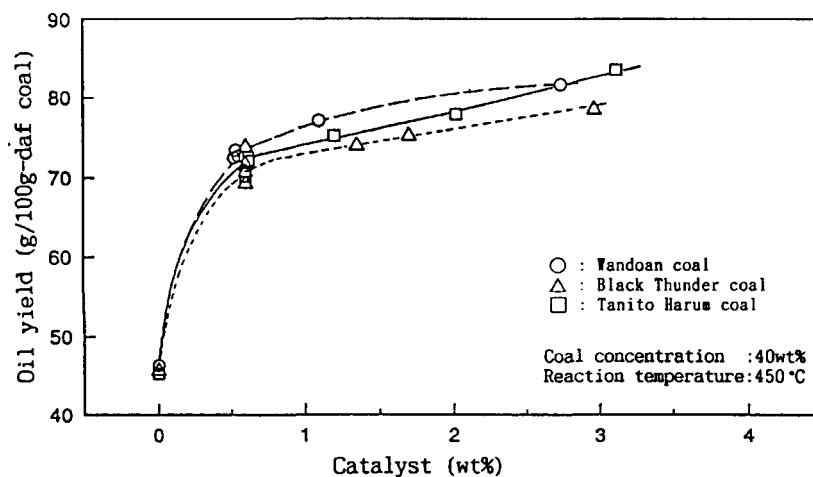


Fig.3 Oil yield vs. amount of catalyst
(Comparison between coals)

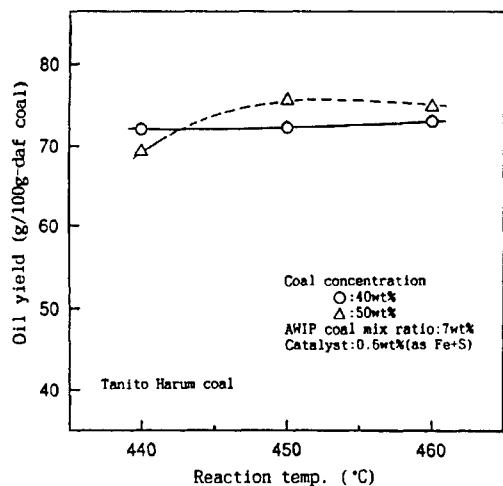


Fig. 4-1 Oil yield vs. reaction temperature
(Comparison between coal conc., batch test)

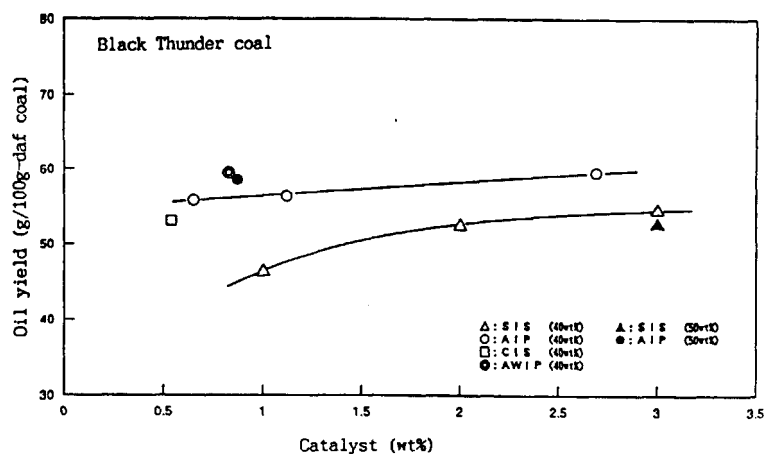


Fig. 4-2 Oil(HS) yield vs. reaction temperature
(Comparison bet. catalysts, continuous test)

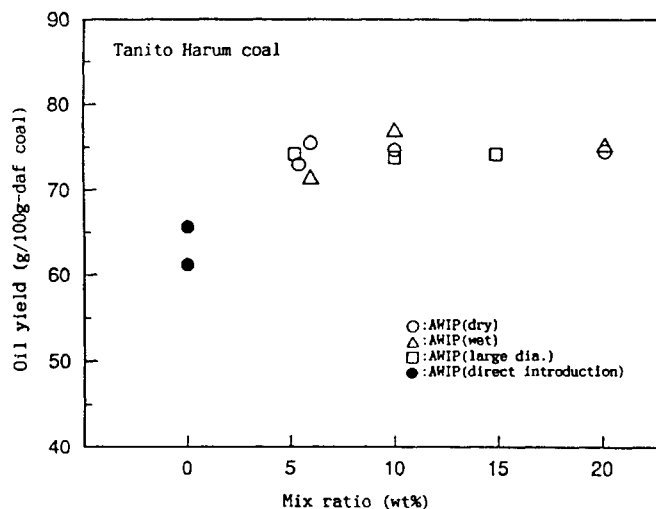


Fig. 5 Oil yield vs. mix ratio of AWIP coal
(Catalyst: 0.60-0.64wt% as Fe+S)

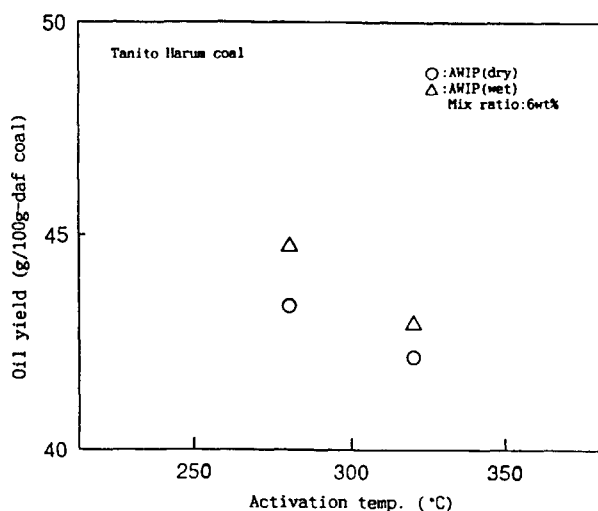


Fig. 6 Oil(450°C) yield vs. activation temperature
(AWIP dry/wet, continuous test at 450°C)

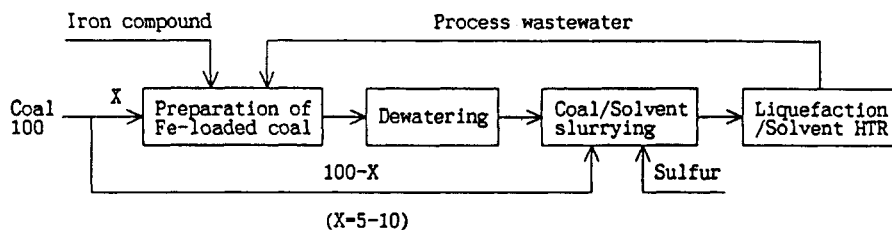


Fig. 7 Flow diagram of AWIP preparation and liquefaction system

Coal Liquefaction under Advanced Conditions

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New Energy and Industrial Technology

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Objectives

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

Work Program

- (1) Liquefaction reaction of finely pulverized coal:
Experimental investigation of the effect of particle size on the liquefaction of coal.
- (2) Basic studies on the technologies for mild conversion of coals: Active pretreatment of coals by the media of the nonequilibrium plasmas and the microwave, and heteroatom removal and dearomatization of condensed aromatics by the plasma hydrogenation and hydrocracking.
- (3) Basic studies on the structure of low rank coals and their liquefaction reactivities: Structural analysis of hydrogenated products derived from various natural organic materials and hydrous pyrolysis of plant constituents.
- (4) Biotreatment of sulfur containing compounds in coal-derived oil: Advanced biological desulfurization and development of energy saving biological desulfurizing methods.
- (5) Investigation of coal liquefaction residues: The genesis and fate of carbonaceous materials during coal hydrogenation and the significance of such materials in the operation of continuous coal hydrogenation reactors.

Summary (1993-94)

1. For FY 1993

- (1) Liquefaction reaction of finely pulverized coal
The effect of particle size on the liquefaction of coal was experimentally investigated. It was provided that the higher HS yield was obtained with the finely pulverized coal sample. The reason of obtained results was discussed.
- (2) Basic studies on the technologies for mild conversion of coals
For the estimation of influence of the microwave electromagnetic field, the coals treated by the microwave and helium and hydrogen plasma field were subjected to elemental analysis, FTIR spectrometry, ESR measurement, heat of adsorption of methanol by FMC.
- (3) Basic studies on the structure of low rank coals and their liquefaction reactivities
The liquid phase alkylation of biphenyl with alkenes was studied over zeolites with twelve-membered pore openings, H-mordenite, HY, and HL.
- (4) Biotreatment of sulfur containing compounds in coal-derived oil
Twenty bacteria strains, which were able to degrade more than 100 ppm of 4,6-dimethyl-dibenzothiophene. Thiobacillus thioparus TK-m was grown on thiosulfate first to obtain a large amount of cell biomass in a short time, and then on dimethyl sulfide to

induce the production of the thio-degrading enzyme.

(5) Investigation of coal liquefaction residues

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 1994

(1) Liquefaction reaction of finely pulverized coal

The effect of the Fe₂O₃-sulfur catalyst concentration on the liquefaction of finely pulverized coal and conventional particle size coal (-100 mesh) was experimentally compared. Finely pulverized Taiheiyo coal (average particle diameter, 4 μ m) was prepared using a slurry jet mill. Conversions of the two coals, on a daf basis, calculated from THF insolubles, were similar (95-96 wt%) in either cases. However, the finely pulverized coal showed a much higher HS yield of 45.1 wt%, while the conventional particle size coal had only 39.5 wt% HS yield at catalyst concentration of 4.4 wt%, daf coal. Similar differences in HS yield were seen at lower concentration of iron catalyst. The higher HS yield obtained with the finely pulverized coal sample may be attributed to the enhanced contact among the components of the coal-catalyst-solvent slurry, resulting in lower amounts of retrogressive products. To examine the effective dispersion among the components in the slurry for liquefaction, the effect of surfactant addition on the yield of liquid product and the conversion from liquefaction was examined. In the case of finely pulverized coal, the HS yield increased to 52.4 wt% by addition of nonion mixed with anion surfactants, while the HS yield, obtained without surfactant, was 45.1 wt%. The increased conversion and HS yield from the -100mesh coal with the surfactant were also observed as similar as the finely pulverized coal. Finely ground coal has attracted attention because of its favorable liquefaction behavior. The gas production behavior during pyrolysis that reflects the oxidation degree of coal was also studied. The gas production behavior of finely ground coal during pyrolysis in nitrogen atmosphere was almost same as that of raw coal with few hundred micron in diameter. In hydrogen atmosphere, finely ground coal, however, produced less amount of hydrogen sulfide in relatively high temperature range than raw coal. The change in hydrogen sulfide production indicates small degree of oxidation of finely ground coal.

(2) Basic studies on the technologies for mild conversion of coals

Tanito Harum and Yallourn coals supplied by Kobe steel industry were tested. These coals treated with helium plasma and subjected to elemental analysis, FTIR measurement, heat of adsorption of methanol by FMC technique, T₁ and T₂ measurement by spin echo technique. In order to investigate the effect of plasma treatment, reaction activity of the coals treated were determined by an autoclave test. Some results indicate that OH groups of the coals were drastically eliminated. This is caused by liberation of hydrogen bondings of the coals. However, the liberation of the hydrogen bondings can not be concluded in the connection with the progress of the reactivity in the liquefaction.

(3) Basic studies on the structure of low rank coals and their liquefaction reactivities

In order to better understand the chemical structures and reactivities of low rank coals, cellulose and Japanese red pine were thermally decomposed in water at 200 C, and the chemical structures of the residual products and their hydrogenation products were compared with those of Morwell brown coal and coalified wood. Solid state ^{13}C -NMR analyses of the hydrous pyrolysis residues showed that carbohydrate structure in cellulose disappeared after 20 hours at 200 C and the residual product had similar amounts of aromatic and aliphatic carbons. The contents of carbon, hydrogen, oxygen, and oxygen functional groups of the residual product from cellulose were similar to those of Morwell brown coal, and their contents of the residual product from Japanese red pine were similar to those of Morwell woody brown coal. The major hydrogenation products of cellulose were hexane, methylcyclopentane, and C1-C5 hydrocarbons. The hydrogenation of the hydrous pyrolysis residue from cellulose provided cyclohexanes, polycyclic compounds, and nondistillable material which were little produced in the hydrogenation of cellulose. These results would show that cellulose was converted by hydrous pyrolysis at 200 centigrade into the polymeric material having similar chemical structure to Morwell brown coal.

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

(a) Advanced biological desulfurization

Microorganisms degrading dibenzothiophene (DBT), a model substrate for heterocyclic sulfur compound in crude petroleum or carbonized component of coal, under the microaerobic conditions, a nitrogen gas-substituted conditions, were tested. Six Gram negative bacteria, which have shown the ability of degrading dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DM-DBT), were characterized. Judging from morphological, cultural and chemically classified characterization, the strains were identified.

(b) Development of energy saving biological desulfurizing methods

At first the influence of pH on the activity of the enzyme was determined. The enzyme had enough high activity at the pH range of 6.5 to 9.0. The optimum pH was from 7.5 to 8.5. Next, the effect of inhibitors on the activity was studied. Sulfate ion, zinc ion, nickel ion, cadmium ion, or EDTA had no effect on the enzyme. Cupric ion was shown to inhibit the enzyme activity. Then, the degradation rate of various mercaptans by the enzyme was estimated. Ethyl mercaptan was degraded as fast as methyl mercaptan. However, the degradation rate of n-propyl mercaptan and n-butyl mercaptan was half, and that of benzyl mercaptan was less than one tenth of that of methyl mercaptan. The degradation rate of n-propyl mercaptan and n-butyl mercaptan decreased as the degradation time was longer. Though one of the products of the reaction, aldehyde, was supposed to inhibit the activity of the enzyme, aldehyde was found to have no inhibition on the enzyme activity.

(5) Investigation of coal liquefaction residues

The hydrogenation characteristics of partially oxidized or

partially carbonized coal holds significant interest as such material could constitute an important factor in the formation of blockage materials in continuous coal hydrogenation reactors. The occurrence of coaly particles of very high reflectance contained in carbonaceous deposits of a bench scale continuous reactor has been reported. These particles were suspected to have been derived from partially oxidized or carbonized coal. If liquid products from partially oxidized coals are the source of coke, such material in its intermediate progression to coke may act as a binder to form aggregates of solid residues, which would accelerate blockage of reactor tubes. In order to investigate these possibilities, a series of batch autoclave experiments and subsequent microscopic observation of residues was carried out. In contrast with the homogenization effect of carbonization, the oxidation created a new form of heterogeneity, that is oxidation in marginal parts and carbonization in core parts of the vitrinite particles. It was illustrated that pre-oxidation gives more complicated effects than pre-carbonization on the subsequent hydrogenation of the treated vitrinite particles. Partially carbonized and oxidized vitrinite is likely to become massive vitroplast and then massive anisotropic particles without passing through the liquid phase. If such particles accumulate in a reactor while they are still plastic, they may coalesce. This in turn may promote the blockage of small diameter reactor tubes or enhance the formation of solid deposits in large diameter reactors.

Future Tasks

(1) Liquefaction reaction of finely pulverized coal

Based on the effect of size distribution on liquefaction yield and the thermal reactivity of finely pulverized coal, liquefaction tests are to be performed under various conditions with different catalyst concentrations. In addition, liquid yields will be investigated under the hydropyrolytic conditions.

(2) Basic studies on the technologies for mild conversion of coals

In order to investigate a relation between structural modification of plasma treated coals and their reactivity, the radical distribution and relaxation of treated coal are to be measured using ESR. Structural modification of coals will be analyzed from measurements of heat of adsorption and desorption of various solvents against treated coals and their swelling behaviors.

(3) Basic studies on the structure of low rank coals and their liquefaction reactivities

Chemical structures of low rank coals by decomposing them under mild conditions and by analyzing produced liquids.

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

Advanced biological desulfurization and development of energy saving biological desulfurization methods are succeeding and have been progressed.

(5) Investigation of coal liquefaction residues

Conversion process of liquid products to mesophase is to be investigated through autoclave experiments. A possibility of re-hydrogenation of carbonized residue obtained from continuous reactor is to be investigated, as well.

APPLICABILITY STUDY OF COAL LIQUEFACTION TECHNOLOGY

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OBJECTIVES

- (1) To investigate the applicability of coal liquefaction technology to various foreign coals through the international cooperation in R & D, and to receive and cultivate the engineers from proper countries.
- (2) To contribute toward the domestic and overseas progress of coal liquefaction technology through interchanging the information between the advanced countries.

WORK PROGRAM

- (1) Applicability study

Liquefaction characteristics, as well as the general analyses, are to be carried out using both Indonesian and Russian coals as the promising coals for liquefaction. Field survey is also to be made in these countries.

- (2) International exchange and investigation of coal liquefaction technology

Investigations are to be carried out on the trend of technology and the new technology of coal liquefaction. Expert meeting, field survey and invitation of engineers are to be held between Indonesia.

SUMMARY

1. Up to FY 1993

a) Russian Republic

We visited both Fossil Fuel Institute, IGI, in Moscow, and the coal liquefaction plant(ST-5) in Tula city in 1992 on purpose of exchange and investigation of coal liquefaction technology. We investigated the situation of R & D of coal liquefaction in Russia and discussed the possibility of technological cooperation. In 1993, we visited above institutes, as well as International Center of Business Cooperation in Kurasnoyarsk city and Borodin Open Cut Mine on purpose of exchange, investigation of coal liquefaction technology and field survey. Agreement was made in this visit to transport three kinds of coal mined in Kansk-Achinsk area.

b) Republic of Indonesia

BPPT of Republic of Indonesia requested NEDO on the technological cooperation of coal liquefaction in 1993. In January 1994, MOU of research cooperation was interchanged between NEDO and BPPT, describing several activity plans such as expert meeting, invitation and cultivation of Indonesian engineers in Japan, cooperative field survey and so on. In March 1994, the first survey was held in Sumatera island, where we obtained both three kinds of coal samples and the data of the coal deposits and distributions of coal seams.

2. For FY 1994

(1) Applicability study

① Field survey and sample collection

a) Indonesia

1 ton coal sample was collected from south Banko area located in the southern part of Sumatera island for the use of BSU operation and small amount of samples were also collected around this area. Organizations of Indonesian Government concerned fully cooperated in this field survey and sampling work.

b) Russia

To investigate the liquefaction characteristics of Russian coal, three kinds of coal sample were transported to Japan from Kansk-Achinsk area under the cooperation of an institute of Russian Academy of Science.

② Analysis results of coal samples

a) Indonesian coal

Indonesian coal samples (South Banko, Central Banko and Banjarsali) contained relatively small amount of ash (1.4~2.1wt%). Water and oxygen content of these samples was also low (15~20wt%). H/C ratio of these coals was higher than ordinary brown coal. Si and Al content in ash was high and Na and Mg was low for these samples. Cl content was negligible.

b) Russian coal

Water content of Russian coal was at the same level of Indonesian coal (16~18wt%) but ash was at higher level (5~10wt%). Ash of these samples contained much amount of Fe, Si and Ca. Na content was low and Cl was negligible.

③ Coal properties and slurry viscosity

Specific surface area of Australian, Indonesian and Russian brown coal

measured by BET method using nitrogen gas was at same level. Pore volume of Indonesian coal measured by mercury penetration method was lower than those of Australian and Russian coal. Slurry viscosity was measured varying solvent/coal ratio at 50°C. Viscosity of Indonesian and Russian coal slurry was lower than that of Australian coal. This result indicated that low solvent/coal ratio must be adaptable in the case of Indonesian and Russian coal.

④ Thermal decomposition behavior

Thermogravimetric change of Indonesian south Banko coal and Russian Beryozovo coal showed same tendency. During heating up, gas generation was observed around 300 °C and was at maximum level between 400 ~450 °C. Generation of CO₂, H₂O and CO gas also showed same behavior for these samples.

Coal samples were heated up to 450°C in high temperature ESR spectrometer under nitrogen atmosphere. Radical concentration was measured during heating up and at 450 °C. Though radical concentration of South Banko coal at room temperature was relatively high, increase of radical concentration during heating up was relatively small. Rapid increase of radical concentration started around 400°C was due to the thermal decomposition of coal. And this behavior coincided with the result of TG - MS.

⑤ Liquefaction characteristics

Liquefaction characteristics of 4 kinds of Indonesian coal and 3 kinds of Russian coal were evaluated using autoclave. 1-methylnaphthalene and γ -iron oxyhydroxide was used as the solvent and catalyst respectively. Russian Borodino coal and Beryozovo coal showed good liquefaction activity and Beryozovo coal was best among Russian coal.

In the case of Indonesian South Banko coal, amount of CO₂, H₂O and CO was small and high oil yield of 70~75wt% was expected from the total value of distillate and CLB yield.

South Banko coal was evaluated using BSU. Creosote oil was used as the solvent. Solvent/coal ratio, reaction temperature and pressure of this operation was 2.0, 450°C and 14.7Mpa respectively. Gas and CLB recycle were not adapted. Almost same result as autoclave test was obtained from this evaluation. And BSU operation was carried out without trouble.

It was confirmed by high temperature and high pressure viscometer that slurry viscosity of South Banko coal was decreased during heating up to reaction temperature.

(2) International exchange and investigation of coal liquefaction technology

① Cooperation with Indonasia

Based on the MOU interchanged between NEDO and BPPT, cooperative field survey, coal sample collection, evaluation of Indonesian coal, invitation and cultivation of Indonesian engineers and expert meeting were carried o u t .

FUTURE TASKS

- (1) Evaluation of South Banko coal is to be continued in more detail.
- (2) International exchange and investigation of coal liquefaction technology
- ③ Proper works written in MOU are to be continued.

Preliminary survey on the Mongolian Coal

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Objectives

This survey is to investigate the status of resources and energy, infrastructure, system organization of research and development, and suitable coal conversion processes in Mongolia. Moreover, the necessity of the guidance for improvement and diffusion of coal utilization technologies is also investigated.

Work Program

- (1) Investigation of Governmental policy for Energy, resources, technical potentiality by published data
- (2) Preliminary evaluation test of Mongolian coal
- (3) Evaluation of the applicability of liquefaction technology
- (4) Invitation of Mongolian engineers
- (5) Visiting Mongolian research organization for survey of present status

Summary

1. Up to FY 1993

Resources, energy status, suitable coal conversion technologies and requirement of the technical assistance were studied based on literature and on-the spot survey in 1993. Moreover coal analysis as preliminary tests were conducted over the coals provided by Mongolia.

(1) Resources and Energy status of Mongolia

Although all petroleum products, 600,000 tons a year, are imported, 10 billion tons of coal deposits seems to be existing and 6 million tons of coal are produced in a year. Almost all the product is consumed only power stations.

(2) Preliminary tests of Mongolian coals

It is said that ash content of Mongolian coals are high and sulfur content are low. On the basis of the analysis and liquefaction tests, it was found that the coals provided by Mongolia were two kinds of brown coals and one sub-bituminous coal and that characteristics of these coals were similar to those of the coals that seems to be suitable for coal liquefaction.

(3) Evaluation of suitability for coal liquefaction

It was concluded that low temperature carbonization technology is suitable for producing liquid fuels from coal, judging from the present status of transportation and power generation fuels in Mongolia, contribution of

decreasing import of petroleum products, results of the coal analysis and the data of a demonstration plant having been operating in USA.

(4) Research and Development Potential and Organization

For accepting the technology transfer from developed countries, it is important for engineers and researchers to have a high educational level. Therefore, educational system and a period devoted to coal utilization technology were investigated. In Mongolia, an entering rate to primary schools is 100 % and literacy rate is 89%. Moreover, in 1992, there are 28 universities and 1,8000 students enrolling in universities.

2. For FY 1994

Coal analysis, and liquefaction and carbonization tests were conducted as preliminary investigation for evaluating liquefaction characteristics, and besides, Mongolia engineers were invited and visited national and private research organizations for discussing coal utilization progress. Moreover, on the spot survey was conducted for investigating recent energy status and visiting related organizations in Mongolia.

(1) Situation of Mongolia

a. Social and economics situation

In accordance with the democratization of the politics, an economic reform has progressed rapidly. Although the socialism and planned economy have been changing to democracy and market economy, respectively, Mongolia is in a chaotic situation on their economy. Twenty-five percent of the population concentrates in Ulaanbaatar of the capital and employment rate for engaging in stock farming is 36 % (on 1992).

Although they have a large area of land, the population density is too low and transportation facilities are not well organized. On the other hand, educational system is well prepared and literacy rate is more than 97 % and there are 28 of universities in the country.

b. Energy situation

As there is no petroleum production, whole amount of petroleum consumed (0.6 to 0.7 million tons/y) is imported from Russia. However, it is said that estimated amount of coal deposits is 10 billion tons and that the amount is in top ten in the world. Eighty percent of energy is supplied by coal.

In the capital and large cities, central energy system is adopted and electricity, steam and hot water are supplied by the system. On the other hand, residents in rural area and nomads use electricity from small sized diesel power generators, coal and dung for cooking and heating.

(2) National Development plan

a. Long term plan

After break of a five year plan, a three year plan has been conducted since 1993. Moreover, a new long term plan for coal utilization is in consideration and will start from 1995.

b. Energy development plan

Since Mongolia is depending on Russia to supply petroleum, they feel uneasy about it. Therefore, the following new energy plan is progressing under the collaboration of developed countries.

- (a) Mongol Petroleum Project for investigation of domestic petroleum resources
- (b) Mongol Gasoline Project for development of producing liquid fuel from coal
- (c) Master plan regarding coal (renovation and rehabilitation of coal mines, comprehensive coal utilization plan)

(3) Status of research and development

a. Education

Educational system in Mongolia consists of four organizations such as general educational institutions, higher educational institutions, special educational institutions and infant educational institutions. Number of students enrolling in these institutions is more than 420,000 and is equivalent to 20 % of the population.

b. Research institutes and fields for energy related development

As shown in Table , there are following research institutes related energy development in Mongolia.

Table . Research Institute in Mongolia

Name of Institute	Fields of Work
National Research Center of Chemistry and Technology of Coal	Coalgasification and Liquefaction Smokeless fuel production
Institute of Energy	Supplyplan for Electricity, steam and Hot water Rehabilitation plan for power station
Mining Institute	Coal mining, briquette production Coal analysis for power station
Institute of Chemistry	Coal science and Chemistry
Institute for Renewable Energy	Solar, Wind power, Geothermal and Hydraulic Energy

c. Research facility

National Research Center of Chemistry and Technology of Coal (NRCCTC) has only facilities for elemental analysis and proximate analysis. They have not a facility for development of coal utilization technologies.

d. Research personnel and research item

- (a) Each institute is controlled by Science Academy or each ministry and has almost 18,000 research personnel. National Research Center of Chemistry and Technology of Coal (NRCCTC) has 34 research personnel and several personnel out of 34 graduated engineering colleges of Russia.
- (b) Two engineers were invited to Japan and learned coal utilization technologies through observation of facilities, acquisition of technical information, study of evaluation experiments.
- (c) Twenty-two reports regarding coal related research were found in the survey at Japan. There are 7 resource related reports, 7 coal liquefaction, 5 coal science and 5 trace element of coal and almost all the reports were born from collaboration work with the former Soviet Union.
- (4) Preliminary analysis and Evaluation of Mongolian Coal
- a. Proximate and Ultimate analysis

Table 1. and 2. show the results of the ultimate analysis for Uvdughudag, Hootiin Honhor and Shivee-Ovoo coal with the results of Wyoming coal as reference.

Table 1. Results of proximate analysis under equilibrium moisture basis (wt %)

Kind of coal	Uvdughudag	Hootiin honhor	Shivee-Ovoo	Wyoming
Moisture	21.1	16.8	15.4	25.80 **
Ash	8.6	15.4	9.0	7.02 *
Volatile Matter	33.9	33.7	35.5	43.78 *
Fixed Carbon	36.4	34.1	40.1	49.20 *
Calorific Value daf base cal/g	6,470	7,150	6,730	7,034
Sulfur(daf wt%)	3.78	1.02	1.18	0.54 *

*:dry basis **: as received

Table 2. Results of Ultimate analysis (daf basis wt. %)

Kind of coal	Uvdughudag	Hootiin honhor	Shivee-Ovoo	Wyoming
Carbon	67.56	74.60	73.83	75.41
Hydrogen	4.70	5.01	4.47	5.03
Nitrogen	0.74	2.29	0.77	1.03
Oxygen	23.74	17.34	20.92	18.45
Combustible S	3.2	0.76	0.01	0.07

b. Maceral group and reflectance

Table 3. shows the analysis results of maceral components of Mongolian coals.

Table 3. Results of Maceral analysis and Reflectance (vol. %)

Maceral Group	Uvdughudag	Hootiin honhor	Shivee-Ovoo	Wyoming
Vitrinite	83.9	85.4	63.9	83.0
Exinite	1.2	3.0	1.0	4.4
Total Reactive	85.1	88.4	64.9	87.4

Inertinite	7.8	0.6	28.9	9.0
Mineral Matter	7.1	11.0	6.2	3.6
Total Inert	14.9	11.6	35.1	12.6
Reflectance				
Mean	0.32	0.47	0.34	n.a

c. Liquefaction test of Mongolian coal

Liquefaction tests over three kinds of Mongolian coal samples were conducted using autoclave reactor with Tetraline and synthetic pyrite.

Experimental conditions were based on the conditions of the NEDOL process.

The test results are indicated in Table 4.

Table 4. Product yields (wt% daf coal basis)

	Uvdughudag	Hootiin honhor	Shivee-Ovoo	Wyoming
Product Gas	17.53	16.00	18.71	17.26
Product water	14.91	12.51	13.24	11.45
Oils	55.56	55.29	42.30	56.57
Asphaltene	10.12	13.31	11.66	11.03
Preasphaltene	1.57	3.03	3.12	3.93
Unreacted Coal	4.33	4.40	15.46	3.90
Total Products	104.02	104.60	104.49	104.14
Hydrogen Cons.	4.02	4.60	4.49	4.14
Conversion	95.67	95.60	84.54	96.10

As shown in Table 4, it was found that almost same results as those of Wyoming coal were indicated in coal liquefaction yields of the Mongolian coals except Shivee-Ovoo coal. Low oil yield and high unconverted coal yield of Shivee-Ovoo were seemed to be caused by high content of inert material shown as Table 3.

d. Low temperature carbonization test

Carbonization test was conducted over Shivee-Ovoo coal sample on 6 °C/min. of heating up rate, atmospheric pressure and 550 °C of carbonization temperature. Product yields and properties of product char are indicated in Table 5 and 6.

Table 5. Product yield (wt% dry base)

Product Char	Product Oil	Product water	Product Gas	Loss	Total
63.17	10.50	8.36	10.97	7.00	100.00

Loss shown in the above Table was mainly water and light hydrocarbons associated with exhaust gas.

Table 6. Product Char characteristics (wt% dry base)

Volatile Matter	Fixed Carbon	Ash	Carbon	Hydrogen	Nitrogen	Oxygen	Sulfur
18.72	66.94	14.34	89.25	3.37	1.05	4.67	1.66

Note : Ultimate Analysis based on wt. % daf coal basis.

Low product yield and high gas yield seemed to be caused by high content of functional oxygen group and inert materials. Sulfur content of product char was 1.68 % and some treatment process will be required for usage of product char as low pollution fuel.

(5) Study for Applicability to liquefaction technology

Results of the study for applicability of liquefaction technologies are summarized as follows based on the results of coal analysis and liquefaction tests.

- a. Mean reflectance of three coals is below 0.5 and this value indicates that the coals are easy to be liquefied. The order of the reflectance is as follows.

Hootiin Honhor > Uvdughudag > Shivee-Ovoo

The reflectance of Hootiin Honhor is slightly high and involved in subbituminous coal rank. However, Uvdughudag and Shivee-Ovoo are classified in brown coal rank.

- b. It is indicated that coals containing much Inertinite has a high yield of coke in a pyrolysis process.
- c. Reactive like Vitrinite and Exinite are easy to be liquefied. The reactive content of Shivee-Ovoo is about 65 % and the others are over 85 %. This means the coals except Shivee-Ovoo are easy to be liquefied.
- d. In a view point of product yield, liquefaction characteristics are arranged in order as follows.

Uvdughudag > HootiinHonhor > Shvee-Ovoo

Future Tasks

The following tasks are required for meeting the demands of Mongolian energy development based on the survey conducted.

1. There are abundant coal resources and personal having high potential. However, assistance from foreign countries is required for the energy development judging from the country status.
2. As there is no enough apparatus and equipment for research and development, assistance from foreign countries is inevitable
3. Level-up of the technical performance of researchers and engineers is required. The methods of the level-up are summarized as follows.

- a. To train researchers and engineers by providing technical information, dispatching trainers and inviting trainee for learning research methods and evaluation methods of the research results.
 - b. To provide the assistance for drawing up development plan and repletion plan of facility over coal utilization technology.
4. Analysis of the other coals rather than coals tested are required for evaluation of the Mongolian coals over liquefaction adaptability. In this investigation, one out of three kinds coals was placed at liquefaction tests. Therefore, the further investigation is required to select suitable coals for liquefaction through liquefaction tests.

5. DEVELOPMENT OF COAL-BASED HYDROGEN PRODUCTION TECHNOLOGY

(1) Design, Construction and Operational Research of a Pilot Plant for Coal-Based Hydrogen Production

Design, Construction and Operational Research of
a Pilot Plant for Coal-Based Hydrogen Production

New Energy and Industrial Technology
Development Organization (NEDO)

Objectives

The objective of the research and development (R&D) aims to produce hydrogen, as one of more clean energies which will be expected to increase the demand for wider applications such as for petroleum refining, chemical raw materials, fuel and coal liquefaction etc., from coal by gasification. The design and construction of the pilot plant was completed by 1990. And the operational research of the pilot plant was started since FY 1991.

Work Program

1. The development target for the pilot plant operation :
 - (1) Carbon conversion : More than 98%
 - (2) Cold gas efficiency : More than 78%
 - (3) Continuous operation time : More than 1,000 hours
 - (4) Gasifying pressure : 30kg/cm²g
2. The work program of the FY 1994:
 - (1) Study of used materials in the pilot plant
 - (2) Collection of the achievements and the results of development of the coal-based hydrogen production technology
 - (3) Proceeding for applications of the laws and regulations

Summary

1. Up to FY 1993

In FY 1985, the basic conceptual design of the pilot plant has been carried out for the purpose of developing a basic constitution of the pilot plant.

In FY 1986, the basic design and the primary detailed design have been carried out. And composed equipments of supporting section were fabricated. The pilot plant site was prepared and the diverted equipments from the Hybrid gasification plant have been taken care of.

In FY 1987, the design conditions and specifications for equipments, piping and design of the control systems for each section have been carried out for the secondary detailed design. And some equipments were fabricated. The diverted equipments were fabricated after transferred.

In FY 1988, some equipments of the gasification section and a part of

piping on the pipe rack including steel structural supports have been designed as for the tertiary detailed design.

The main equipments such as a gasifier and a heat recovery boiler were fabricated and installed.

In FY 1989, some equipments of the gasification section and a part of piping on the pipe rack including steel structural supports have been designed as for the fourth detailed design.

In FY 1990, some equipments of the gasification section and utility facilities were fabricated and installed, and the pilot plant was completed. Mechanical running test and part of trial operation were performed on all of its sections and facilities.

In FY 1991, the following were performed: operational research of the pilot plant, research on gasification of liquefied coal residue, and proceeding for applications of the laws and regulations.

In FY 1992, the operational research and the proceeding for applications of the laws and regulations were performed.

In FY 1993, the further operational research and proceeding for applications of the laws and regulations were performed.

2. For FY 1994

(1) Study of used materials in the pilot plant

In order to the design and evaluation of operation for the future demonstration plant, study of used materials in the pilot plant were carried out.

(a) Inspections and Materials Sampling

Before the materials sampling the inspection of the pilot plant were carried out and the material cut out points were decided. Shell thicknesses of the pressure vessels at the gasifier, waste heat boiler, cyclones and several hoppers were measured. Those thicknesses were compared with the values at turn around inspection, that confirmed the durability of the all pressure vessels. Also the durability of the tube sheet of the heat exchanger was inspected by penetration examination.

Replica sampling of micro structure on the surface of high temperature parts of hoppers in the char recycle system. Several parts sampling were performed after the site inspection and those samples were sent to the laboratory for analysis.

(b) Sample Analysis and Observation

Samples were generally inspected as a state of arrival at laboratory and cleaned the surface. Many data were gathered by thickness measurement, micro and macro structure inspection, tensile test, EPMA and so on.

Inspection results of main equipments are as following.

① Gasifier

Refractory of the gasification wall had been exposed in the whole three years. Its lower part thickness was slightly thin compared with the upper part because of high temperature. However wall itself was firmly sustained with studs and not observed falling off. Developed refractory material verified its reliability.

Refractory material of the gasifier bottom used through RUN-8-1 to 9-2 (1,468 hours, covered with iridium on the slag and gas taps) and RUN-9-3 (109 hours, without iridium cover) were inspected. After 1,149 hour the former portion was observed only melting of the iridium cover on the gas tap, however all taps and bottom floor surface were severely eroded after 1,468 hours. These portions might be exposed in the relatively high temperature atmosphere. As to the later refractory, the portions of the taps above bottom floor surface were eroded. However floor itself was not so severely eroded. Scale of iron sulfide and oxide were observed on the surface of the water cooled tubes, however tube thicknesses were not reduced.

② Waste Heat Boiler

Corrosion and thickness reduction of the boiler tubes by sulfurization and oxidation were observed on the surface. The thickness reduction was observed.

This corrosion was inferred mainly due to down time that suggests corrosion protection during down time is important.

③ Cyclone

The thickness reduction was observed due to high temperature gas attack and erosion by solid particles.

④ Water Washing Section

Few SCC were observed at venturi scrubber etc.

⑤ Piping

Erosion at the bends of coal feed piping was observed.

⑥ In-plant Test Coupon

In results of the comparison with turnaround sample, corrosion was divided into two categories, high temperature gas attack and down time corrosion.

Corrosion rates identified to the chromium content in the several test coupons, which will greatly assist material selection in next stage.

(2) Collection of the achievements and the results of development of the coal-based hydrogen production technology

Conceptual design and feasibility study of the hydrogen production and fuel cell (MCFC) use were performed.

Evaluation of the nine-year HYCOL technology development was executed and results were summarized in the final report.

- (a) Basic technology feature of the HYCOL coal gasification, entrained bed with one-chamber and two-step spiral flow, was verified. And many useful technologies, dry coal feed system, hot direct char recycle, slag self-coating and hot gas self-circulating type slag tap etc. were developed.

These means HYCOL technology is established at the level of pilot plant.

- (b) All targets of the pilot plant operation; carbon conversion 98% or more, cold gas efficiency 78% or more, continuous operating 1,000 hours or more, gasifying pressure 30kg/cm²g, were achieved at 99%, 79%, 1,149 hours, 30kg/cm²g respectively. These results give great promise of level up to the one of most excellent coal gasification technology in the world.

Further high level results will be obtained on the large scale demonstration plant.

- (c) HYCOL technology should be polished up at demonstration stage not only for the hydrogen production but electric power generation.

(3) Proceeding for applications of the laws and regulations

According to the suspension of operation and abolition of the pilot plant, notification to relevant government offices related to the following laws and regulations were performed and accepted.

- ① Air Pollution Prevention Laws
- ② Water Pollution Prevention Laws
- ③ Law of Wastement Treatment
- ④ The anti-noise Law
- ⑤ Labor Safety and Health Law
- ⑥ Munincipal Fire Prevention Regulations
- ⑦ Electricity Enterprises Law
- ⑧ High-pressurized Gas Treatment Regulations
- ⑨ Disaster Prevention and Relief law

6. DEVELOPMENT OF TECHNOLOGY FOR ENTRAINED FLOW COAL GASIFICATION

(1)Development of Entrained Flow Coal Gasification Power Generation Plant

(2)Coal Selection for Conversion

(3)Development of Coal Conversion Technology Data Processing System

Development of Entrained Flow Coal Gasification Power Generation Plant
Dr. Shigeru Ueda
Director General of Clean Coal Technology Center, New Energy and
Industrial Technology Development Organization (NEDO)

Objectives

To develop, as a means to enlarge coal utilization, an entrained flow coal gasification combined cycle power generation system which is considered to provide for improved thermal efficiency and environmental acceptability, and to have excellent load following characteristics, a wide scope of applicability for different coal types, and adaptability for larger capacities. Also conducted will be, aside from element studies, design, manufacture, and installation of a pilot plant followed by test adjustments, adjustment operation and overall operation and test studies.

Work Program

1. Element Studies

- (1) Study through gasification tests using a 2ton/day gasifier.

Data of gasification and operation characteristics are obtained, using a 2ton/day gasifier, for particular coal types intended for the pilot plant. These data are reflected on the conditions of operation tests.

- (2) Study on a large size gas turbine combustor for the demonstration plant.

A life size combustor for low calorie gas necessary for the development of a large gas turbine for the demonstration plant is designed and manufactured, and compatibility thereof to the demonstration plant is evaluated through full pressure combustion tests using actual gas from the pilot plant.

- (3) Study on simulation of combined cycle power generation systems.

To establish a total control system to ensure safe and optimum operation of the pilot plant, operation characteristics of the plant as a whole are determined and the control system verified through simulation.

At the same time, a simulation program for combined cycle power generation system is constructed with which to estimate the load following characteristics of combined cycle power generation system.

- (4) Study on slag utilization technology

Study is conducted on the effective utilization of slag discharged from the coal gasifier including tests to determine fundamental physical properties of slag.

- (5) Aside from the above, fundamental tests are also conducted in relation to the safety of gasifier and others.

2. Construction, Adjustment Operations and Overall Research Operation of Pilot Plant

Construction and installation at site are conducted for each component facility. After

installation, tests and adjustments for each equipment, adjustment operations and overall operation and test studies are conducted.

- Gasifier facility (pressurized, two-stage entrained flow slag tap type)
- Dry type gas clean-up facility (two-stage fluidized bed type desulfurization unit, granular bed type dust remover)
- Gas turbine (open simple cycle, single shaft type)
- Full pressure and full size combustor testing stand
- Safety and environmental control facility (gas treating equipment, denitrification unit using dry ammonia selective catalytic reduction method, desulfurization unit using wet limestone-gypsum method)
- Total control system (including electric and telecommunicate facilities)
- 66kV/6.9kV indoor switchgear
- Civil engineering and construction facilities
- Common facilities

3. Feasibility Study Concerning Demonstration Plant

For a demonstration plant scale of coal gasification combined cycle power generation, research on its conceptual design is conducted.

Summary [FY 1986-1993]

FY 1986 Out of the ten-year plan of this project, the first five years were spent for design and construction of the pilot plant.

In the first year, 1986 basic design of the pilot plant was conducted, with element studies started simultaneously.

FY 1987 While element studies were continued detailed design of the pilot plant was developed with results of element studies reflected thereon.

Manufacture of some equipment was also started.

With construction permit received in January, preparation for civil engineering work started at site.

FY 1988 Element studies were conducted, and results thereof reflected on the detailed design of pilot plant.

While manufacture of equipment continued, civil engineering and construction work was started at site.

FY 1989 While element studies were continued, study was made on the operation conditions of pilot plant.

In succession to the previous year, manufacture of equipment and civil engineering and construction work were continued.

Installation of large equipment was also started at site.

FY 1990 Element studies were continued, and study was made on the operation conditions of pilot plant.

Also conducted were installation of all facilities, test adjustment, and experimental operation of individual equipment.

FY 1991 Element studies were conducted.

Adjustment operation of each facility of the pilot plant was conducted successively, and research operation using adjustment coal (Taiheiyō coal) was conducted.

30hours 16 minutes), gas passing operation to gas clean-up facility and gas turbine was conducted.

ii) As the weight increase rate of slag discharge tank was noticed being slowed down, various controls were tried to improve slag discharge rate but all efforts were in vain. As slag was seen depositing in the slag hopper, it was considered difficult to continue operation so that the gasifier operation was manually stopped.

(Results of operation study)

i) Oxygen concentration control test was conducted utilizing recovery oxygen for the air fed to the gasifier, and it was confirmed that the oxygen concentration in the air supplied to the gasifier was properly controlled. Also confirmed was the fact that the heating value of product gas increased as the amount of recovery oxygen was increased.

ii) In the minimum load condition confirmation test, the lower limit was found at the heat input of 41% because of limitation of amount of secondary air. However, operational conditions of gasifier were stable, and slag discharge from slag tap was also satisfactory.

(b) Run D4 operation study (gasifier operation test using coal only) (May, 1994)

(Conditions of operation)

i) Gasification loaded operation with conducted at gasifier load of 55-60% (operation time: 8hours 38minutes).

ii) Temperature of slag hopper water tended to go down with the weight increase rate of slag discharge tank also slowing down. Various recovery measures were tried in vain, eventually leading to manual shutdown of gasifier.

(Result of operation study)

i) As to the slag flow-down from the slag during operation using coal only, it was surmised that slag was discharged satisfactory since the differential pressure across the gasifier wall was found stable, although it could not be confirmed through the monitoring TV because of high brightness of flames flowing in from the combustor chamber.

(c) Run D5 operation study (confirmation of measure against R-system overfeed, operation test using coal proper) (June, 1994)

(Conditions of operation)

i) Gasification loaded operation was conducted at gasifier load of 55-100%. (operation time: 32hours 14minutes)

ii) Differential pressure across the gasifier wall and slag flow-down are found generally satisfactory.

(Result of operation study)

i) In the confirmation test for measure taken against R-system overfeeding, it was found that the overfeeding was difficult to occur as the weight of measuring hopper at the time of receiving was greater, that is, as the layer of pulverized material because thicker.

(d) Run D6 operation study (operation test fueled with coal only) (June, 1994)

(Conditions of operation)

i) Gasification loaded operation was conducted at the gasifier load of 55-59% (operation time: 9hours 12minutes).

ii) Slag hole tended to clog. Various measures were tried to bring up temperature within the combustor, but none was effective. It became impossible to determine whether or not slag was flowing down. When the differential pressure across the gasifier wall was found

suddenly rising, we judged that the slag hole was completely clogged, so that the gasifier was manually shut down.

(Results of operation study)

i) As a result of checking made to the inside of gasifier after the completion of test, the slag hole was found completely clogged, but no slag was found deposited on the water-cooling jacket of the light oil combustion chamber.

(e) Gasifier remodeling work (July-November, 1994)

(Description of work)

i) Gasifier remodeling work was conducted mainly aiming at anti-slugging measures including modifications of diffuser and pressure vessel itself.

ii) For other facilities, checking and overhauling of equipment, piping and valves were conducted.

(f) Run D7 operation study (confirmation test to determine the effect of gasifier remodeling work, gas turbine high load test, integrated load pressure control test) (November, 1994-February, 1995)

(Conditions of operation)

i) Gasification loaded operation at gasifier load of 53-100% (operation time: 268hours 36minutes) as well as gas passing operation to the gas clean-up facility and gas turbine were conducted.

(Results of operation study)

i) As a result of checking made to the inside of gasifier after completion of test, formation of slag was found at the lower end of low temperature water tube panel which looked like eaves, but aside from that no adhesion nor deposit of slag causing problems was found. Thus, the effect of remodeling was confirmed.

ii) After the receiving kick program of R-system measuring hopper, it was confirmed that no over-feeding occurred at the load of 100%.

iii) For gas turbine, 3/4 and 4/4 load tests and load cut-off test were conducted. Results were all satisfactory.

iv) Pressure controllability tests were conducted at the gasifier input mode and gasturbine output mode. The pressure was confirmed to be controlled almost satisfactory.

(g) Run D8 operation study (reliability confirmation test (long-term continuous test)) (March-April, 1995)

(Conditions of operation)

i) Gasification loaded operation at gasifier load of 65-100% (operation time: 787hours 00minutes) as well as gas passing operation to the gas clean-up facility and gas turbine were conducted.

ii) Shlls, etc., were attached to the inlet of fine tubes of condenser, reducing the cooling capability, and thus gradually bringing up the temperature of condensed water until it got close to the limit value. As a countermeasure, a part of main steam was blown out of the system.

iii) The sulfur condenser of desulfurization unit of gas clean-up facility tended to clog, so that the operation to melt and remove attached was conducted. As a result, normal condition was restored, but only temporarily, and the same problem occurred again. Finally the device was disassembled, checked and cleaning conducted. After restoration, gas passing operation was resumed again.

(Results of operation study)

- i) 789hours of gasifier coal gasification continuous operation was accomplished.
- ii) Gas fueled load test of gas turbine was successfully conducted for 312hours and 15 minutes.

(3) Feasibility study concerning demonstration plant.

For a demonstration plant scale of coal gasification combined cycle power generation, various types of study results, etc., necessary for establishing concept of basic design of a demonstration plant, were put together based on the results of pilot operation studies conducted in previous years and of the feasible study made in relation to demonstration plant, and selection of fundamental systems and determination of working formula were performed.

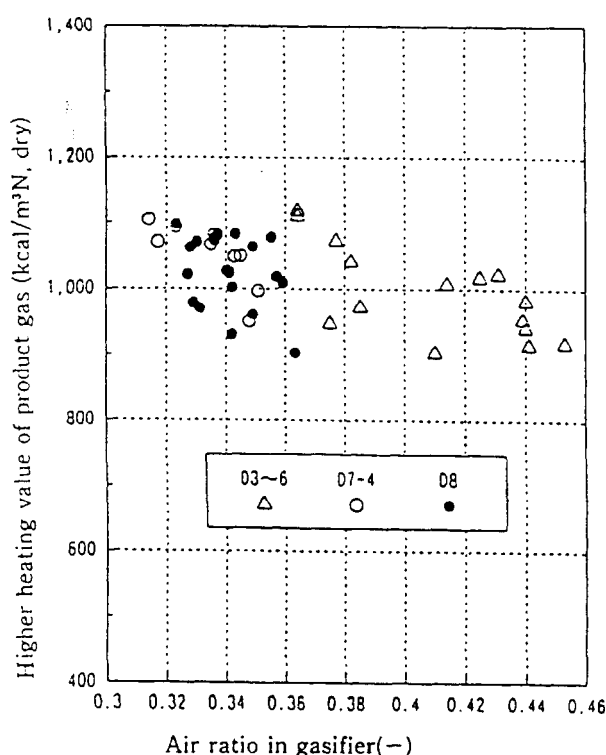
Future Tasks

- ① Confirmation of controllability of total system.
- ② Expansion of coal type applicability.

Results of Sulfur Concentration Measurements at Inlet and Outlet of Desulfurization unit

Inlet concentration (ppm)	Outlet concentration (ppm)	Desulfurizing rate (%)
H ₂ S: 400-600 COS: 60-160	H ₂ S: 20- 70 COS: 10-150	87-95

Heating value of Product gas



Results of Dust Concentration Measurements at Inlet and Outlet of Dust Remover

Inlet concentration (mg/m ³ N)	Outlet concentration (mg/m ³ N)
66-267	lower1-4

Results of Study:

Industrial Properties, Technical Guidance, Papers and Lectures, Oral Reports, etc.

(1) Oral reports

Subject	Speaker	Name of Meeting
i) Development of IGCC System by Means of a 200t/d Pilot Plant	S.Araki IGC Engineering Research Association	3rd Japan/EC Workshop Minimization of CO ₂ related problem
ii) Test Results of Hot Gas Clean-up Facility (Desulfurization Unit) for 200t/d Entrained Flow Coal Gasification Pilot Plant	T.Sugitani Ishikawajima-Harima Heavy Industries	Technical Exchange with KEMA, Netherlands

(2) Published Papers

Subject	Author	Published Paper
i) Status of Research and Development of a 200t/d Entrained Flow Coal Gasification Power Generation Pilot Plant	IGC Engineering Research Association	Overseas Version of Nippon Kogyo Shinbun "Japan 21st"

Coal Selection for Conversion

S. Ueda

Director General

Clean Coal Technology Center (CCTC)

New Energy and Industrial Technology Development Organization (NEDO)

Objectives

To determine the properties of feedstock coals for liquefaction, to relate the above to the liquefaction potentials of the coals, to characterize the residue from NEDOL process liquefaction as a gasification feed and to provide a basis for selection of feedstocks to permit more effective conversion.

Work Program

The work program includes the investigations of

- (1) the geologic and chemical properties of various coal seams distributed in the circulative Pacific countries,
- (2) the liquefaction potentials of the coals through the hydrogenation experiments in the presence of solvent, iron/sulfur catalyst and hydrogen gas by using agitated batch reactors,
- (3) the physicochemical properties and gasification characteristics of the residues from NEDOL process liquefaction, and
- (4) the compilation of the data as the Coal Data File for Conversion.

Summary (1980-1994)

1. Up to FY 1993

The coals ranging in rank from lignite/brown coal to high volatile bituminous were obtained from 136 coal mines or deposits in Australia, China, Canada, USA, Indonesia, New Zealand, Japan, etc. The coal samples were investigated by using combined chemical and petrographic techniques. The coals were liquefied in the batch autoclave to relate their properties to conversion potentials. The hydrogenation under the rapid heating condition in the mode of NEDOL batch reaction was carried out by using the micro reactors. Gravity separation fractions of Taiheiyō coal and Tatung coal from China, which were previously deashed by the hydrofluoric/hydrochloric acids treatment, were gasified through a thermobalance method. The initial reaction rates during gasification were investigated in connection with the maceral composition of each fraction. An impact of coal properties was discussed on the basis of the analytical and experimental results.

2. For FY 1994

(1) Combustion characteristics of coal under gravity and microgravity conditions

A pressurized thermogravimetric analyzer (TGA) and a high pressure drop-tube reactor (HP-DTR) were used to estimate the combustion reactivity of the coal for effect of coal rank and pressure. For TGA tests, the behavior of the volatile matter release in inert gas was independent of pressure, kinds of inert gas and particle size. It was seemed that the coal combustion was not individual coal particle but bulk, because TGA was fixed bed. As oxygen enters smaller pore of coal at higher pressure, exothermic reaction increased with increasing oxidation reaction rate and ignition temperature of coal was lower. For HP-DTR tests, when the coal combustion under pressurized was used that an index of unburned carbon (Uc%) on pulverized coal combustion was 30 to 50% at atmospheric pressure, Uc% decreased 2 to 3% and combustion reactivity of the coal was improved. Evolution of volatile matter and its concentration around particles for diffusion coefficients proportional to $1/P$ increased with increasing pressure. Consequently the coal particle rise of temperature at ignition was higher under pressurized than at atmosphere pressure and char combustion of next stage was accelerated. For occurring partial rise of temperature, it was found that melt of ash particle proceeded and its formed bigger spherical ash.

Pulverized coal combustion tests were also conducted in microgravity field and clarified the combustibility in the field to obtain the fundamental data which contributes to the optimum design of coal gasified system. Ten seconds microgravity environment which is available at JAMIC (Japan Microgravity Center), Hokkaido, was used to attain a spatially homogeneous and quiescent distribution of pulverized coal and the environment where the flame propagation is not affected by natural convection, buoyancy. Comparison of flame propagation speed has been carried out for various oxygen concentration and kinds of coal. Image of burning process of a coal particle has been carried. Two color image of flame propagation has been carried out to obtain temperature of coal particle. Coal particle and gas after combustion has been sampled to clarify burning process of a coal particle.

(2) possible impacts of coal properties on the coal conversion technology

Some possible impacts of coal properties were given on the future coal utilization technologies, especially coal liquefaction technology, based on the data obtained from analytical and experimental tests. Our previous works have illustrated that the relationship between the property of coals and their liquefaction characteristic can be developed, and that the degree of coalification and petrographic composition are important coal parameters. From the viewpoint of liquefaction, low inertinite content and subbituminous-class coals are suitable stocks. The variation in inertinite content shall be seized in advance. Liquefaction characteristics of the coals particularly abundant with liptinite macerals are excellent. A demonstration-scale, high efficiency NEDOL system is

planned to have a liquefaction capacity of 30,000 tons of coal per day, integrating a 7,400 tons of coal per day IGCC plant and a HYCOL plant which processes daily 2,060 tons of coal and 10,220 tons of liquefaction residue. In this study, three cases of coal usage were imaginable; using only a feed coal for both liquefaction and gasification, using a coal for liquefaction and another coal for gasification, and using a part of a coal which is produced from the coal by utilizing its physical properties for liquefaction and using the residual coal from the coal for gasification. These cases were compared with each other. Liquefaction suitability of coals has so far been discussed based on coal type, and it seems necessary to propose general criteria for their classification.

(3) Coal properties, utilization, and carbon dioxide emission

Heat values of the products of coal conversion technologies, assuming the theoretical reactions, were calculated for various types coals with different ranks, brown coals, vitrinite-rich and inertinite-rich subbituminous coals, and low-rank bituminous coals. Then, they were compared with the overall CO₂ emission, which includes the product's combustion and the CO₂ from the coal conversion technologies. The ratio of the CO₂ emission to the heat value of the products by the conversion technology shows the quality of the conversion technology, but the ratio also depends on the properties of coals. We must define the most suitable technology for each coal in order to use coal in the highest efficiency. A fundamental stage investigation was conducted for the purpose of considering the relationship between properties of coal and coal utilization technology. In conclusion, the carbon content per heat value of brown coals are generally higher than that of subbituminous and bituminous coals, so that it is said that the use of brown coals should be restrained from the viewpoint of mitigating global warming. Although subbituminous coals within similar rank given by the carbon content and Ro%, their theoretical efficiency and CO₂ emission are significantly different due to their maceral composition. In the development of a utilization technology of subbituminous coals, it is essential to consider the characteristics of individual coals. The theoretical efficiency and the CO₂ emission of direct coal liquefaction is less than that of the gasoline production through the gasification. The progress of coal science is essential to control these characteristics, and also to develop the most efficient utilization technology for individual coals.

Future Tasks

- (1) Further investigation of the relationships between the properties of feedstocks and their conversion potentials is presently continuing for the coals through statistical analysis.
- (2) To increase the understandings of overall potential of a whole mine or coalfield, the liquefaction in the mode of NEDOL batch reaction is also being performed by using

micro reactors.

- (3) To determine the physicochemical properties and gasification characteristics of the residues from NEDOL process liquefaction.
- (4) The data will be compiled as the progressed Coal Data File for Conversion, and compiled data will be evaluated by using a matrix data analysis method.

Development of Coal Conversion Technology Data Processing System

Dr. Shigeru Ueda
Director General of Clean Coal technology center,
New Energy and Industrial technology Development Organization (NEDO)

Objective

The research aims at the development of a data control system for coal conversion technology (gasification and liquefaction) as well as a data collection and processing system for reports of the results of pilot plant operation and support research and at the effective use of the obtained data to carry the research forward to the next step such a conceptual design of the commercial plant. The research conducted in fiscal 1994 aims at the development of the general technical information database.

Research Program

1. Development of the general technical information database
 - (1) Design of data input system
 - (2) Design of management and operation system
 - (3) Evaluation of data input system
2. Pilot survey of COAL DATA BANK
 - (1) Survey of coal databases in Europe

Research Progress

1987

The requirement for the database and database utilization method were studied to establish a concept of the whole system by the research group with NEDO, an expected main user of the system, at the core. In addition, an analysis was made on the general technical information retrieval system, and a conceptual drawing of the basic functions of system were prepared.

1988

Storage conditions of various data obtained in experimental plants in the past were investigated to study a hierarchical structure of the data. Concerning the general technical information database, made were the sample design of input/output layout, division of the system into functional subsystems and examination and study of the hardware.

1989

Functions required for the system were filed to study the hardware and software. Moreover, basic specifications of the data structure were designed. Concerning the general technical information database, studied were control of the terms which are the point of the retrieval and applicability of the commercially available software.

1990

Based on the results obtained in 1989, sample design of the input and output layout and design of the retrieval structure were made.

1991

A keyword dictionary for the general technical information database was compiled. Approximately 3,500 words, most of them are related to coal conversion technology, were collected and translated into English, and synonyms were controlled. Keyword category codes were prepared for the utilization of the dictionary.

1992

The general technical information database was designed in detail. Selection of basic software and investigation of hardware were carried out.

1993

As the development of the general technical information database, carried out were layout of master file, design of retrieval system and output system, input of test data and retrieval test. Furthermore, to realize the 'COAL DATA BANK' plan, a pilot survey was started.

Research summary

1. Development of the general technical information database

(1) Design of data input system

A direct data input system by indexers were developed through integration of indexing and data input processes. The system was named CADIS (Computer Aided Input System).

Introduction effects of CADIS are as follows:

- a. Reduction of indexing process
- b. Elimination of errors
- c. Supports for indexers

(2) Design of management and operation system

Management system was designed to meet the characteristics of the database system that requires four access levels according to users. It includes registration of users, recording of use, and charging system. Moreover, methods of operation were investigated: monthly operations of data renewal and backup, dairly ones of starting-up and shutting-off.

(3) Evaluation of data input system

CADIS was proved to have good performance through data input test.

2. Pilot survey of COAL BATA BANK

(1) Survey of coal databases in Europe

To realize the 'COAL BATA BANK' plan, a pilot survey was carried out. Databases of coal samples have rarely been developed in Japan. So the pilot survey was conducted in research institutes in Europe.

Institution	Country	Kinds of Coal	Items of Analysis
N M I	Netherland	1 8 0	1 8 0
D E C H E M A	Germany	1 2 0	3 1
C R E	U. K	—	3 0

Future Tasks

1. Peripheral systems will be designed: linkage to image files, connection to networks.
2. Management system of numerical data will be investigated.
3. A data input program will be planned.
4. As the pilot survey of 'COAL DATA BANK', databases of coal specimen will be surveyed.

7. THE ASSESSMENT OF COAL HYDROGASIFICATION

The Assessment of Coal Hydrogasification

New Energy and Industrial Technology Development Organization (NEDO)

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 consumers. 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. Process studies, and cost and engineering studies were carried out for coal hydrogasification technology, which directly produces methane from coal, and for other coal gasification technologies.

Research subjects are currently being extracted by surveying the technologies for the hydrogasifier and related equipment. An optimum process system is being discussed for obtaining high thermal efficiency and low gas cost. R&D items of the pilot plant and a timetable from PDU to commercial scale are being researched. The outlined design for a pilot plant is being discussed.

2.Work Program(1994)

- (1)The importance of coal hydrogasification research and development activity
- (2)The development plan for ARCH hydrogasification process
- (3)The trend in world coal gasification process development

3.Outline(1990~1993)

3-1. Up to FY 1990

- (1)Necessity for SNG production from coal
- (2)Study of SNG process from coal and cost and engineering study
- (3)Fundamental research on coal hydrogasification and process development

(4)Clarification items for development of coal hydrogasification

3-2. For FY 1991

- (1)Research on the utilization of SNG in the city gas industry and in other industries
- (2)Investigation and evaluation of technologies in hydrogasification
- (3)Development of hydrogasification process
- (4)Guidelines for scale-up leading to industrial use
- (5)Outlined design of a pilot plant

3-3. For FY 1992

- (1)Research on new circumstances concerning coal hydrogasification technologies
- (2)Study of new coal hydrogasification process
- (3)Gasification characteristics of hydrogenated char

3-4. For FY 1993

- (1)Research on role of coal hydrogasification technology development
- (2)Study of coal hydrogasification process development
- (3)Fundamental properties of hydrogenated char

4.Summary(1994)

In 1994, the final fiscal year for this assessment, the committee completed an investigation on coal hydrogasification.

- (1)The importance of coal hydrogasification research and development activity

In Chapter 1, the importance of coal hydrogasification research and development activity is emphasized to reflect the committee's work over the past four years. This work considered recent changes in the energy situation, progress in research and development, and various new aspects.

The use of LNG in electric power generation and city gas production has been continually increasing. Worldwide demand for LNG is expected to rise due to growing demand from developing countries and its low environmental impact. However, LNG will likely be produced under severe conditions from wells located in remote areas. The purity of natural gas from these wells is also expected to be low due to CO₂ content. Costs associated with production at remote sites and costs required for long-term development will eventually cause LNG prices to rise and potentially create fear of a supply shortage. Japan currently produces 73.6% of its city gas from imported LNG. To prepare for the future shortage of LNG as well as to maintain bargaining power and national security, Japan must have as many options as possible available to maintain sufficient natural gas supplies. Coalbed methane and methane hydrates have been researched as alternative sources of natural gas. Coal as a raw material for SNG production can be imported due to worldwide abundance and wide geographical distribution of its reserves.

The conditions for building SNG production facilities in Japan have been investigated: locations in the vicinity of big cities and the ability to be coupled with electric power stations or iron/steel production works which already have coal-related facilities for production of electric power and chemicals. Clean utilization of coal has the potential of reconciling energy and environmental issues while producing a product transportable by a domestic and international natural gas pipeline currently under consideration.

In the ARCH process proposed by the committee, the price of SNG produced depends on the quantity and price of BTX produced with methane. If the prices of coal and natural gas change at the current rate, SNG from the ARCH process can compete with LNG in price circa 2010. From environmental standpoints, sulfur, nitrogen, ash and so on from coal can be removed using ARCH, resulting in the clean conversion of coal to SNG. This technology has a theoretical thermal efficiency near 80%, offering an excellent method for abating CO₂

emissions. If low-grade natural gas contaminated by 50% CO₂ is used, ARCH produces less CO₂ than a comparable LNG-based process.

If SNG is used in the near future as a medium for transporting and utilizing hydrogen supplied by WE-NET or other facilities, the highly reactive component of coal can be converted to SNG by an advanced hydrogasification process based on ARCH, while the less reactive char can be partially oxidized and converted to methane. This combination can produce SNG with a lower consumption of hydrogen and higher efficiency.

(2) The Development Plan for ARCH Hydrogasification Process

Chapter 2 describes basic concepts and the development of the entire ARCH system, including the hydrogen/oxygen burner and injector systems. ARCH utilizes a two-stage gasifier. In the first stage, pyrolysis is carried out at a high temperature. In the second stage, hydropyrolysis at an optional temperature and time is performed mainly to control BTX formation. Consequently, three different optimal operation modes exist for the attainment of the best SNG yield, the best thermal efficiency, and the best BTX yield, respectively.

The target of this plan is to develop a process which produces 3 million Nm³ of SNG per day. Four years of fundamental research is to be followed by an eight-year operational study using a 50 tons coal per day capacity pilot plant focusing on the development of the gasifier and its supplementary systems. Then scale-up to a 500 tons coal per day demonstration plant will be conducted and subsequently operated in conjunction with a hydrogen production plant.

The design of the hydrogen/oxygen burner was obtained by an extensive literature and patent search, including searches for a suitable physical structure, ignition method, and burner monitoring technique. A plan for testing and improving the injector using a cold/hot model equipped with the proposed hydrogen/oxygen burner is being developed.

Basic research prior to the development of key technologies has been performed, such as: 1) prediction of gasifier performance and the optimum gasification conditions for the production of liquid products, through the use of a process simulator, 2) visualization and analysis of gas and solid flow in the gasifier using the Laser Sheet Method, and 3) determination of the heat transfer characteristics of the fluidized bed-type char cooler.

(3) The Trend in world coal gasification process development

In Chapter 3, views of the current and future trends in coal gasification process development are discussed, and the development of ARCH is evaluated from this standpoint. The trend in world coal gasification process development is to advance a high-efficiency integrated gasification combined cycle power generation system which would reduce the cost of electricity and raise the environmental acceptability of coal-based power generation systems. Improvement of the oxygen-blown entrained flow gasifier is directly connected to the optimization of ARCH's hydrogen-producing stage, which subsequently determines the efficiency of the entire system.

From the international perspective, each country will consider coal hydro-gasification as a natural gas source, depending on its particular energy situation. For example, China is considering the use of natural gas as an issue to be solved by close international cooperation. Since ARCH is capable of meeting a wide range of requirements, the committee strongly feels that ARCH must be developed as quickly as possible.

8. INTERNATIONAL CO-OPERATION

(1) IEA Contribution

IEA CONTRIBUTION

S.NAKAYAMA

New Energy and Industrial Technology
Development Organization (NEDO)

Objectives

1. Cooperation to IEA Coal Data Base by inputting coal-related bibliographic information in Japan.
2. Search of bibliographic information from Coal Data Base produced by international cooperation.
3. Literature search for the purpose of R & D.

Work Program

1. Domestic coal-related bibliographic information collected by NEDO are to be provided to IEA Coal Research as input information to IEA Coal Data Base.
2. Literature of specific area is to be retrieved from IEA Coal Data Base, and copies of original papers retrieved are to be obtained.
3. In order to cooperate to work of preparing "Coal Research Project in the World" which will be published by IEA, coal-related research themes are to be collected by NEDO and supplied to IEA Coal Research.

Summary(1992 - 1994)

1. Up to Fy 1993

- (1) NEDO provided domestic coal-related literature to IEA Coal Research as our cooperation of inputting to IEA Coal Data Base.

- (2) Japanese information on coal-related research themes was collected and sent to IEA Coal Research.

2. For FY 1993

- (1) The number of domestic coal-related literature sent to IEA Coal Data Base as our cooperation is as follows.

Period of time	Apr. 1994 to Mar. 1995
Number of literature	430

- (2) Literature retrieval using IEA Coal Data Base
NEDO retrieved some themes which were "Coal utilization technology" and others through Data Base System constructed by NEDO.
- (3) Japanese information on coal-related research themes was collected and sent to IEA Coal Research. The number of themes is 330.

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