Research and development of pretreatment technology for vacuum residue

1. Contents of empirical research and development
The purpose of our research was to reduce the production of heavy oil, especially vacuum residue, to increase the production of middle distillation and gasoline, and to develop process technology and the following catalysts for cracking of heavy oil.

1) Develop catalysts and process technology to serve as preliminary processing (direct desulfurization pre-treatment).

2) Use direct desulfurization as secondary treatment and develop a catalyst for the same.

Taking Kuwait vacuum residue as the feedstock base, the following specific target values were established.

<table>
<thead>
<tr>
<th></th>
<th>Direct desulfurization pre-treatment</th>
<th>Post direct desulfurization (final target)</th>
<th>(Feedstock)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Vacuum residue conversion rate:</td>
<td>25% or more</td>
<td>45% or more</td>
<td></td>
</tr>
<tr>
<td>2) Conradson carbon residue (CCR):</td>
<td>15 mass % or less</td>
<td>8 mass % or less</td>
<td>(23 mass%)</td>
</tr>
<tr>
<td>3) Metals (Ni + V):</td>
<td>60 ppm or less</td>
<td>25 ppm or less</td>
<td>(160 ppm)</td>
</tr>
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</table>

In 1998, the final year, the following tests and studies were conducted.

1.1 Practical application tests using industrial equipment
In order to fully complete the process technology for practical application, a commercial unit was charged with developed catalyst and tests were performed on practical performance. Process data on the commercial unit was obtained.

1.2 Examination of practical applicability
Concurrent with the aforesaid practical performance testing, long-term bench plant tests were performed with vacuum residue treatment of the developed catalyst using a midget plant, etc. Detailed process data were obtained, and the design was evaluated as a commercial unit in a vacuum residue pre-treatment system.

1.3 Development and/or improvement of catalyst
Along with evaluating the developed catalyst from the standpoint of industrial manufacturing, in order to further improve and optimize the developed catalyst and process technology, catalyst trial production, screening, and examination of structural analysis methods for produced oil and catalysts were undertaken.
1.4 Examination of catalyst performance estimation method
In order to establish technology for estimating catalyst performance, studies were done on catalytic properties and catalytic activity, and the behavior of reactions under catalytic combinations was investigated.

2. Empirical research results and analysis
2.1 Practical application tests using commercial unit
2.1.1 Manufacture of catalyst developed for practical application testing
As the catalyst developed for practical application testing, it was decided that a direct desulfurization pre-treatment catalyst, developed by the year 1997, would be used in combination with two types of post direct desulfurization catalyst.

The direct desulfurization pre-treatment catalyst that was developed (catalyst 1) is a binary oxide supported catalyst. The two types of post direct desulfurization catalyst (catalysts 2 and 3) are metal oxide supported catalysts, and they are unique in terms of pore structure and metal activity. In comparison to conventional catalysts, these catalysts exhibit high-performance and the following unique properties in terms of activity.

1) In comparison to commercial catalysts for HDM, catalyst 1 exhibits high-performance, being three times greater in terms of vacuum residue conversion capacity, which is essential for treatment of vacuum residue, and 1.3 times greater in terms of metal capacity. This is because catalyst 1 is slightly acidic and has a very large pore diameter. Demetalized catalysts with acidity could not be obtained in the past, and such a catalyst was made practical by curbing its acidity to a suitably low level. Slightly acidic substances elevate catalytic strength, and the past problem of the inverse proportionality between pore diameter and strength in demetalized catalyst, has been resolved so that the catalyst can be successfully made to exhibit high levels of metal capacity while having adequate strength for practical application.

2) In comparison to desulfurized catalysts available on the market, catalyst 2 exhibits high-performance with 1.3 times greater hydrogenation activity that exhibits HDCCR activity.

3) The original hydrogenation activity of catalyst 3 is high, and when this catalyst is combined with catalyst 1 and 2, it exhibits high performance, its hydrogenation activity being two times greater than that of catalyst sold on the market. Like catalyst 2 and 3, it also has a high surface area not found in catalysts on the market sold for hydrogenation of residual oil. Even higher hydrogenation capacity is exhibited when this catalyst is used in combination with catalyst 1, which has high pre-treatment capacity.

Production on an industrial scale of the three catalysts mentioned above was undertaken in prescheduled volumes. These catalysts satisfied prescribed specifications in terms of chemical composition and physical properties and it was confirmed that they exhibit performance as expected in terms of catalytic activity.

2.1.2 Commercial operation testing
In order to test practical operations, the direct desulfurization units at Sakaide laboratory No. 31 were charged with the aforesaid catalysts developed for testing of practical operations, and operations were started at the beginning of August 1998.
After charging industrial equipment with the catalyst, the catalyst was presulfurized. The presulfurization process took place in a prescribed procedure of wetting, primary sulfurization and secondary sulfurization, and after the target sulfur adsorption volume had been reached, feedstock was substituted. During presulfurization there were no rises in temperature caused by such things as a violent advance of sulfurization at each stage of temperature rise, and the developed catalyst could be sulfurized at a regular preset sulfurization temperature. In testing mixtures with a vacuum residue, a feed filter device was introduced for removing impurities from feed oil. Also, a feed filter backwash device was introduced for removing impurities accumulated inside the feed filter device, along with a heavy oil metal analyzer for measurement of the metal content accumulated on the catalyst.

Upon completion of sulfurization, operations were performed using residual oil of normal pressure as crude oil, and such things as catalytic activity, pressure loss and temperature distribution were checked. The trends in required temperatures for developed catalysts in industrial equipment are shown in Figure 2.1-1. The required temperature which means catalytic activity, following an initial deactivation, gradually showed the trend toward stabilization, and the high catalytic performance prescribed was demonstrated also in the industrial equipment. Then, after catalytic activity stabilized, three tests with vacuum residue mixtures were conducted, and it was confirmed that stabilized processing capacity is exhibited, as prescribed, with no sharp drops in activity.

At the laboratory stage, pressure drop arising from charge of the developed catalyst into practical equipment, which cannot be checked accurately, and abnormal temperature distribution arising from channeling were not noted. What is more, in tests of vacuum residue mixtures, pressure loss and temperature distribution followed smooth trends with no sharp increases.

![Figure 2.1-1 Trends in required temperature of developed catalyst in industrial equipment](image)

| Equipment:  | Direct desulfurization unit at Sakaide laboratory No. 31 |
| Catalyst:   | Direct desulfurization pre-treatment catalyst + post direct desulfurization catalyst |
2.2 Examination of practical applications

2.2.1 Midget plant operation

Concurrent with testing of vacuum residue mixtures employing industrial equipment. A 100% throughout test vacuum residue was undertaken at the midget plant, concurrent with testing of vacuum residue mixtures employing industrial equipment. Long-term bench plant tests were performed combining 2 midget plants as direct desulfurization pre-treatment equipment and post direct desulfurization equipment.

Shown in Figure 2.2-1 are the trends in required temperature for direct desulfurization pre-treatment catalyst. Long-term bench plant tests were carried out in actual equipment running modes using improved catalyst having a high pre-treatment capacity and weak acidity. Liquid space velocity at the midget plant was kept constant, and long-term bench plant test was performed while adjusting the reaction temperature in line with deactivation of catalytic activity so that the HDM of vacuum residue and the feedstock would be constant. Although the temperature required for exhibiting catalytic activity rose sharply following initial deactivation, it stabilized after about 20 days and exhibited soft stabilized deactivation. After 190 days of operation, the required temperature reached the operation temperature upper limit, and tests were continued after switching to a separate reaction column charged with a new catalyst.

**Figure 2.2-1** Trends in required temperature of direct desulfurization pre-treatment catalyst
Feedstock: Kuwait vacuum residue
LHSV: standard 1
Hydrogen partial pressure: constant
The trend in required temperature for post direct sulfurization catalysts is shown in Figure 2. 2-2. A catalytic system designed for improving reactivity by means of the synergetic effect of pre-stage catalysts was used as the catalytic combination. At the initial stage of reaction, Kuwait residual oil of normal pressure was used as the feedstock so that catalytic activity would be stabilized. Thereafter, two midget plants were connected, and the feedstock was replaced with vacuum residue pre-treatment oil produced after being processed with pre-stage direct desulfurization pre-treatment catalyst. Operation was continued while gradually changing the reaction temperature in line with deactivation of the catalyst. After substituting with vacuum residue pre-treatment oil, the catalyst deactivated slightly and the temperature required for obtaining the production oil properties targeted followed an upward trend, stabilized after twenty or thirty days, then changed to a stable pattern of gentle slope.

![Graph showing trend in required temperature for post directly desulfurized catalyst](image)

**Figure 2.2-2  Trend in required temperature for post directly desulfurized catalyst**
Feedstock:  vacuum residue pre-treated oil
LHSV:  standard 2
Hydrogen partial pressure:  constant

### 2.2.2 Process design
A direct desulfurization pretreatment device using the vacuum residue pre-treatment catalyst that was developed, was designed in outline.

The majority of hydrogenation desulfurization processes for residual oil implemented commercially in Japanese oil refining plants are directed at residual oil of normal pressure. Although equipment for vacuum residue is operated at one plant, the defect is that the cycle is short, lasting about five months at the most. The purpose of this process is to reduce the residual carbon, metal and asphalt fraction in residual oil after processing to allow vacuum residue and other residual oils of poor quality to be treated with conventional equipment for hydrogenation and desulfurization (direct desulfurization equipment) of residual oil of normal pressure, and thereafter, to facilitate treatment with equipment for hydrogenation and desulfurization of residual oil of normal pressure. Another function of this process is to use the high reaction temperatures reached in the course of the reaction to feedstock middle distillation.
A schematic illustration of the pre-treatment device designed is shown in Figure 2.2-3. As in the case of the conventional process for hydrogenation and desulfurization of residual oil, the reaction takes place in the presence of a solid-body catalyst in a hydrogen atmosphere. Although catalytic life varies with severity, because the life of this catalyst is shorter than the catalytic life in the process of hydrogenation and desulfurization of residual oil of normal pressure, this deactivated catalyst must be replaced. For this reason, the process concept called for continuous operation while switching among a multiple number of reactors.

2.3 Development and/or improvement of catalyst
Additional research and development activities were carried out this year for the purpose of improving still more direct desulfurization pre-treatment catalysts and catalysts for previous-desulfurization equipment. For trial production of catalysts, catalysts for both pre-treatment device and previous direct desulfurization were designed, and they were produced both laboratory level and through outsourcing.
2.3.1 Direct desulfurization pre-treatment catalyst

Further studies were done on catalysts with slight acidity added, that were discovered to have a high pre-treatment capacity had been manufactured on an industrial scale. The relative relationship between metal capacity and demetallization activity is shown in Figure 2.3-1. It was found that demetallization activity could be improved without lowering the level of metal capacity by extending large pore diameter or highly active metal content to standard catalysts. It was also confirmed that even catalysts without additional weak acidity have the same level of metal capacity and demetallization activity as catalysts with weak acidity if the former has the same properties as the latter. However, with very large-pore diameter, catalytic strength drops sharply, reaching the minimum catalytic strength for usage. In contrast, by using catalyst with slight acidity added, pore diameter could be enlarged and catalytic strength could still be maintained.

![Figure 2.3-1 Relative comparison of metal capacity and of demetallization activity in trial catalysts with weak acidity added](image)

*Feedstock: Boskan crude oil
Reaction temperature: 395°C, LHSV: 0.5h⁻¹*

Shown in Figure 2.3-2 is a relative comparison of activity in a trial catalyst. This catalyst, which has an affinity with hydrocarbons, was found to exhibit continuous long-term pre-treatment capacity and it was subjected to improvement studies. By improving the catalyst carrier shape, desulfurization activity was improved. Along with improvement of desulfurization activity, however, demetallization activity dropped. It was then discovered that demetallization activity could be maintained and desulfurization activity could be improved through the processing for changing catalytic shape, for instance, and for retaining highly active metals.
Standard catalyst
Change of catalyst carrier shape
Highly active metal A
Highly active metal B

Desulfurization activity
Demetallization activity

Figure 2.3-2 Relative comparison of desulfurization activity and of demetallization activity in trial catalyst of hydrocarbon affinity
Feedstock: Boskan crude oil
Reaction temperature: 395°C, LHSV: 0.5h⁻¹

2.3.2 Previous direct desulfurization catalyst

Shown in Figure 2.3-3 is a relative comparison of desulfurization activity in trial previous desulfurization catalysts. Taking a conventional desulfurization catalyst as the standard catalyst for comparison, it was confirmed that desulfurization activity could be improved through processing involving a combination of factors including higher relative surface area, addition of a new component, control of pore diameter, and active metal stabilization.

Figure 2.3-3 Relative comparison of desulfurization activity in trial previous desulfurization catalyst
Feedstock: Residual oil of normal pressure
Reaction temperature: 385°C, LHSV: 0.4h⁻¹
2.4 Evaluation of catalyst performance estimation

In regards to reaction temperature in a direct desulfurization pretreatment device, studies were conducted this year for the purpose of clarifying the impact of vacuum residue pre-treatment oil on direct desulfurization devices from the differences in chemical structure of the oil produced and for the purpose of identifying reactivity forecasting factors stemming from chemical structure. Characterization was performed on three types of pre-treated oils of different reaction temperature (high-temperature, intermediate temperature, low temperature processing), on a direct desulfurization oil product made to react in a previous direct desulfurization device, and on a vacuum residue which was the feedstock. Except for reaction temperature, all other operating conditions of desulfurization pretreatment devices were held constant; the operating conditions of the previous desulfurization device were also held constant.

2.4.1 Type analysis of molten fraction by mass spectrometry

By column chromatography, molten fraction was separated into saturation fraction and aromatic fraction, and the aromatic fraction was separated into aromatics of 1 ring, 2 rings and 3 or more rings by HPLC. Each fraction was analyzed by field desorption mass spectrometer (FDMS), and type analysis was made based on the Z number obtained from the mass spectrum.

The composition of saturated fraction by Z number is shown Figure 2.4-1.

In high-temperature pretreated oil, the percentages of paraffin fraction and of one-ring naphthene are high. Respecting the distribution of paraffin chain length, there is a shift to the low molecular side. Hence it was acknowledged that hydrogenation and compound cracking are advanced through pre-treatment at high temperature. Similarly, among oils produced by direct desulfurization, it was found that the percentages of paraffin fraction and of single-ring naphthene in oils pretreated at high temperature are large, and cracking is most advanced. As for the aromatic fractions, overlap of each fraction is severe, and no significant differences were found between pretreated oil and oil produced by direct desulfurization.

2.4.2 Average structure by nuclear magnetic resonance

With respect to resin fraction and asphaltene fraction, average structure analysis was performed through computations using proton nuclear magnetic resonance (1H-NMR) and carbon nuclear magnetic resonance (13C-NMR).
An average structure model of resin fraction is shown in Figure 2.4-2. In respect to the structure of resin fraction in each type of pretreated oil, no striking differences could be noted in the cluster structure, but cluster count and molecular weight were the smallest in oil pretreated at high temperature, and it is believed that this causes cracking to be most advanced. It also becomes clear from the structure model that among oils produced by direct desulfurization, those pre-treated at high temperature undergo the most advanced hydrogenation, and it is believed that because the change in molecular weight is slight, cracking is the rate-determining step.

![Structure models of resin fraction](image)

**Figure 2.4-2 Average structure models of resin fraction in feedstock and in each type of produced oil**

Shown in Figure 2.4-3 are average structure models of asphaltene fraction. Concerning the structure of asphaltene fractions in each type of pretreated oil, it appears that cracking is most advanced in oils pretreated at high temperature because cluster count and molecular weight in these oils are smallest. Among direct desulfurization oils, it was indicated that hydrogenation of aromatic rings progresses in those oils subjected to pre-treatment at high temperature.

Based on the studies, following an examination of structural factors affecting the reactivity of vacuum residue pretreated oil, it was found that the specific structural factors of asphaltene contribute largely to reactivity.
3. Results of empirical research

(1) Since the developed catalyst is being manufactured on an industrial scale and expected performance is being obtained, commercial operation tests were performed by charging operational equipment with the developed catalyst, practical performance was investigated in this equipment, and tests were run on vacuum residue mixtures. For these, feed filter devices were introduced, along with feed filter backwash devices and test equipment for analysis of metals in heavy oil.

(2) Using midget plants, long-term bench plant tests were performed on the developed catalyst through 100 percent processing of vacuum residue and detailed data on process reactions were accumulated. In addition, the operational data obtained through conduct of the aforesaid practical application tests (for example, data on vacuum residue mixture treatment facilities) were analyzed, and residual oil pre-treatment technology was evaluated for practical performance.

(3) In order to improve the performance of catalysts still further, research on catalyst development was conducted. Trial catalysts were designed for experimentation and trial adjustments were consigned to outside resources. To investigate catalyst-refining technology, studies were done on refinements of new catalysts inside the Company, which possesses refining know-how. Trial produced catalysts were subjected to preliminary evaluations, for example, using a micro-reactor in order to obtain fundamental data on catalyst activity. After separating asphaltene fraction and molten fraction from feedstock and produced oils, the molten fraction was further separated by column chromatography into saturation fraction, aromatic fraction, and resin fraction, and methods were established for characterization of each fraction.
(4) Using equipment for separation and testing of pretreated produced oils, reactive produced oils were distilled continuously, the properties and yields of produced oil obtained by 100 percent processing of vacuum residue by midget plant were determined; the structures of produced oils were analyzed, and the structural factors relevant to the reactivity of vacuum residue pretreated oil were investigated.

4. Summary

By conducting preliminary treatment (direct desulfurization pre-treatment) in order to remove catalytic toxic substances from vacuum residue, the load on direct desulfurization equipment was reduced drastically. In this way, upgrading functions (high resolution, CCR removal, etc.) could be added with direct desulfurization devices and cracking of heavy oil could be stepped-up. For this reason, R&D was conducted on direct desulfurization pre-treatment catalyst processing technology and on post direct desulfurization catalyst technology.

By combining midget plants and conducting long-term continuous testing using the developed catalyst to convert vacuum residue, operations could be implemented for obtaining produced oils as targeted. In conducting practicability tests using industrial equipment, it was found that the developed catalyst, manufactured commercially, could be used with in-service equipment. The target values of R&D could thus be reached. It is believed that the basis for vacuum residue pre-treatment technology was established by such means as testing of practicability in the final year, trial manufacture of catalyst on a laboratory scale as practiced heretofore, activity screening and testing of catalyst life. Charging practical equipment with the developed catalyst and then operating this equipment for one year are of great significance in working toward practicability.

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