1. Introduction

Slurry-type hydrocracking processes have the potential to meet future oil market demand by converting ultra-heavy oils, increasing production of transportation fuels, and meeting demanding new environmental constraints. Therefore, Kobe Steel, Ltd. and Chiyoda Corp. have been developing an innovative process, called the KOBELCO SPH process (SPH process), which applies our previous experience with the slurry process, and the well-established brown coal liquefaction technology. The SPH process can be installed as an upgrading technology either in upstream processing or at refineries.

Reaction models for the slurry phase of the heavy oil upgrading process have yet to be proposed, mainly because the slurry phase reaction for heavy oils, such as oils with API gravity of less than 20, involves various reaction pathways and mechanisms, catalyst deactivation, and sludge formation. Many reaction lump models have been proposed for the present designs of hydrocracking and thermal cracking processes. One of the vacuum residue (VR) hydrocracking reaction model\(^1\) uses a five-lump model based on the VR of Maya crude to estimate the yields of the vacuum gas oil (VGO), distillates, naphtha, and gases. The thermal cracking and dry sludge formation model\(^3\) proposed a reaction model and a prediction model to predict the maximum extent of conversion minimizing dry sludge formation. However, the slurry phase reaction model must incorporate the changes in the catalyst performance and reaction rate with sludge formation on the catalyst.

Our reaction performance experiments in an autoclave indicate that our proposed model effectively represents the complicated phenomena occurring in residue hydrocracking, and can predict the optimum reaction conditions in a slurry process.

2. Experimental

2.1. Outline of Gas Flow Type Autoclave Reactor

Figure 1 shows the outline of the autoclave reactor, which is the gas flow type of 1-liter capacity. The VR is charged into the reactor with the catalyst (pulverized limonite in oil) and sulfur. Hydrogen is introduced
into the reactor under pressure using an air-driven compressor. The flow rate is adjusted with a mass flow controller (MFC). During the hydrocracking reaction, hydrogen gas and product gas are passed from the top of the reactor to a double-tube high-pressure cooler (refrigerant circulation), partially condensed, and then sent to the cold high pressure separator (CHPS). External cooling via Coolnx refrigerant circulation in the CHPS causes further condensation. The CHPS distillate is collected as a light decomposition solution. The required amount of catalyst was suspended in light cycle oil (LCO) to form a slurry, then added with the VR to the reactor, and the reactor temperature and pressure increased with stirring using a magnetic type stirrer. After reaching the target temperature and pressure, hydrogen gas was circulated to start the experiment. The fractional components in the outlet gas were separated by the later stage separator and collected, as the F product, O/T-F (Once Through) liquid, or fractioned distillate obtained through Once Through operation. The residue remaining in the reactor after the once-through reaction was considered the P product: O/T-P product. Both O/T-F liquids and O/T-P products were separated with the solvent fractionation method as described later, and the physical properties and atomic balance analyzed.

2.2. Reaction Conditions for Hydrocracking

The reaction conditions for the hydrocracking reaction experiment using the autoclave reactor were selected to achieve 95 wt% of 525 °C+ in VR conversion rate and 85 wt% or higher oil yields to establish economical operation of a commercialized plant. The reaction pressure of 15 MPaG is the standard reaction pressure based on previous experiments conducted by Kobe Steel, Ltd.\(^4\),\(^5\). Therefore, the reaction pressure range was set as 12-20 MPaG, similar to other slurry process licensors’ reaction conditions, as shown in Table 1\(^6\).

In addition to the above references, the reaction temperature of the Super Oil Cracking (SOC) process implemented by Chiyoda Corp. was considered\(^7\),\(^8\), and 450 °C was used as the standard temperature. Furthermore, the reaction temperature range was set at 415-470 °C so that the 525 °C+ conversion rate and the amount of coke formation could be reflected in the modeling.

Reaction time of 60 min is the standard, as the 525 °C+ conversion rate and the oil yield are expected to achieve our target based on past test results obtained in autoclave tests conducted by Kobe Steel, Ltd. For the range of the reaction time, about 10 min of temperature rising and temperature cooling for the autoclave test were predicted to be necessary in the preliminary temperature rising test. The thermal stability of the reaction temperature during the autoclave test after reaching the target of greater than 400 °C as well as past test data obtained through coal liquefaction indicated that hydrogen consumption should increase after the reaction time reaches 10 min, so the minimum reaction time was considered to be 10 min. The longest reaction time was based on the cracking rate of the feedstock oil peaking at 60 min in a previous autoclave test by Kobe Steel, Ltd., so was expected to decrease thereafter. Therefore, a 90-min reaction time, 1.5 times longer than 60 min, was selected.

The catalyst was a limonite catalyst from Brazil. The catalyst was pulverized in oil to form a slurry with average particle size of 1 μm or less to increase the specific surface area and obtain reaction characteristics close to a synthesis catalyst such as NiMo/CoMo hydrogenation catalyst\(^9\),\(^10\). LCO was selected for catalyst solvent use as it is less likely to cause reaggregation of the catalyst due to the high content of aromatic compounds compared with conventional gas oil, as well as the expectation that it would suppress the formation of sludge in the reactor. The catalyst concentration is expressed in wt% to indicate the amount of limonite catalyst (as Fe with catalyst concentration indicated as wt%) continuously injected with respect to the mass flow rate of the feedstock (similar to feed oil ratio). The makeup concentration of 1 wt% as Fe was sufficient in the 3 barrels/day bench scale unit (BSU) operated by Kobe Steel, Ltd., since 95 wt% of 525 °C+ cracking rate was obtained with the 1 wt% catalyst. In addition, the reaction performance was close to saturation at 1 wt%, and the result was almost constant even at higher concentration.

2.3. Feed Oil Preparation

The feed oil used in the experiment was a mixed

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Table 1 Reaction Conditions for Hydrocracking

| Reaction pressure | [MPaG] | 12-20 |
|-------------------|--------|-------|
| Reaction temperature | [°C] | 415-470 |
| Reaction time | [min] | 10-90 |
| Catalyst addition | [wt% (as Fe wt% on feed oil)] | 0-2.0 |
crude oil from the Middle East, and VR oil obtained through distillation was used as the feedstock for the SPH process as shown in Table 2. Predetermined amounts of the VR, limonite, sulfur, and LCO were prepared, and the reaction was carried out under predetermined conditions with the hydrogen flow rate maintained with a compressor, as shown in Table 3.

The catalyst used in the experiment was the catalyst slurry obtained through pulverizing limonite in LCO until average particle size becomes 1 μm or less. Preliminary sulfidation of limonite was carried out with a method based on the past pilot test results of coal liquefaction at Kobe Steel, Ltd. In the commercial SPH process, sulfidation during the start-up operation is planned using dimethyl disulfide (DMDS) or solid sulfur, as pre-sulfurization with hydrogen sulfide in the recycle gas is practical during normal operation. However, in this autoclave test, sulfidation used solid sulfur for handling reasons during the test. The catalyst slurry shown in Table 3 was adjusted based on the above preparation procedure.

### Table 2 Properties of Feedstock Used in Hydrocracking Experiments

| Property                          | Value          |
|----------------------------------|----------------|
| Sp. Gr. [d (15/4 °C)]            | 1.035          |
| C [wt%]                          | 84.3           |
| H [wt%]                          | 9.2            |
| Sp. Gr. [wt%]                    | 4.56           |
| N [wt%]                          | 0.36           |
| V [wppm]                         | 127            |
| Ni [wppm]                        | 43             |
| Fe [wppm]                        | 18             |
| Na [wppm]                        | 19             |
| CCR (Conradson Carbon Residue)   | 23             |
| HI (Heptane Insoluble)           | 9.2            |
| HI-TS (Heptane Insoluble Toluene Soluble) | 11.7 |
| TI (Toluene Insoluble)           | 0.02           |
| Distillation                     |                |
| 200-343 °C                       | 0.6            |
| 200-343 °C                       | 1.4            |
| 450-525 °C                       | 7              |
| 525 °C +                         | 90.9           |

### Table 3 Properties of Slurry

| Component            | Brazil        |
|----------------------|---------------|
| Feed oil [g]         | 600           |
| Slurry [g]           | 0-72.1        |
| LCO (Light Cycle Oil) [g] | 0-49.6 |
| Limonite [g]         | 0-22.5        |
| Powder sulfur [g]    | 0-13.78       |

| Element | Limonite [mass%] |
|---------|------------------|
| Fe      | 0.30-0.85        |
| Ni      | 0.97-1.42        |
| Cr      | 1.46-2.47        |
| Al      | 1.92-2.36        |
| Si      | 1.01-1.07        |
| O @balance | 41.36-43.22    |
| Total   | 100.00          |

2.4. Analysis Method

The P liquid (product liquid left in the reactor after the autoclave reaction experiment) contained both soluble and insoluble components, but the sample amount of P liquid obtained after the reaction test was not necessarily sufficient since the gas flow type autoclave had a volume of only 1 liter, and the amount of P liquid obtained after the reaction inevitably decreased. Moreover, the P liquid contains solid content including the catalyst, so an efficient separation operation to minimize the product’s loss is also required for the analysis. Uncracked oil as the residual fraction from the autoclave bottom (AC-BTM), which contains the dissolved and insoluble components, underwent a small number of filtration steps to minimize the analysis procedure, as shown in Fig. 2. In this method, the sample was considered to be uniformly mixed.

C, H, S, and N in THFS (tetrahydrofuran soluble) and THFI (tetrahydrofuran insoluble) components of the P liquid and the fraction separated and recovered from the gas were analyzed. To estimate the reaction rate in the O/T operation, experiments were conducted with different reaction temperature, reaction time, reaction pressure, and catalyst addition amount, allowing mass balance data to be obtained.

3. Results and Discussion

3.1. Effect of Reaction Time on Hydrocracking during O/T Operation

The effects of reaction time were investigated on VR conversion, H₂ consumption, product yields, and yields of insoluble materials. The effect of the reaction time at reaction temperature of 450 °C was determined in experiments with reaction time of 15, 30, 60 and 90 min. Since the autoclave reactor cannot perform pulse-like temperature increases/decreases, the corrected reaction time (θ_correct) was calculated from both reaction
temperature and activation energy to account for the additional reaction time required to reach the set reaction temperature and to cool down after the experiment. For example, in an experiment with a set time of 30 min, activation energy of 50 kcal/mol for the SPH cracking reaction was used to correct the reaction time. That is, the liquid temperature of the reactor measured every second during the heating process and the activation energy of 50 kcal/mol are considered for the correction of feed oil cracking during heating up the autoclave. The corrected reaction time ($\theta_{corr}$) from the Arrhenius equation was calculated as 47 min, which is 1.5 times longer than the set time.

The VR (feed oil) cracking rate and the amount of hydrogen consumption increased with longer reaction time as shown in Fig. 5, where VR conversion was calculated as the cracked quantity of 525 °C+ component in Fresh Feed (FF). However, the VGO fraction, the 343-525 °C fraction, shows that the produced VGO and its VGO cracking rate were balanced up to 70 min, and that further VGO cracking occurred over the VGO production as the reaction time increased as shown in Fig. 3. The fraction of the 171-343 °C light oil fraction did not significantly increase even with reaction time of 70 min or longer, where the heptane insoluble component gradually decreased as the 525 °C+ was cracked, as shown in Figs. 4 and 5.

3.2. Effect of Reaction Pressure on Hydrocracking during O/T Operation

The rates of VR conversion and H$_2$ consumption
remained the same between 12 MPaG and 15 MPaG as shown in Fig. 6. However, VR conversion slightly decreased and H₂ consumption decreased by 18 % at 20 MPaG. The yield of the middle 171-343 °C distillate increased from 12 to 15 MPaG, then became saturated at reaction pressure of 15 MPaG or higher as seen in Fig. 7. On the other hand, the yield of 343-525 °C decreased from 12 to 15 MPaG, then became saturated at 15 MPaG or higher. The yield of 525 °C increased at reaction pressure of 15 MPaG, different trend from the yield trends of 171-343 °C and 343-525 °C.

Figure 8 shows the decreasing tendency of HI, TI, and THFI yields with higher reaction pressure. Presumably the polycondensation reaction (dry sludge generation) rate decreased as H₂ pressure increased, because HI, TI, and THTF yields proportionally decreased with higher hydrogen pressure as well. That is, the polycondensation reaction and VR conversion were both suppressed. Free radicals of different carbon numbers will produce a greater range of products, but the reaction pressure of 20 MPaG is presumably the region in which the catalytic H₂ quench of free radicals is increased, leading to the decreases in VR cracking reaction rate. Also, the aromatic saturation reaction is likely to be saturated between 12 MPaG and 15 MPaG considering that H₂ consumption is constant. Furthermore, hydrogenation of the heavy components, such as HI, is more likely to occur than cracking of the 525 °C as VR conversion decreases with higher H₂ pressure. Further experiments are planned in the future to verify these assumptions.

3.3. Effect of Catalyst Concentration on Hydrocracking during O/T Operation

The effect of catalyst concentration was investigated using 0.1, 0.2, 0.5, 1, and 2 wt% as Fe on VR, including a control thermal cracking experiment without the addition of catalyst. VR (feed oil) conversion was not significantly affected by the amount of added catalyst as shown in Fig. 9. However, H₂ consumption in Figs. 9 and 11 indicated that hydrogenation increased with higher catalyst concentration, and the insoluble content decreased until the catalyst concentration reached 1.0 wt%. The naphtha fraction (C₅H₁₂-171 °C) and the 525 °C also tended to decrease, and the middle fraction (171-343 °C) and the VGO fraction (343-525 °C) increased with higher catalyst concentration up to 1.0 wt%, then these fractions and insoluble content
plateaued at catalyst concentration higher than 1.0 wt%. These findings probably show that the hydrogen donation ability increases with higher catalyst concentration up to 1.0 wt%, the radical molecules generated by the thermal cracking reaction are hydrogenated to suppress the polycondensation reaction, and the insoluble content is greatly reduced. In particular, the catalytic reaction effect was remarkable from no catalyst to catalyst concentration of 1.0 wt%. Although suppression of the polycondensation reaction was still observed at the higher catalyst concentration of 1.0 wt%, no remarkable addition effect was seen.

Furthermore, as an example of the catalytic effect, the state of coke adhesion around the impellers and plate in the reactor after the experiment was compared as shown in Figs. 12-1 and 12-2. During thermal cracking (without catalyst), a large amount of coke was deposited on the impellers and plate with very high TI yield of 16.6 wt% (coke precursor and coke). As the amount of the catalyst increased, the amount of coke deposition decreased, and catalyst concentration of 0.2 wt% or more significantly reduced coke deposition, and no coke deposition occurred with the standard 1.0 wt% catalyst. Based on these results, the polycondensation reaction, especially formation of TI (coke precursor and coke), was largely suppressed by the SPH catalyst.

The SPH process system uses inexpensive limonite catalyst, which does not require any synthesis, so that catalyst regeneration is not required. Therefore, based on the test results, the spent catalyst activity can be maximized and the amount of catalyst introduced into the system can be minimized, which will lead to a more economically feasible process. Establishment of the function (equation) of the spent catalyst activity and the catalyst concentration for economic optimization of the process will achieve the optimum uncracked oil recycle flow rate, fresh catalyst amount, and sludge control. So far, 1 wt% catalyst concentration has been the standard condition, and 1 wt% was confirmed as the optimum amount of catalyst to be added.

3.4. Effect of Reaction Temperature on Hydrocracking during O/T Operation

Higher reaction temperature increased the VR (feed oil) cracking rate (525 °C conversion) and the cracked oil yield (C5H12-525 °C) as shown in Figs. 13 and 14. The vacuum gas oil (VGO) (343-525 °C) fraction was maximum at around 450 °C, and decreased above that reaction temperature because cracking of VGO (343-525 °C) also occurred. On the other hand, hydrogen consumption tended to increase in proportion to the reaction temperature, so desulfurization may also occur. Furthermore, with respect to the yield of the insoluble content, cracking of HI occurred at 450 °C or less, whereas the yields of both TI and THFI remarkably increased at 450 °C or higher, presumably because polycondensation occurred, as shown in Fig. 15.

4. Hydrocracking Reaction Modeling

Optimization of the SPH process requires a reaction model which considers first the cracking reaction of the bottom recycle oil (uncracked oil), then the catalyst activity of fresh catalyst and the spent catalyst. Therefore, the present reaction model was first proposed based on O/T test results, then the parameters were adjusted to create the basis for the reaction modeling of this hydrocracking process. Based on this base model, reaction modeling of the bottom recycle will be proposed in our next achievements to finally optimize the remainder of this process.

4.1. Proposed Reaction Model

The hydrocracking reaction model to achieve the optimum mass balance, including recycling of the uncracked oil, incorporated the following assumptions into the proposed lump reaction model, as shown in Fig. 16.

(i) The hydrocracking reaction of the autoclave reactor was assumed to incorporate no residence time distribu-
(ii) Under the reaction conditions, the light fraction below the middle distillate fraction generated by hydrocracking was obtained in the vapor phase, so the reaction time was short, with no cracking pathway from the middle distillate.

(iii) To optimize the cracked oil recycling model in the future, the proposed reaction model in Fig. 16 investigated the contribution of the bottom recycle oil to the improvement of the cracked oil yield based on equilibrium reaction pathways such as $k_{21}$ and $k_{32}$.

(iv) H$_2$S and NH$_3$ were collectively treated as a single gas component.

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**Fig. 12-1** Coke Formation Control Effect of SPH Catalyst

**Fig. 13** VR Conversion Rate/Desulphurization/H$_2$ Consumption and Reaction Temperature

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**Thermal cracking**

![Thermal cracking diagram](image)

**Hydrocracking**

![Hydrocracking diagram](image)
This reaction model incorporated equilibrium reactions such as $k_{12}$ and $k_{21}$, $k_{32}$ and $k_{23}$, and was devised to be easily and accurately express the rates of the hydrocracking reaction and the polycondensation reaction.

Abbreviations in Fig. 16 are as follows.

- C1: 525 °C-HS fraction (mass%)
- C2: HI-TS fraction (mass%)
- C3: TI-THFS fraction (mass%)
- C4: THFI fraction (mass%)
- C5: VGO: 343-525 °C fraction (mass%)
- C6: middle distillate: 171-343 °C fraction (mass%)
- C7: naphtha: C5H12-171 °C fraction (mass%)
- C8: gas: CH4-C4H10, H2S, NH3 (mass%)

The reaction rate equation of the hydrocracking reaction model is as follows:

\[
\frac{dC1}{dt} = -k_{12}C1 - k_{15}C1 - k_{16}C1 - k_{17}C1 + k_{21}C2 \tag{2}
\]

\[
\frac{dC3}{dt} = k_{12}C1 - k_{23}C2 - k_{25}C2 - k_{26}C2 - k_{27}C2 - k_{28}C2 + k_{32}C3 \tag{3}
\]

\[
\frac{dC4}{dt} = k_{23}C2 - k_{34}C3 \tag{4}
\]

\[
\frac{dC5}{dt} = k_{13}C1 + k_{25}C2 - k_{56}C5 - k_{57}C5 - k_{58}C5 \tag{5}
\]

\[
\frac{dC6}{dt} = k_{56}C5 + k_{16}C1 + k_{26}C2 \tag{6}
\]

\[
\frac{dC7}{dt} = k_{57}C5 + k_{17}C1 + k_{27}C2 \tag{7}
\]

\[
\frac{dC8}{dt} = k_{58}C5 + k_{18}C1 + k_{28}C2 \tag{8}
\]

4.2 Tuning Results (reaction time) for Autoclave Test Results

Figures 17 and 18 show both the obtained autoclave results and simulation results by fitting the autoclave results with minimum deviation. However, some plots did not exactly fit the simulated lines in Figs. 17 and 18. For example, reaction yields of 525 °C-HS and 343-525 °C at 22.8 min and 525 °C-HS at 107.8 min did not perfectly fit with the reaction model. In this section, these two reaction mechanisms are discussed.

4.2.1 Changes in Overall Reaction Rate for VR with Wide Molecular Distribution

VR has a molecular structure that is easy to crack (i.e. the reaction rate is fast) and another molecular structure that is difficult to crack (i.e. the reaction rate is slow) due to the wide range of molecular distribution. Therefore, the reaction order for severe VR cracking has been experimentally observed to follow pseudo-second-order reaction if the VR fraction is considered as one fraction. However, our SPH reaction model was focused on accurate prediction of individual product yields by separating the VR fraction into four fractions. Specifically, dependent on whether the VR was...
soluble in solvents or not, C1 (525 °C-HS), C2 (HI-TS), C3 (TI-THFS), and C4 (THFI) were considered as a part of the VR fraction but with different molecular distributions, and incorporated into our model based on our past experience of thermal cracking modeling \(^ {12} \). Following separation of the VR fraction into these four fractions, the molecular distribution was narrowed down so that uniform first order reaction rates could be expressed more precisely in our proposed reaction model than if the VR fraction was considered as only one fraction.

4.2.2. Reaction Rate Changes in Each VR Fraction with Effect of Catalyst Deactivation

Figures 19 and 20 show that the simulated lines and the reaction test data at 22.8 min fitted well if the reaction rate constants were mainly adjusted for 22.8 min reaction time, but the data deviated more at reaction times longer than 22.8 to 107.8 min. Similarly, Figs. 21 and 22 show that the simulated lines and the reaction test data at 107.8 min fitted well if the reaction rate constants were focused on 107.8 min, but deviated more at shorter reaction times than 107.8 min. These adjustments indicate that the reaction pathways cannot be expressed by a single reaction rate during the reaction time or in each fraction of VR. That is, the limonite catalyst activity during the reaction time was considered to change from the initial stage of the reaction to the late stage of the reaction.

Assuming such changes leads to the proposal that catalyst deactivation function should be incorporated into the current SPH reaction model in the future to reflect catalyst deactivation at each stage. Table 4 shows that the reaction rate changes occur probably because of different catalyst deactivations at different reaction times. For example, \( k_{12}, k_{15}, k_{16}, k_{34}, \) and \( k_{57} \) are considered to undergo kinematic changes with reaction time. Also, the coking formation rate (reaction rate from VR to coking formation) in the thermal crack-
The reaction rate in SPH is slower than thermal cracking. In addition, although the reaction rate of \( k_{34} \) temporarily increased during the initial stage of the reaction in the SPH process, coking formation was largely suppressed by the hydrogen and the catalytic effect. Given these nonuniform changes occur in all reaction paths at various reaction times, the effect of thermal cracking and catalytic hydrogenation on reaction rates must be considered in the future because the hydrogen, catalyst, and high temperature/high pressure reactions interact to affect product yields in complex ways.

The future reaction model should also incorporate the function of residence time distribution, because the SPH process involves an uncracked oil recycle system in which multiple stages of the continuous stirred tank reactor (CSTR) reaction model must be considered\(^\text{1}\). Using this model can construct an operation-optimized flow that minimizes sludge formation and maximizes the VR (feed oil) cracking rate and oil yield of the feedstock oil.

### 4.3. Tuning Results (temperature) for Autoclave Reactor Test Results

The standard reaction temperature of SPH is 450 °C with 60 min reaction time, as discussed here. Based on these conditions, the predicted yields from the reaction model are shown in Figs. 23 and 24 with the frequency factor and activation energy of each reaction route determined according to the Arrhenius equation. Comparison of the product yields with the expected yield from the reaction model shows that the 525 °C-HS yield, HI-TS yield, and 171-343 °C yield deviate if the reaction temperature changes from the standard reaction temperature. In particular, the deviation from the model is increased as the reaction temperature exceeds 460 °C. If the reaction temperature is within 460 °C, the assumed reaction rate of hydrocracking shows a good fit. However, if the temperature reaches 460 °C or higher, the yields of 525 °C-HS, HI-TS, and 171-343 °C deviate from the experimental yields because sampling uniformity in the autoclave at higher reaction was not always maintained at higher temperature, mainly due to the phase separation caused by the high degree of thermal cracking and the polymerization reaction. For example, as coking increases, the liquid product remaining in the autoclave was more viscous and difficult to sample due to the high degree of thermal cracking and coking generation with free radical reactions.

### 5. Conclusion

The SPH reaction model was proposed for slurry-type hydrocracking reaction of heavy oil based on the experimental autoclave results. The decomposition reaction pathway of the VR includes two equilibrium reactions, which indicate that the polymerization is mitigated by

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**Table 4 Changes in Reaction Rate Constants in the Initial and End Stage Periods**

| Reaction pass at 22.8 min | at 107.8 min |
|--------------------------|-------------|
| \( k_{12} \) | 1.0 (base) | 0.4 |
| \( k_{15} \) | 1.0 (base) | 0.5 |
| \( k_{16} \) | 1.0 (base) | 0.7 |
| \( k_{17} \) | 1.0 (base) | → |
| \( k_{18} \) | 1.0 (base) | → |
| \( k_{23} \) | 1.0 (base) | 0.8 |
| \( k_{25} \) | 1.0 (base) | → |
| \( k_{26} \) | 1.0 (base) | → |
| \( k_{27} \) | 1.0 (base) | 1.1 |
| \( k_{28} \) | 1.0 (base) | → |
| \( k_{34} \) | 1.0 (base) | 0.1 |
| \( k_{40} \) | 1.0 (base) | → |
| \( k_{50} \) | 1.0 (base) | 7.3 |
| \( k_{58} \) | 1.0 (base) | → |
| \( k_{60} \) | 1.0 (base) | → |
| \( k_{21} \) | 1.0 (base) | → |
| \( k_{22} \) | 1.0 (base) | → |

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hydrogenation. By adding this reaction route, a complex reaction path for the hydrocracking model can be proposed, which enables optimization of the autoclave test plan and the development of a process system that leads to optimization of the reaction yield. In the future, we will adopt the CSTR reaction model from the plug flow reactor (PFR) reaction model, by considering uncracked oil recycling and varying catalyst deactivation rates into our reaction model, to develop a commercial reaction model that incorporates residence time distribution.

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要旨

リモナイト触媒を用いたスラリー型ハイドロクラッキングの反応モデル

川井 英司，藤井 重孝，佐藤 秀紀，和田 幸隆，武田 大

(株)日柄製薬所と千代田化工建設(株)が、90%を超える分解率を持つ究極の重質油改質プロセスとして共同開発したKOBELCO SPH（スラリー型水素化反応プロセス）は、上流の油井での重質原油アップグレードへの適用、または製油所での減圧残油（VR）アップグレードへの適用が可能である。一般に重質油の水素化分解では、熱分解によって引き起こされるラジカル反応と高分子化合物の縮合反応により、分解率が高くなるにつれてスラッジ生成速度が増加する。本研究目標は、95 wt%を超えるVR分解率、80 wt%を超える油収率、かつスラッジ生成の最小化を達成する最適化された反応条件を見つける、パイロットおよび商業装置のプロセスシステム構築に適用することである。この目的のために、1L容積のオートクレープ試験装置を用い、反応時間、触媒リモナイト濃度、反応圧力、および反応温度を変化させ、最適な反応条件を見つけた。また、この反応条件を理論化し、将来のパイロット・商業装置への適用性拡張を行うためには今までにない新しい反応モデルが必要である。本研究では、その新しい反応モデルを提案し、実験結果をシミュレートすることで反応モデルの妥当性の検証を行うとともに、将来への課題・展望を述べる。