

A PREDICTION MODEL FOR DRY SLUDGE FORMATION IN RESIDUE HYDROCONVERSION

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Among the various residue upgrading processes in use, conventional hydrodesulfurization (HDS) units operated at elevated temperatures are widely employed for cracking of inferior crudes with a high metal content, such as Middle East or South American crude. Such a high-temperature operation results in inducing dry sludge formation in product oil and maximum conversion is regulated by that limitation. With a combination of hydrovisbreaking and hydroconversion by asphaltene bottom cracking (ABC) catalyst the maximum conversion was improved by as much as 15% for inferior crudes. The advantage of the higher conversion was proved by characterizing the reaction mechanism in the process. And, the reaction mechanism model and prediction model for compatibility of product oil proposed for the prediction of maximum conversion will also be a tool for optimizing various types of residual hydroconversion processes.

Introduction

Japan's refining industry has encountered changes in product demand, namely a decrease in heavy fuel oil demand and an increase in gasoline and middle distillate demand, while crude throughput has decreased. Recently, it has become very popular to operate residue HDS units at elevated temperatures to hydroconvert residual bottoms to a more valuable product in trade-off of hydrogen consumption⁵⁾ to cope with these changes. The higher-temperature operations resulted in shorter catalyst lives and induction of dry sludge formation in product oil. After the formation of dry sludge in product oil the unit can hardly be operated, because the sludge deposits in flush drums, fractionators, product rundown heat exchanger and lines of the unit. Additionally, the properties of the product are far from acceptable.

The maximum conversion attainable in residue hydroconversion is determined by this limit of dry sludge formation in product oil, not by the limit of fixed bed catalyst activity, and it is around 45 to 50 wt% of 538°C above conversion depending upon feedstock in the conventional hydrodesulfurization (HDS) process with a fixed-bed reactor. A combination²⁾ of asphaltene bottom cracking (ABC) catalyst⁶⁾ and hydrovisbreaker increased maximum conversion up to more than 60 wt% of residue feed.

The mechanism of dry sludge formation is too complicated to analyze and understand without suit-

able mathematical models. The proposed model well represented the complicated phenomena taking place in residue hydroconversion and it became possible to predict the maximum extent of conversion within the limit of no dry sludge formation.

1. Components Breakdown for Reaction Analysis

When residue is converted beyond a certain limit, condensed carbonaceous material (dry sludge) precipitates in product oil.

The phenomena of dry sludge formation are very intangible. In the hydrovisbreaking heater, asphaltene content increases but product oil is rather stable up to a certain level. On the other hand, dry sludge easily precipitates at a lower level of asphaltene content in the catalytic hydroconversion reactor. Dry sludge precipitation is comprehended to be triggered by the incompatibility of polymerized and condensed asphaltenic bottom component in product oil.

For the analysis of component compatibility in the product oil along with residue conversion, maltene portions of residual oil (heptane-soluble component) were developed into four segments as shown in **Fig. 1**: saturates, aroma-I, aroma-II and resin by use of thin-layer chromatograms.³⁾ When reaction takes place, the contents of those segments and asphaltenes (heptane-insoluble component) were observed to change with a specific rate of reaction depending on the processing conditions.

Segmented components are those illustrated in **Fig. 2**, if represented by average molecular structures. Saturates and aroma-I have a simple structure and are

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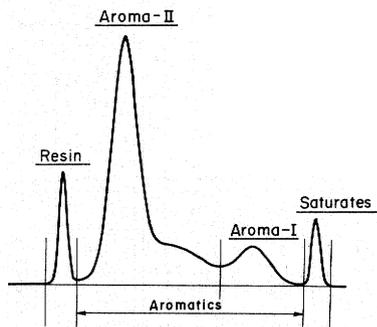


Fig. 1. Typical TLC/FID chromatogram of maltenes

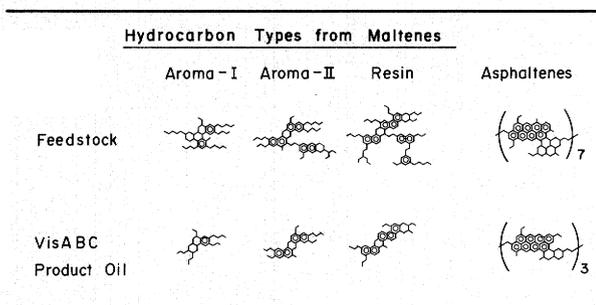


Fig. 2. Possible molecular structures

regarded as the final products in reaction systems such as in a hydroconversion or hydrovisbreaking reactor, where thermal cracking results in a driving force of cracking. On the contrary aroma-II and resin have molecular structures with a weak bond energy like a bibenzyl structure in them. They have a rather fast cracking rate at high temperature.

Figure 2 also shows the average structural models of asphaltene. It is easily cracked on ABC catalyst with the unit structure left almost constant but the number of unit cells decreased drastically.⁶⁾ However, it is easily polycondensed at elevated temperatures in the absence of hydrogen and catalyst.

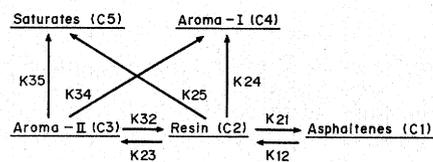
2. Reaction Model

Figure 3 shows reaction mechanism models for the hydrovisbreaking reaction in the heater and the hydroconversion reaction in the following fixed-bed reactor. They are derived from the previous discussion of the reaction potential of each component.

Both models have the same reaction paths K_{24} , K_{25} , K_{34} and K_{35} in cracking reaction to produce saturates and aroma-I from aroma-II and resin. They are thermal cracking paths from residue. Condensation and polymerization take place (K_{32} and K_{21}) along with cracking reactions in the hydrovisbreaking reaction. Catalytic reaction is observed only in the hydroconversion reaction of bottom cracking paths (K_{12} and K_{23}).

The concentrations of components are predicted by solving the following differential equations simul-

Reaction Model



Relative Rate Constant

Kx	HYDROVISBREAKING		HYDROCONVERTING
	ABC	HDS	HDS
K35	1.00	1.00	1.69
K34	0.99	0.81	1.64
K25	2.15	2.36	4.07
K24	0.60	1.00	2.84
K23	—	5.03	4.06
K32	0.13	—	—
K12	—	7.08	5.18
K21	0.35	—	—

Fig. 3. Reaction mechanism model

taneously.

For hydroconversion reaction:

$$dC_1/dt = -K_{12} \cdot C_1 \quad (1)$$

$$dC_2/dt = K_{12} \cdot C_1 - K_a \cdot C_2 \quad (2)$$

$$dC_3/dt = K_{23} \cdot C_2 - K_b \cdot C_3 \quad (3)$$

$$dC_4/dt = K_{24} \cdot C_2 + K_{34} \cdot C_3 \quad (4)$$

$$dC_5/dt = K_{25} \cdot C_2 + K_{35} \cdot C_3 \quad (5)$$

where

$$K_a = K_{23} + K_{24} + K_{25} \quad (6)$$

$$K_b = K_{34} + K_{35} \quad (7)$$

For hydrovisbreaking reaction:

$$dC_1/dt = K_{21} \cdot C_2 \quad (8)$$

$$dC_2/dt = K_{32} \cdot C_3 - K_a \cdot C_2 \quad (9)$$

$$dC_3/dt = -K_b \cdot C_3 \quad (10)$$

$$dC_4/dt = K_{24} \cdot C_2 + K_{34} \cdot C_3 \quad (11)$$

$$dC_5/dt = K_{25} \cdot C_2 + K_{35} \cdot C_3 \quad (12)$$

where

$$K_a = K_{21} + K_{24} + K_{25} \quad (13)$$

$$K_b = K_{32} + K_{34} + K_{35} \quad (14)$$

The numbers tabulated below Fig. 3 are representative relative rate constants observed in the data fitting. For the prediction of product oil components, relative reaction rates are important rather than absolute values. In hydrovisbreaking, the value of $k_{25} + k_{35}$ is smaller than that for hydroconversion, indicating that less saturates are produced in hydrovisbreaking than in hydroconversion. A tendency was also found for less saturates, less asphaltene and more aromatics in product oil with ABC catalyst in

hydroconversion than with conventional HDS catalyst.

3. Prediction of Product Oil Components

Simulations were carried out with the rate constants shown in Fig. 3 to predict how the components change in the hydroconversion of residual feed. Hydroconversion schemes employed in the simulations were as follows:

Case 1 Combined Hydroconversion Mode

1-a HVB-ABC

1-b HVB-HDS

Case 2 Conventional Catalytic Hydroconversion Mode

2-a ABC

2-b HDS

HVB: Hydrovisbreaking

ABC: Hydroconversion with ABC catalyst

HDS: Hydroconversion with conventional HDS catalyst

Predicted results are illustrated in Fig. 4 and 5 for each case. Distinctive features of each scheme, especially around the maximum conversion, can be summarized as follows:

Mode	Case 1 Combined Hydroconversion	Case 2 Conventional Hydroconversion
Saturates	+	++
Aroma-I	+	++
Aroma-II	-	--
Resin	--	--
Asphaltenes	--	--

+: increase, ++: increase more

-: decrease, --: decrease more

with the effect of catalyst on reaction rates:

	ABC	HDS
Saturates	+	+
Aroma-I	+	++
Aroma-II	-	--
Resin	-	--
Asphaltenes	--	-

+: increase, ++: increase more

-: decrease, --: decrease more

The results indicate that product components are very different in each hydroconversion scheme. Those differences of components affects the compatibilities of product oil and regulates the maximum extent of

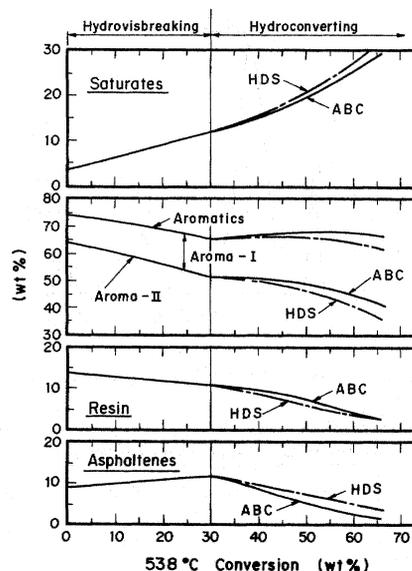


Fig. 4. Components prediction for VisABC process

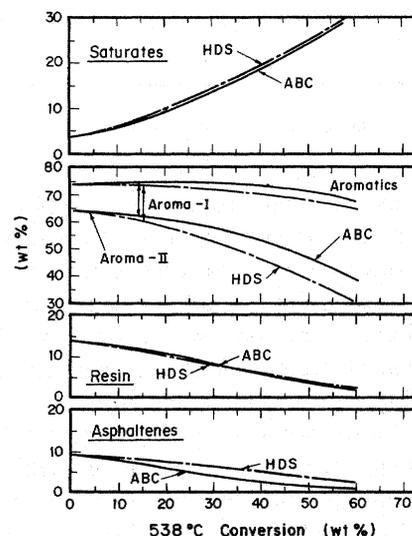


Fig. 5. Components prediction for conventional hydroconversion process

conversion, as will be discussed in later sections.

4. Predicting Model for Compatibility of Product Oil

As experienced, the condition of

- less saturates
- more aromatics
- more resin
- less asphaltenes

is believed to be a better condition for the compatibility of product oil or stable product oil against sludge formation. This is comprehended as asphaltene is dissolved more stably in the product oil if their properties are closer each other. It indicates Hildebrand's solubility theory⁴⁾ is applicable with simulated component breakdowns to predict the compatibility of product oil.

$$\frac{(X_2)_{ideal}}{X_2} = \exp[(-V_2 \cdot A_{12} \cdot \Phi_1^2)/RT] \quad (15)$$

$$A_{12} = (\delta_1 - \delta_2)^2 + 2l_{12} \cdot \delta_1 \cdot \delta_2 \quad (16)$$

The solubility parameters actually depend upon temperature by the definition. But, they were predicted by the following empirical equation¹⁾ in the model,

$$(10^3)^{1/2} \cdot \delta = 14.8 - 11.8 \cdot \{1/(1 + C/H)\} \quad (17)$$

because the values of their differences can be regarded as independent of temperature and the binary parameter l_{12} was fixed, as shown in Fig. 6, to work for all the effects of temperature on A_{12} .

Then, dry sludge formation in product oil is calculated.

$$Cd = C_1 - C_1^* \quad (18)$$

with the assumption:

$$\frac{(C_1^*)_{ideal}}{C_1^*} = \frac{(X_2)_{ideal}}{X_2} \quad (19)$$

The solubility parameter of product oil (δ_1) is not so far from that of asphaltenes (δ_2) at the low conversion. Product oil has very high solubility against asphaltenes. When conversion is increased, the solubility parameter of product oil tends to have a smaller number with components of more saturates, less aromatics and less resin against the large number of asphaltenes as shown in Fig. 7. It means the difference of δ_1 and δ_2 is increasing and that the solubility of asphaltenes in product oil is getting worse.

As indicated the logarithm of solubility is linear against the function of solubility parameters in the Hildebrand's theory. Figure 8 shows the asphaltene content against the function of solubility parameters, when dry sludges were just observed in product oil. The observed data are shown to fit the formula of Hildebrand's theory very well.

5. Control of Compatibility of Product Oil

Figure 9 shows a ternary composition diagram depicted on the model calculations. It predicts compatibility or product stability against sludge formation for simulated results of case-1 and case-2 which were discussed in the previous section. It shows out that asphaltene solubility greatly depends upon the components of product oil and that it is very important to control the compatibility of product oil to attain a high conversion. Roughly, line A and line B are comprehended to be the maximum conversion boundary regulated by asphaltene content and the hydrogenation extent of product oil, respectively.

Figure 10 shows the predicted amount of dry sludge sedimentation. Maximum conversion is more clearly

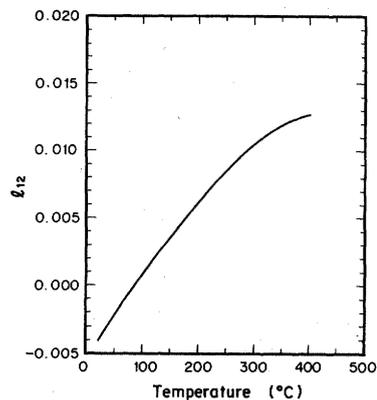


Fig. 6. Binary parameter for asphaltene solubility prediction

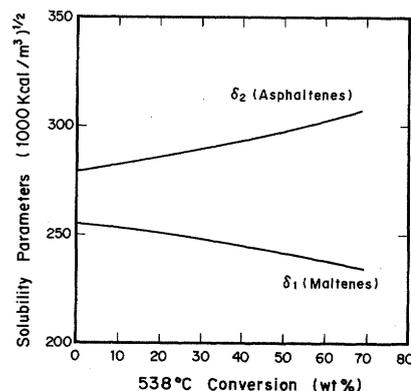


Fig. 7. Solubility parameters

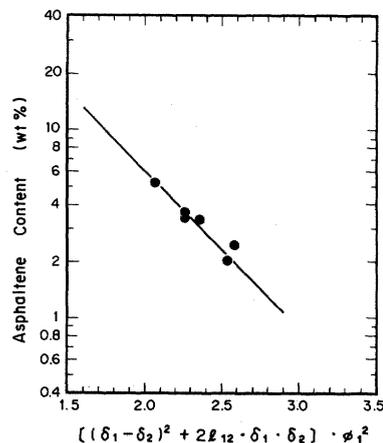


Fig. 8. Data fitting for Hildebrand Theory

indicated for each processing scheme. It is shown that the combination of HVB and ABC is an optimal system integration from the view point of compatibility control of product. In the hydrovisbreaking reaction, thermal cracking reaction is very dominant and high conversion is achieved. On the contrary, hydrogen is selectively consumed in a radical quenching against polymerization and condensation of asphaltenic bottom compounds. Following hydroconversion on ABC catalyst enables superior function of

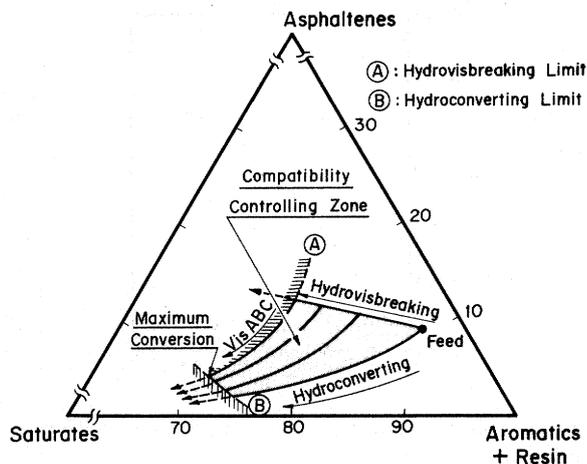


Fig. 9. Compatibility control diagram

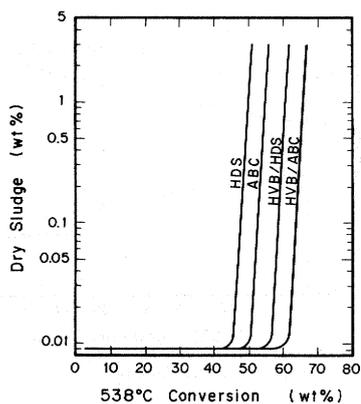


Fig. 10. Limit of 538°C conversion

asphaltene cracking and moderate hydrogenation of cracked oil as well as further cracking of residual portion. Less asphaltenes and proper hydrogenation lead to good compatibility of product oil and higher conversion is realized throughout the operation time.

Figure 4 implies a close performance of HDS catalyst to ABC catalyst, and a maximum conversion with HDS catalyst is predicted to be 57% against 62% with ABC catalyst in Fig. 10. However, this is based on catalyst performance after MOR (middle of run). Approximately before 500 h of operation time HDS catalyst has too strong a hydrogenation activity to control compatibility of product oil and dry sludge is easily formed as shown in Fig. 11. Moderate hydrogenation activity of ABC catalyst throughout the operation time is well appreciated in the control of compatibility of product oil.

Conventional hydroconversion process even with ABC catalyst has lower maximum conversion. Without hydrovisbreaking more hydrogenation is taking place than cracking. It results in poor compatibility with highly saturated components, and dry sludge easily precipitates in the product oil.

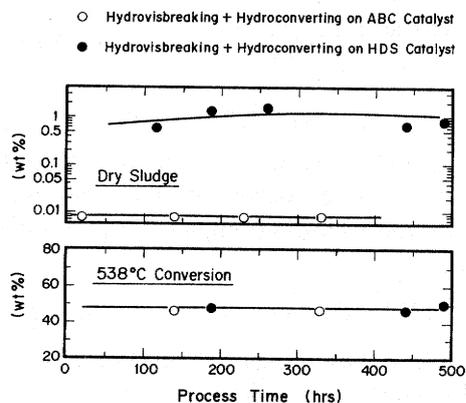


Fig. 11. Catalyst effect on dry sludge formation in early stage of operation

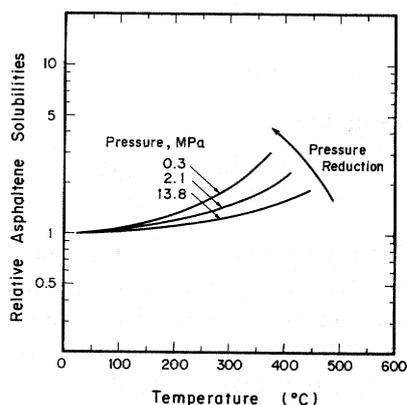


Fig. 12. Asphaltene solubilities for product oil states

6. Dry Sludge Sedimentation in Down Streams of the Unit

Dry sludge sedimentation is brought about in down streams of the unit by letting the states of the product oil be changed. Asphaltene is estimated to be dissolved in product oil stably in a reactor, even though down streams suffer from problems caused by dry sludge sedimentation. At higher temperatures, as in a reactor, lighter portions of cracked oil normally with paraffinic characteristics are vaporized. That should make the solubility parameter of product oil closer to that of asphaltene and improve the compatibility of product oil with relatively higher asphaltene solubility as shown in Fig. 12. Asphaltene is kept from sedimentation. But compatibility could turn out worse when effluent from the reactor is cooled by heat exchanger, because light cracked oil is condensed into product oil. Figure 13 shows that maximum conversion is raised to a greater extent if product oil is allowed to be cooled to a limited level.

On the contrary, too much vaporization of product oil, such as pressure reduction of reactor effluent at elevated temperature, sometimes seems to accelerate dry sludge formation in product oil. That is a predictable result from Fig. 13, which indicates that max-

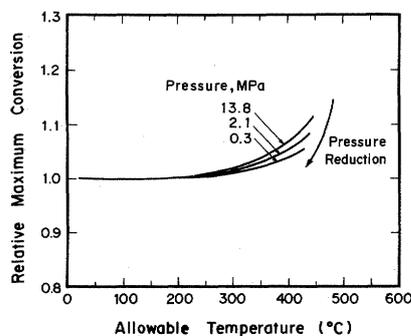


Fig. 13. Allowable temperature for product oil cooling against dry sludge formation

imum conversion is lowered by pressure reduction. In this case, the amount of maltene component as a solvent to dissolve asphaltene is considered to decrease by its vaporization from the product oil, though solubility itself is not worse, as shown in Fig. 12.

Such phenomena collected from operation in the field are rather hard to analyze for lack of quantitative data. The newly developed compatibility prediction model is useful for understanding the tendencies of those field data and to find methods of dealing with problems. If the state of product oil is allowed to change to a limited level and aromatic solvent or something with a proper solubility parameter, for example, is mixed into product oil to improve compatibility before it is changed further, conversion is expected to be raised to a greater extent as predicted in Fig. 13.

Conclusions

- 1) Maximum conversion is attained by controlling the compatibility of product oil in the state of nonformation of dry sludge.
- 2) The newly developed mathematical model gave excellent maximum conversion predictions for two types of hydroconversion process and two kinds of catalyst.
- 3) The diagram of product oil compatibility de-

icted in the model calculations indicated that more asphaltene cracking and moderate saturation of cracked oil are the optimal roots for maximizing a residue conversion.

4) Conventional HDS catalyst has too strong a hydrogenation activity at elevated cracking temperature in the early stage of operation. This results in easy formation of dry sludge or limited conversion.

5) The prediction model for product oil compatibility can be of great help in a diagnosis of downstream problems of the hydroconversion process caused by dry sludge sedimentation.

Nomenclature

C_i	= concentration	[kg/kg]
$(C_i^*)_{ideal}$	= ideal solubility of asphaltene	[kg/kg]
C_1^*	= solubility of asphaltene	[kg/kg]
C/H	= carbon to hydrogen atomic ratio	[kg mol/kg mol]
K_{ij}	= reaction rate constant of C_i to C_j	[1/h]
l_{12}	= binary parameter	[—]
R	= gas constant	[kcal/kg mol K]
T	= temperature	[K]
t	= reaction time	[h]
V_2	= molar volume of asphaltene	[m ³ /kg mol]
$(X_2)_{ideal}$	= ideal solubility of asphaltene	[kg mol/kg mol]
X_2	= solubility of asphaltene	[kg mol/kg mol]
δ_1	= solubility parameter of maltene	[(kcal/m ³) ^{1/2}]
δ_2	= solubility parameter of asphaltene	[(kcal/m ³) ^{1/2}]
ϕ_1	= volume fraction of maltene	[m ³ /m ³]

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