

## UPGRADING OF SHALE OIL BY AN EBULLATED-BED REACTOR

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## ABSTRACT

Proposed is a refining system composed of ebullated-bed type hydro-refining (1st stage treating) and processing of a mixture of syncrude and petroleum by use of conventional petroleum refining technologies (2nd and 3rd-stage treating) which upgrades the quality of shale oil containing large quantities of olefins and nitrogen compounds, to the level of current petroleum products. To conduct an evaluation of this system, an ebullated-bed type bench plant processing 1.5 Bbl/day of shale oil was used to perform a hydrorefining test and a fixed bed type bench plant was used to perform 2nd and 3rd-stage treating tests. After the evaluation of the operating conditions and the products, the feasibility of this system was confirmed.

## 1. Introduction

Shale oil, one of the alternatives to petroleum resources, includes a large quantity of impurities such as olefins and nitrogen compounds, compared with current petroleum crudes. With conventional hydrorefining processes in fixed bed, there exist numerous problems such as blockage in catalyst layers, elimination of reaction heat, rapid catalyst deactivation caused by increasing reaction severity, and so on.

To surmount the above problems, an ebullated-bed type reactor, which can maintain the activity of catalyst by changing it continuously and uniform temperature profile, is used for the purpose of evaluating the refining system (Figure 1) for shale oil.

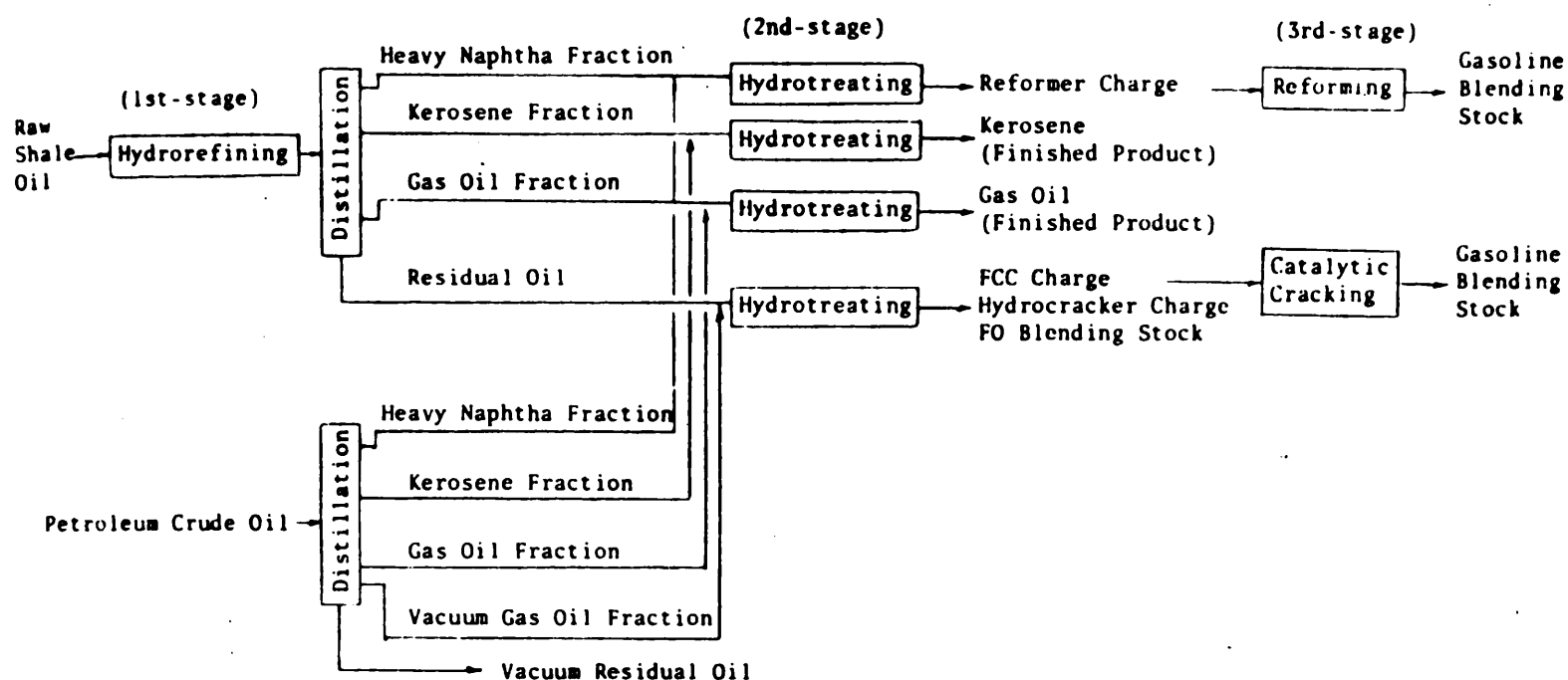


Figure 1. Refining System for Shale Oil

## 2. Experimental Method

### 2.1 Samples

Samples used in these experiments are American shale oil H; Chinese shale oil A; and Australian shale oil C. They are all whole range fractions by retorting. The feedstock properties are as shown in Table 1.

Shale oils A and C are made from the pilot plant of JNOC/JOSECO processing 300 T/day.

### 2.2 Catalysts

The catalysts used for the 1st and 2nd-stage treating were the Ni-Mo catalyst named NM-8 (NiO: 4 wt%; MoO<sub>3</sub>: 20 wt%) processed according to the specified pre-sulfiding method.

For the 3rd-stage treating, a commercial bi-metallic catalyst, which was used normally for catalytic reforming process, was used.

### 2.3 Experimental Apparatus and Method

#### (1) 1st-stage treating

Small-scale bench plant was used with a shale oil processing capacity of 0.05 Bbl/day, a diameter of 60 mm, a length of 400 mm, and a liquid inner circulation reactor with a catalyst capacity of 300 ml. For purposes of investigation, hydrorefining was performed under the condition of a reaction temperature of 360-420°C, a pressure of 100-140 kg/cm<sup>2</sup>G, and

a LHSV of  $0.35-1.0\text{hr}^{-1}$ . On the other hand, large-scale bench plant was also used, having a shale oil processing capacity of 1.5 Bbl/day, a diameter of 150 mm, a length of 3000 mm, and a liquid outer circulation reactor with a catalyst capacity of 24  $\ell$ . For purposes of obtaining chemical engineering data such as hold-up of gases, solids, and liquids by a scanning type  $\gamma$ -ray densimeter, and of manufacturing feedstocks for the 2nd and 3rd-stage treatings, hydrorefining was performed under the condition of a reaction temperature of  $360-420^{\circ}\text{C}$ , a pressure of  $135\text{ kg/cm}^2\text{G}$ , and a LHSV of  $0.33-1.0\text{hr}^{-1}$ .

#### (2) 2nd-stage and 3rd-stage treating

For the 2nd-stage treating the fixed bed reactor used had a diameter of 26 mm, a length of 1600 mm, and a catalyst capacity of 100 m $\ell$ . For the investigation of reaction condition optimization and for obtaining the feedstocks for the 3rd-stage treating, the treating conditions were a temperature of  $280-350^{\circ}\text{C}$ , a pressure of  $30-50\text{ kg/cm}^2\text{G}$ , and a LHSV of  $3-4\text{hr}^{-1}$ . For the 3rd-stage treating with the same type of reactor, the test was carried out at a temperature of  $470-490^{\circ}\text{C}$ , a pressure of  $11.7\text{ kg/cm}^2\text{G}$ , and a LHSV of  $1.0\text{hr}^{-1}$ .

### 2.4 Analytical Method

Shale oil properties were analysed by the standard test methods specified in JIS and ASTM.

The gaseous hydrocarbons was analysed by TCD and FID gas-chromatography.

## 3. Test Results and Conclusions

### (1) 1st-stage treating

#### 1) Reaction characteristics

At the time of the 1st-stage treating, kinetic study was given to the most important issue, that is, denitrogenation.

The ebullated-bed reactor has a greater inner circulation volume compared with the volume of liquid feed to the reactor; therefore this is considered to be a complete mixing tank, and the denitrogenation reaction can be considered as the pseudo-first order reaction. The following equation is confirmed:

$$K_N = (F/W) \times \frac{(N_F - N_p)}{N_p} \quad (1)$$

The temperature dependency on the denitrogenation rate constant of various shale oils calculated from equation (1) is shown in Figure 2. This shows that the temperature dependency is apparently almost the same regardless of various oils. The reaction data obtained from the small-scale bench plant are shown in the same Figure. This data shows good correspondence with these from the large-scale bench plant. From this result, it may be confirmed that the shape and structure of the reactors do not make a difference in ebullated-bed reactors.

## 2) Chemical engineering aspects

It is very important to maintain a catalyst level constant in order to obtain a uniform temperature profile in the reactor with a catalyst supply and withdrawal system. It is necessary to predict the catalyst level depending on the changes of operation conditions.

$$\frac{L_f(\text{III})}{L_0} = \frac{\epsilon_{SO}}{1 - \frac{1}{\epsilon_{SO}} A \left( \frac{U\ell}{U_t} \right)^a \cdot \left( \frac{U\ell U_t}{\sigma\ell} \right)^b + B} \quad (2)$$

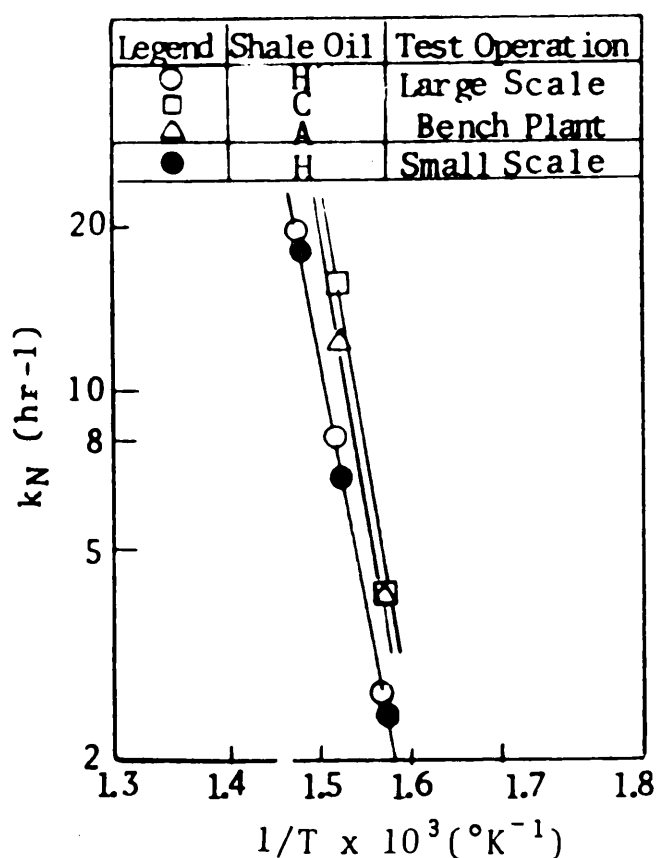


Fig.2 Arrhenius Correlation in Hydrodenitrogenating Shale Oil

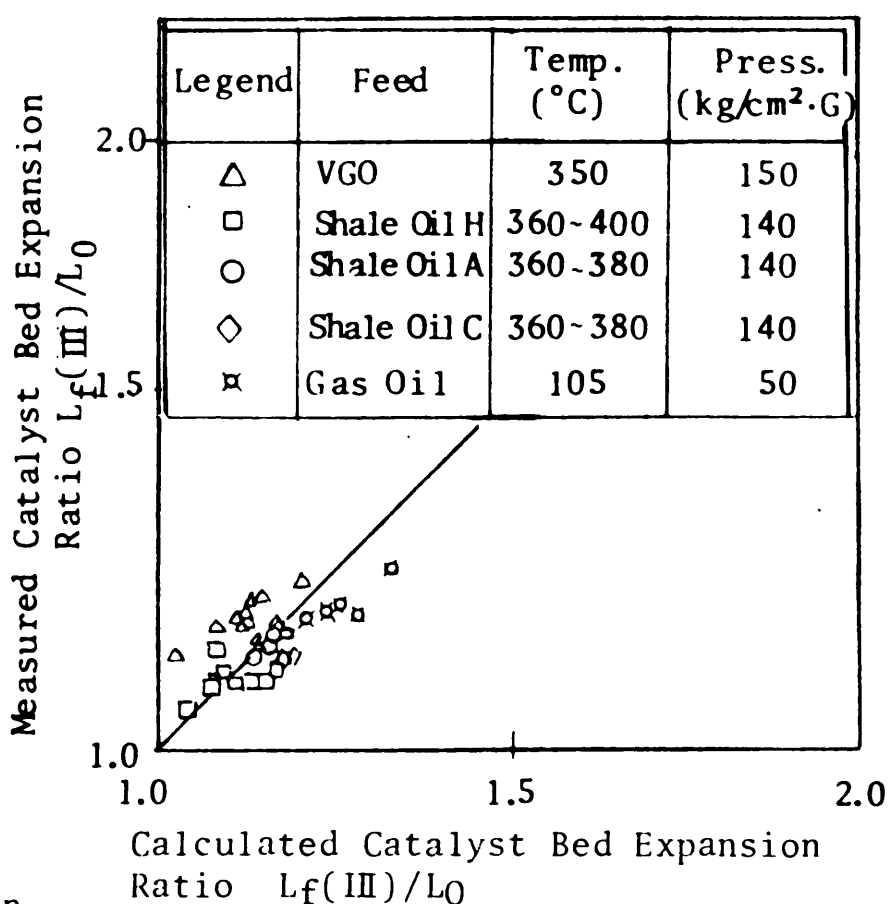


Fig.3 Relation between Calculated Data and Measured Data of Catalyst Bed Expansion Ratio

From this point of view, experiments with various liquids, operation conditions, and ebullated-bed sizes were carried out in cold conditions. The results lead to the above equation (2), that is, equation for predicting the catalyst level.

Figure 3 shows the correlation between catalyst levels calculated using equation (2) and the actual catalyst levels. The two coincide very well regardless of the feedstock properties changes and operating conditions; therefore, it may be confirmed that equation (2) is applicable to hydrorefining shale oil under a high temperature and a high pressure.

## (2) 2nd-stage treating

To evaluate the applicability of the refining system for shale oils shown in Figure 1, 2nd-stage treating of heavy naphtha fractions from syncrude (shale oil H), made by large-scale bench plant, was conducted and following result were obtained. The properties of the feedstocks are shown in Table 2.

### 1) Hydrotreating of mixed heavy naphtha fractions

As Table 2 shows, heavy naphtha fractions of syncrude from shale oil H includes 198 wt ppm of nitrogen. This is extremely high compared with petroleum fraction. In the 2nd-stage treating of heavy naphtha fractions from syncrude it is required that the maximum permissible nitrogen and sulfur content be 0.5 wt ppm and 1.0 wt ppm respectively because of specifications for the catalytic reforming (the 3rd-stage treating) catalyst.

For the desulfurization reaction, the sulfur content in the heavy naphtha fraction from syncrude is extremely small; therefore, as the blending ratio increases, the sulfur content of the mixed heavy naphtha fraction decreases; however, the sulfur content of the product naphtha fraction increases because of the inhibition effect on the desulfurization reaction by the nitrogen compound.

Figures 4 and 5 show the effect of blending ratio on the nitrogen and sulfur content of 2nd-stage treated oil. Figure 4 shows the minimum value of nitrogen content in the 2nd-stage treated oil based on specified reaction temperatures, and this shows that there is a limitation in reaction temperature.

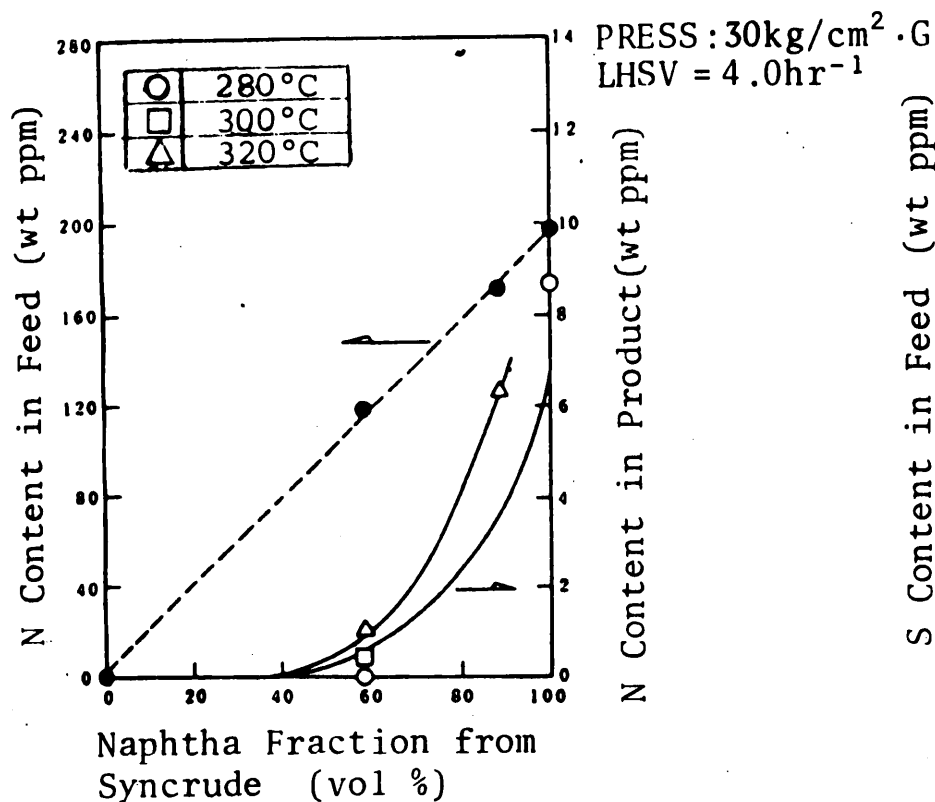


Fig. 4 Effect of Blending Ratio on Nitrogen Percentage of 2nd-stage Treated Oil

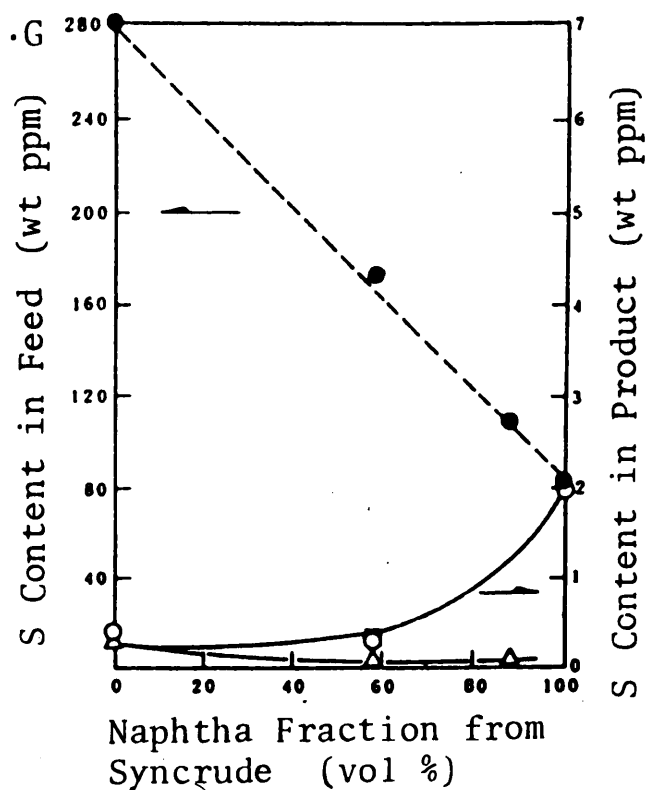


Fig. 5 Effect of Blending Ratio on Sulfur Percentage of 2nd-stage Treated Oil

Table 1 Feedstock Properties

Name		Shale Oil H	Shale Oil A	Shale Oil C
IBP-160°C	vol%	0.6	3.5	1.9
160-240°C	"	14.5	19.2	15.5
240-350°C	"	42.7	34.0	35.5
350°C+	"	42.2	43.3	47.1
C	wt%	84.26	85.11	85.08
H	"	11.86	12.47	11.93
N	"	1.68	1.14	1.13
S	"	1.02	0.41	0.38
O	"	1.18	0.87	1.48
(difference)				
Vis.@50°C	cSt	11.23	5.389	6.716
C.C.R.	wt%	1.71	1.48	1.86
Ash	"	0.03	0.01	0.04
Sp. Gr.	15/4°C	0.9045	0.8884	0.8888
Pour Pt.	°C	+25	+25	+27.5

Table 2 Properties of Heavy Naphtha Fraction (80-160°C)

Name	Syncrude (N=1350ppm)	Petroleum
Yield (vol%)	4.2	14.2
Sp. Gr. (15/4°C)	0.7582	0.7359
N (wt ppm)	198	0.3
S (wt ppm)	82	280
Composition (vol%)		
	A: 9.5	A: 12.0
	O: 0	O: 0
	P: 50.9	P: 68.0
	N: 39.6	N: 20.0

## (3) 3rd-stage treating

Figure 6 shows the effect of reaction temperature on catalytic reforming. Octane number increases as the reaction temperature increases; therefore, when compared with the petroleum fraction, at the same reaction temperature it is 7 octane higher, in other words, the same octane number can be obtained at a temperature 10°C lower.

Hydrogen production increases as the temperature goes up, and at the same time, the liquid yield decreases, as a result, hydrocracking proceeds.

Figure 7 shows the effect of blending ratios on the catalytic reforming. As the blending ratio increases, the octane number and hydrogen production increases. This is based on the high naphthene content in the shale oil.

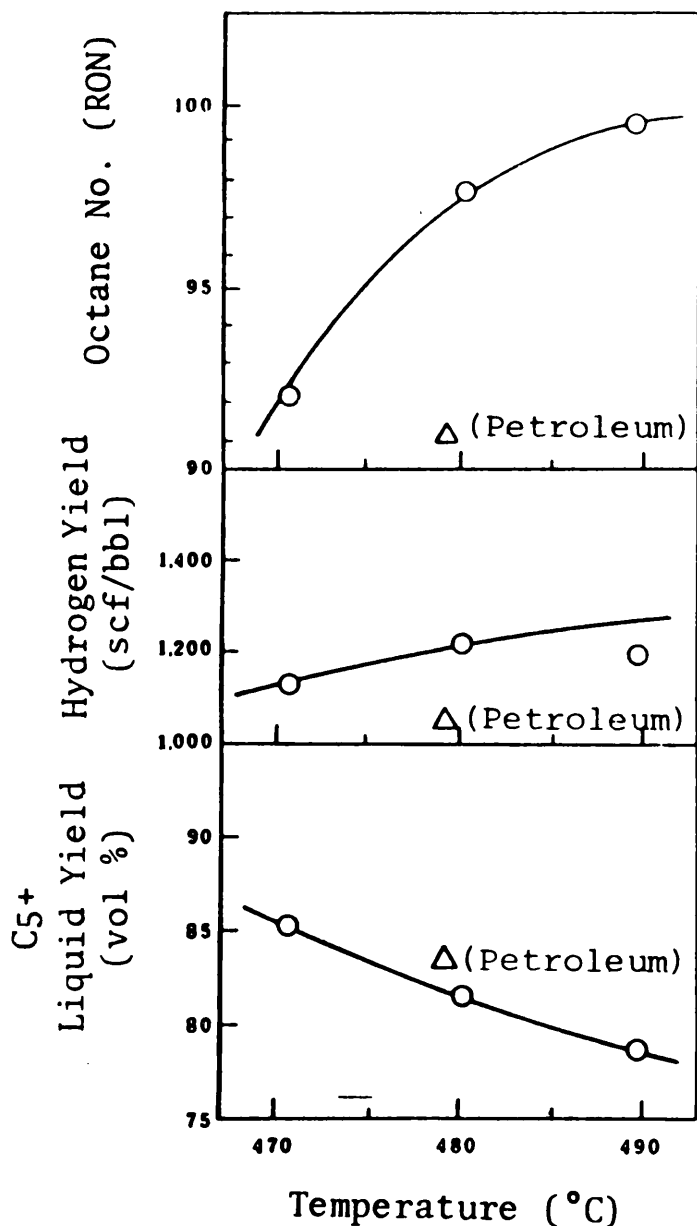


Fig.6 Effect of Temperature on Catalytic Reforming

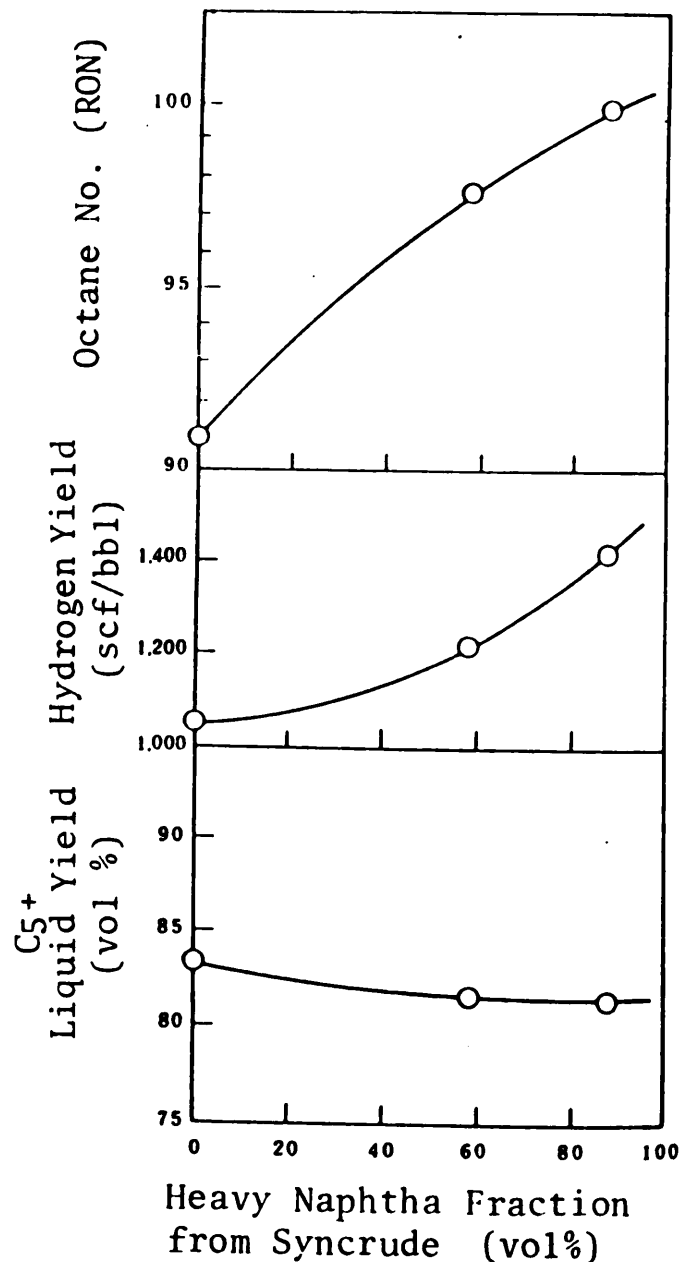


Fig.7 Effect of Blending Ratio on Catalytic Reforming

From the above results, it is confirmed that the 3rd-stage treating of heavy naphtha fractions from syncrude can be carried out by the conventional petroleum refining technology, that heavy naphtha fractions may be sufficient feedstock for catalytic reforming process, and that operating temperature can be lowered by mixing syncrude.

As in the case with naphtha fractions, kerosene, gas oil, and residual oil fractions from syncrude are mixed with petroleum fractions for the 2nd-stage and 3rd-stage treating experiments and conventional petroleum refining technologies were applicable to the refining system for shale oil, as a result, this refining system is confirmed to be effective.

#### 4. Conclusion

- (1) 1st-stage treating : Ebullated bed reactor is an effective reactor in hydrorefining shale oil.
- (2) 2nd-stage treating : Processing is possible, although there is a limitation in blending ratio and in operating conditions.
- (3) 3rd-stage treating : Naphtha fraction from syncrude can be used as a feedstock for catalytic reforming process.

From the above, it is possible to realize the feasibility of a "Refining system for shale oils".

#### 5. Acknowledgements

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