[Note]

Studies on Catalytic Hydrotreating of Heavy Residua (Part 1) Establishment of Handling and Control of Pilot Plant

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In the development of a catalytic hydrotreating process for heavy residua, it is important to evaluate product qualities and yields, and catalyst activity and life. The pilot plant test, therefore, is sufficient for this purpose. The authors have used "microreactors" for exploratory testing and screening of catalysts, "bench-scale test units" to evaluate catalyst performance over its expected life course, by obtaining kinetic data and studying process variables, and "pilot plants", simulating actual process flow and configuration for process configuration, by direct simulation of commercial operations. The test units were equipped with many devices to accommodate sludge and asphaltenic residua, as well as to increase unit reliability and to facilitate long run operations.

1. Introduction

We have conducted investigations into the catalytic hydrotreating of heavy residua. From this research, various processes were developed, such as the Asphaltenic Bottom Cracking (ABC) process^{1)~4)}, which produces lighter hydrocarbon oil from asphaltene-containing residua, and the hydrodenitrogenation (HDN) process^{5)~8)} for Middle East residua. Incidentally, since it is possible to estimate hydrotreating performance from properties of feedstocks and of catalysts, the number of necessary pilot plant runs can be reduced. To develop new processes, however, experimental tests must be conducted with actual feedstocks and catalysts, in order to obtain information on the activity and life of the catalyst, as well as on the properties and yields of product oils. Pilot plants will play, therefore, an important role in the investigation of catalytic hydrotreating of heavy residua.

In the development of a catalytic hydrotreating process for heavy residua, a large number of pilot plants are desirable because each run requires a long period of operation, using only one pilot unit for each catalyst. During operation, a steady state must be maintained, requiring accurate measurement and control of oil flow rates, smooth transfer of heavy oils, and safe oil-sampling methods. Special precautions and techniques are required

for handling ultraheavy fractions, containing asphaltenes or sludge. In the hydroprocessing of heavy oil, laboratory techniques must be systematized prior to the adoption of established computerized automation.

The authors have investigated procedures and methods to utilize pilot plants. In this paper, the authors report the results as follows: (1) the proper use concerning the purpose; (2) the development of equipment to handle heavy residua; (3) the effect of flow in the reactor on catalyst effectiveness.

2. Pilot Plant in Process Development

2.1. Pilot Plant Units

There are various pilot plant units which simulate petroleum processes. They can be classified into three separate categories in terms of process research steps: microreactors, bench-scale test units and pilot plants. The specifications of pilot plant units are outlined in **Table 1**. The number, capacity, and function of these units were determined on the basis of previous trials and operating experience.

2.2. Microreactors

A simplified flow diagram of a microreactor is shown in **Fig. 1**. The feed oil rate is measured by the buoyancy change transmitter (BCT) method as shown in **Fig. 2**. A metering pump, typically used in liquid chromatography applications, was employed as a feed pump after remodeling. The effluent gas from reactor is separated in the high-

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Table 1 Pilot Plants at Chiyoda R & D Center

	Microreactor	Bench-scale test unit	Pilot plant
Total number	20	26	6
Type	1	6	6
Reactor diameter [mm]	12.7	25.4	37
Reactor length [mm]	250	1,100, 2,200	3,320
Catalyst volume [ml]	6-30	100-1,000	500-2,500
Max. oil rate [ml/h]	30	800	2,500
Number of items of data stored	20-30	20-30	50
Functions			
Gas flow mode	Once-through	Once-through or recycle	Recycle
Oil flow mode	Upflow	Downflow and upflow	Downflow
Oil recycle	No	Yes	Yes
Light oil separation	No	Yes	Yes
Production gas analysis	Off-line	On-line	On-line

Fig. 1 Simplified Flow Diagram of Microreactor

pressure separator. At 12 h intervals, the product oil in the high-pressure separator is discharged by the automatic liquid sampling (ALS) system, which is described in a subsequent section. Hydrogen gas passes through the system once, and the pressure is controlled by two self-control regulators. The flow rate of gas is set by a metering valve, installed on the depressurized gas line.

Considering the comparatively small diameter of the reactor, the external temperature of the reactor tube is taken for the reaction temperature. The difference in temperatures during hydrotreating of residue was less than 3°C, as determined by a moving thermocouple probe, shown in Fig. 3. The heater of reactor is separated into three blocks for preheating and for compensation of heat loss.

2. 3. Bench-scale Test Units

A simplified flow diagram of the bench-scale test unit for hydrocracking of residue is shown in Fig. 4. Considering that these reactors are usual-

ly operated in a trickle flow mode, the wetting efficiency of the catalyst is an important property⁹. Bruijn¹⁰ proposed that the catalyst beds should be diluted with small inert particles.

From the results of the electron probe microanalysis (EPMA) of the used catalyst, which will be described later, the precautions for catalyst loading and operation procedures were standardized to avoid partial wetting. The wetting efficiency, f_e , for an extrudate catalyst of 1/32-in diameter was so high that dilution was unnecessary. The f_e of the 1/16-in diameter extrudate, however, decreased with distance down the bed so much that it became necessary to operate the units in upflow mode or in trickle flow and diluted with small inert particles. During the trickle flow mode, a pressure drop occurred at the top of the catalyst bed, caused by the deposition of plugging materials, such as iron and salt, which decreased the voidage of the bed with time.

Activity was higher in the upflow mode. For

Fig. 2 Oil-flow Measurement System by Buoyancy Change Transmitter

the 1/32-in particles, a difference was observed between upflow and downflow, as shown in Fig. 5.

2. 4. Pilot Plants

A simplified flow diagram of an ABC/solvent deasphalting (SDA) combination unit is illus-

Fig. 3 Catalyst Temperature Profile of Microreactor

trated in Fig. 6. Details were reported previously^{1),2)}. In the SDA section, the recovered solvent is recycled after the solvent flow rate is measured by calibrated vessels with the sequence control supplied by a microcomputer.

2. 5. Tactics of Using Pilot Units

The purpose of using pilot plants is to generate data and to evaluate the possibilities for the development of new processes. Microreactors are units of the smallest size among the pilot plants, so they are normally used for exploratory testing and the screening of catalysts, for the testing and

Fig. 4 Simplified Flow Diagram of Bench-scale Test Unit

screening need the most frequent runs. In the catalytic hydrotreating of residua, pressure and

Modes. catalyst: 1/32-in extrudate.

⊙: Upflow mode, △: Downflow mode.

Fig. 5 Comparison of Product Oil Properties between Upflow and Downflow

hydrogen to oil ratios beyond certain limits have little effect on activity^{11,12}, but liquid hourly space velocity (LHSV) has a pronounced effect on catalyst life. Considering that the amount of metal deposit determines the length of catalyst life for heavy oil processing, the amount of oil stock fed to the catalyst must be accurately measured. Tamm *et al.*¹³ showed that the effectiveness factors obtained from the distribution of metal deposits in used catalysts could be useful for investigating catalyst life. The catalyst could be screened both for activity and life, providing a comparative method using the standard catalyst as a reference. Each aging test is conducted over a one-month period, and the depositional profiles of vanadium in the used catalysts, which is one of the important factors dominating the catalyst life, are measured by EPMA. Various catalysts and feedstocks can be tested and evaluated so that subsequent experimental trails can be conducted more accurately. The microreactors were designed to accurately measure and control the feed-oil rate and to facilitate operations. With twenty units, it was possible to operate more than 200 runs a year.

The bench-scale test units, medium in size among the pilot plants, were designed to determine kinetic activity and to study process variables. The length of most runs is typically longer than six months because experiments are conducted to evaluate catalyst performance over its expected life course. Accurate measurements of oil and gas flow rates are necessary to generate a strict material

Fig. 6 Simplified Flow Diagram of Pilot Plant for ABC/SDA Process

balance. Reaction conditions, yields, and properties of products are obtained during this stage of testing. In addition to more automatic control loops, these bench-scale units need higher levels of safety and emergency shut down procedures. Twenty-six units, grouped into six types, can be operated for about fifty runs a year.

The pilot plants, which are the biggest in size and have the best devices to simulate the flow of residue hydrotreating, combined with other processes such as SDA and hydrovisbreaking, are used to study process configuration. They identify the smallest possible systems that still permit direct simulation of commercial operations and often need product recycling and separation. Six pilot plants were designed to be completely automated, and the systems were constructed to save development expenses.

3. Pilot Plant Technology for Heavy Oils

Considering that residua have higher viscosity and pour point than distillate fractions, the size of piping and equipment typically used for distillate fractions may be unsuitable for handling residua. Additionally, the higher boiling points of the residua cause two-phase flow in the reactors and necessitate uniform flow in the catalytic bed in order to effectuate the use of the catalysts. We have developed both hardware and software for treatments of oils as the occasion demands, and have obtained effective results.

3.1. Flow Measurement of Heavy Oils

A weight balance and a level detector are commonly used for extremely small flow measurements of liquids. For this purpose, the balancing method should be very accurate. The system was carefully constructed so that it is free from tension caused by connecting pipe and heating devices. Level detection using a differential pressure transmitter (DPT) is not always reliable because of plugging problems in the pressure-impulse pipe. It is also very difficult to detect the meniscus of black oils in a graduated cylinder.

Shown in **Fig. 2** is the flow measurement system utilizing the principles of the BCT method. The BCT method was highly accurate, with only a $\pm 2\%$ error at a flow rate of 10 g/h. The size of the float and the vessel provided a wide flow range (10 g/h–1,000 g/h) acceptable for use in microreactors and in bench-scale units.

3.2. Flow Control and Transfer of Heavy Oils

A positive displacement pump with steam jacket, such as a plunger type, can be used for the quantitative pumping of vacuum residue. Gear pumps were also useful for the pumping of

Table 2 Heating and Cooling Methods for Pilot Plants

Temperature [°C]	Media	Place
–35––10	Freon	Stabilizer overhead
–10–25	Brine	Naphtha storage
25	Cooling water	Condenser
25–100	Tempered water	Feed vessel Cold separator
160	Steam	Oil line Hot separator
100–300	Heat transfer media (KSK–330)	Extractor DAO/SDA Flash drum
300–500	Electric sheath heater	Reactor Flash drum Tower Oil line

ultraheavy oils such as SDA asphalt. Gear pumps can quantitatively pump heavier oil that is maintained at a suitable temperature. As shown in **Fig. 6**, PU-B is used for the pumping of ultraheavy oil which contains more than 35 wt% asphaltenes and PU-A is used to measure the flow rates of the pilot unit by counting pump revolutions.

3.3. Piping for Heavy Oil Handling

Process piping and other equipment in the pilot plant should be maintained at various temperatures. **Table 2** shows the temperature control methods for the pilot plant shown in **Fig. 6**. The selection of appropriate methods is important for controlling the temperature of heavy oil transfer lines. If an excessive amount of heat is lost from tubes, valves, and fittings; the fluid temperature will drop and result in increased fluid viscosity.

For asphaltene-rich oils, the temperature should be maintained between 310°C and 410°C with an acceptable deviation of $\pm 20^\circ\text{C}$. Plugging occurs at localized spots where the temperature is lower. More suitable methods for avoiding a temperature gradient are as follows:

- (1) Employ electrical sheath heaters at short intervals.
- (2) Place thermocouples at important locations on the line.
- (3) Select appropriate insulation materials.

The pilot plant shown in **Fig. 6** is equipped with 26 temperature control loops. The heat pipe tracing maintains the temperature of the nozzles in the reactors and vessels. The presence of gases, such as hydrogen and C_1 to C_4 hydrocarbons, in the reactor effluent causes partial vaporization of light oils which causes the deposition of sludge materials on the wall of the pipe. Prolonged residence of these unstable materials at high temperatures promotes coking by condensation

polymerization. The process piping, therefore, should be as short as possible and have sufficient slope. Furthermore, both light and ultraheavy oils will require rapid separation, because prolonged residence causes phase separation. To maintain a steady state operation, both a high-pressure hot separator and a high-pressure cold separator, as shown in Fig. 4, are useful. The top and the bottom of the high-pressure hot separator are controlled at two distinct temperatures. The temperature of the liquid phase is set to prevent condensation polymerization and to maintain good fluidity. The temperature of the gas phase allows the flushing of light oils.

A displacement level transmitter of the separator is useful for mild pressure applications, but is not practical for those for high-pressure ones because the design of the transmitter allows for excessive heat loss. For DPT used in the high-pressure section, the deposition of sludge materials should be avoided. That is, the temperature of the pressure-impulse tube should be maintained higher than that for the liquid phase of the hot separator, and the temperature of the DPT should be maintained lower than that of the pressure-impulse tube.

3. 4. Automatic Liquid Sampling

There were no problems during sampling of the final product from low-pressure sections. Sampling of intermediate products from the high-pressure section was often requested by researchers during bench-scale and pilot unit operations.

The ALS system set in the high-pressure section is used for microreactors, as shown in Fig. 1. The system consists of high- and low-pressure vessels and valves with a sequence controller. The liquid sample in the high-pressure vessel is fed automatically to the low-pressure vessel through a valve which is actuated by predetermined sampling cycle. When pressure sensor, at the low-pressure separator, detects rapid pressure change at the completion of sampling, the valve is quickly closed. Owing to the quick response of the system (below 0.1 sec), pressure and the flow rate in the high-pressure section are not disturbed while allowing safe and accurate sampling.

Fig. 7 Vanadium Distribution in Used Catalyst by EPMA

4. Wetting Efficiency in Bench-scale Reactor

The effect of wetting efficiency in the catalytic hydrotreatment of heavy oil was investigated by analyzing vanadium deposit distributions in the used catalysts by EPMA. Depositional profiles of particles from the outlet of the catalyst bed, after 1,000 h of operation on Khafji vacuum residue, are shown in Fig. 7.

The symmetrical distributions of “a” and “e” particles indicated complete wetting. On the other hand, the asymmetrical distribution of particles is due to the partial external wetting, where the demetallation reaction was hindered. In Table 3, the percentages of the partially wetted catalyst-particles at the inlet, midway, and outlet of the catalyst bed, after several runs, are summarized.

For the 1/32-in diameter partially wetted catalyst (Run 2 in Table 3), when the intensity of the high wetting side, *I_h*, had a value of 1.0, the average

Table 3 Partially Wetted Catalyst Particles and Wetting Efficiency

Run No.	Oil flow mode	Catalyst size [inch]	Partially wetted catalyst particles by EPMA [%]			Bed-average wetting efficiency
			Inlet	Middle	Outlet	
1	Up	1/32	0	0	0	1.00
2	Down	1/32	12	19	37	0.94
3	Up	1/16	0	0	0	1.00
4	Down	1/16	12	50	75	0.82
5	Down	1/16	0	0	0	1.00
(with small inert particles)						

relative intensity of the low wetting side, I_l , had a value of 0.5. Assuming that these intensities are proportional to the wetting efficiency, the bed-average wetting efficiency, fe , is expressed as:

$$fe = \{(I_h + I_l)/2\} \cdot R + (1 - R)$$

where R is the average fraction of the partially wetted catalyst particles in the total bed. For the 1/32-in diameter catalyst described above, an fe value of 0.94 was obtained. The results are summarized as follows:

- (1) fe for all upflow operations was 1.0; favorable mode unless some upset should occur.
- (2) fe for downflow operation was lower, 0.94 and 0.82, when catalyst shape was 1/32-in and 1/16-in, respectively.
- (3) fe for all downflow operations decreased with distance down the bed.
- (4) fe for downflow operation of 1/16-in diameter extrudate catalyst recovered up to 1.0, by dilution particles.

Wetting efficiency is one of very important factors for the evaluation of test results and experimental planning of pilot plants. This factor is very important, not only in pilot plants but also in commercial plants.

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要 旨

重質油の接触水素化処理に関する研究 (第 1 報) パイロットプラントの運転制御の確立

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重質油の接触水素化処理プロセスの開発において、製品品質と収率、そして触媒活性と寿命を予測することは極めて大切であり、パイロットプラントを用いた試験が重要な役割を果たす。著者らは、“microreactors”を主に探索テストと触媒選定に用い、“bench-scale test units”を動力学データ採取と反応条件の把握

による触媒性能と寿命の検討に用い、“pilot plants”を実運転の直接的シミュレーションによるプロセス構築に用い、スケール別に使い分けることにより開発の効果を上げた。それぞれのスケールの実験において、重質油を扱う機器を開発して使用し良好な結果を得た。

Keywords

Pilot plant, Hydrotreating, Residual oil, Wetting efficiency, Catalyst performance, Product quality