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Active carbon catalyst for heavy oil upgrading

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Abstract

The active carbon (AC) catalyst was studied by hydrocracking of Middle Eastern vacuum residue (VR) for heavy oil upgrading. It was observed that the active carbon has the affinity to heavy hydrocarbon compounds and adsorption selectivity to asphaltenes, and exhibits better ability to restrict the coke formation during the hydrocracking reaction of VR. The mesopore of active carbon was thought to play an important role for effective conversion of heavy hydrocarbon compounds into lighter fractions restricting carbon formation. The performance of the AC catalyst was exaimined by continuous hydrocracking by CSTR for the removal of such impurities as sulfur and heavy metals (nickel and vanadium), which are mostly concentrated in the asphaltenes. The AC catalyst was confirmed to be very effective for the removal of heavy metals from Middle Eastern VR, Maya/Istmo VR and Maya VR. The extruded AC catalysts were produced by industrial manufacturing method. The application test of the extruded AC catalyst for ebullating-bed reactor as one of the commercially applicable reactors was carried out at the ebullating-bed pilot plant for 500 h. The ebullition of the extruded AC catalyst was successfully traced and confirmed by existing γ-ray density meter. The extruded AC catalyst showed stable performance with less sediment formation at an equivalent conversion by conventional alumina catalyst at commercial ebullating-bed unit. The degradation of the AC catalyst at the aging test was observed to be less than that of the conventional alumina catalyst.

Thus, the AC catalyst was confirmed to be effective and suitable for upgrading of heavy oil, especially such heavy oils as Maya, which contains much heavy metals.

Keywords: Active carbon catalyst; Vacuum residue; Hydrocracking

1. Introduction

Heavy crude contains such constituents as asphaltenes, sulfur, nitrogen and heavy metals (nickel and vanadium). For such hydrocracking processes as fixed-bed or ebullating-bed that use alumina catalyst, the catalyst deactivation due to coking and deposition of heavy metals is critical for their operability and economics. The cracking activity of the conventional alumina catalyst is attributed by the acid sites of alumina support. It is stated that these acid sites suffer from deactivation caused by N-containing compounds or coke formed by poly-condensation of heavy hydrocarbon compounds on the surface [1,2]. In this paper, some fundamental studies on active carbon (AC), which is neutral or weak base support, are introduced and the performance of AC catalysts with unique pore structures for hydrocracking of heavy oil [3–5] are presented and discussed.

For the development of the industrially applicable AC catalyst, the extruded form of AC catalyst, which was produced by industrial manufacturing method, was examined by various kinds of test, such as fixed-bed and ebullating-bed pilot plant using Maya VR and Maya/Isthmus VR. The performance of the extruded AC catalyst including the deactivation behavior is discussed in comparison to the conventional alumina catalyst.

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Table 1
Properties of feedstocks

	Middle Eastern VR(A)	Maya VR(A)	Maya/Istmo VR(A)
API gravity	5.35	1.82	3.77
CCR (wt.%)	22.4	27.7	24.4
Asphaltene (nC7 Insols) (wt.%)	9.1	23.5	16.7
S (wt.%)	4.0	5.3	4.7
N (wt.%)	0.53	0.57	0.50
Ni (wppm)	53	130	110
V (wppm)	180	630	500

The extruded AC catalyst is applicable to such schemes as guard to the existing hydrocracking reactors and synthetic crude production from heavy oils.

2. Experimental

2.1. Preparation and evaluation of active carbon support

Active carbons were prepared by activating granules of crushed Australian Yallourn brown coal char briquette with steam using a laboratory rotary kiln at 1073 K. Activation time was changed to obtain several active carbons with different pore structures. The pore structure was evaluated by nitrogen adsorption method.

Adsorption characteristics of thus obtained active carbons were investigated in relation to their pore structures. Active carbons were immersed into Middle Eastern VR(A) shown in Table 1 under a hydrogen pressure of 10 MPa and at a temperature of 523 K under which conditions cracking was expected not to occur. The amount of adsorbed species was measured as the weight increase of active carbon after Soxhlet extraction with toluene and then vacuum drying. The asphaltene (*n*-heptane insolubles) content remained in the vacuum residue (VR) after adsorption was also measured.

2.2. Fundamental studies of active carbon catalyst

2.2.1. Batch test by autoclave

The fundamental studies of active carbon for the use of heavy oil hydrocracking catalyst were carried out either in the form of the mixture with metal compound or metal impregnated.

The mixture of both powders of active carbon and pyrite was used as one form of the catalyst. The other is the crushed granule AC catalyst (size: 1.2–1.7 mm), which was prepared by impregnating aqueous solution of metal nitrate salt followed by drying at 423 K and calcining at 723 K in nitrogen atmosphere.

In order to study the performance of active carbon in terms of its pore structure and coke formation, hydrocracking tests of Middle Eastern VR(A) shown in Table 1 were carried out at 1-liter semi-batch magnetically stirred autoclave. The hydrogen was introduced at a constant flow rate of 54 Nl/h during the reaction to keep hydrogen partial

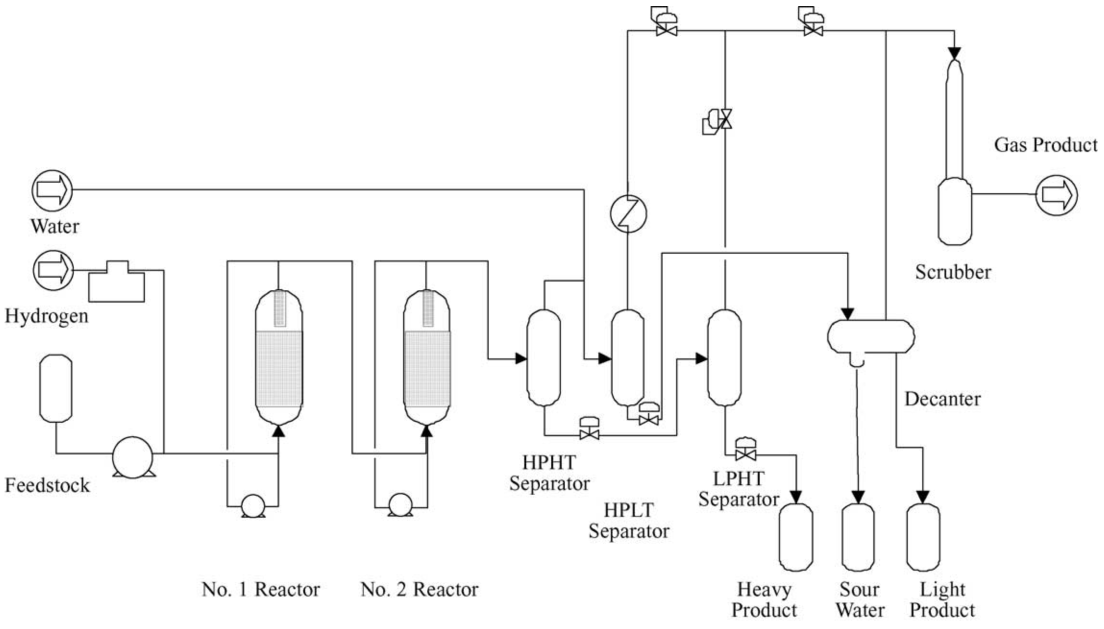


Fig. 1. Flow diagram of ebullating-bed pilot plant.

Table 2
Operation conditions of ebullating-bed pilot plant

Feedstock	Maya (35%)/Istmo (65%) VR(B)
Pressure (MPa)	18.5
LHSV (h^{-1})	0.3
H_2/Oil (SCF/bbl)	7500
Temperature (K)	673–693

pressure constant. Excessive hydrogen and gaseous product were collected for gas analysis. Reaction conditions were as follows: VR charge 300 g, hydrogen pressure 7–10 MPa, reaction temperature 688–718 K, reaction time 60–240 min. The content of residue fraction (798 K^+) in the liquid product was determined by gas chromatography distillation method after separating catalyst and coke from the liquid product by filtration. The conversion was defined as follows: conversion (wt.%) = (100 − wt.% of 798 K^+ in products)/wt.% of 798 K^+ in the feed vacuum residue. The amount of coke was determined as toluene insoluble by Soxhlet extraction.

2.2.2. Continuous test by CSTR

The activities, such as conversion (HDC), hydrodesulfurization (HDS) and hydrodemetalization (HDM) of Iron impregnated (10 wt.%) active carbon AC(C) catalyst were examined by a flow-through type of CSTR unit, which consists of two micro-reactors (250 ml for each) in series, at the conditions of 683–713 K, 10 MPa, oil feed rate 35–100 g/h and H_2 flow rate 90 Nl/h. The crushed granule catalyst (size: 1.2–1.7 mm) was contained in a wire mesh basket of 991 μm sieve aperture, which was set inside of both reactors. The catalyst bed was expanded in the basket by upward liquid flow accomplished by agitator. Details of reactor internals are described in the previous paper [4]. The feed oils for hydrocracking tests were Middle Eastern VR(A) and other extra-heavy oils including Maya VR(A) and Maya/Istmo (Isthmus) VR(A) as listed in Table 1.

2.3. Evaluation of extruded active carbon catalyst

The industrial manufacturing study of the extruded form of AC catalyst based on the results of above fundamental studies is being carried out in collaboration with leading manufactures of active carbon and hydroprocessing catalyst, respectively. Several extruded AC catalyst samples from Australian Yallourn brawn coal char were produced and also commercially available active carbon supports were examined for industrial use by various tests as below.

2.3.1. Fixed-bed test

The hydrocracking performance of the extruded AC catalysts was examined at the fixed-bed unit, which consists of four reactors in a common aluminum block heater and otherwise with four independent feed and product streams, at the conditions of 693–695 K, 18.1 MPa, LHSV 0.25 h^{-1}, H_2/Oil 5, 250 SCF/bbl. The feedstock for the test was Middle Eastern VR(B) with 5.8° API, 22.44 wt.% CCR, 4.6 wt.% S, 0.29 wt.% N, 26 wppm Ni and 85 wppm V.

2.3.2. Ebullating-bed pilot plant test

The extruded AC catalyst (Iron impregnated) was evaluated in terms of applicability to ebullating-bed and hydrocracking performance by using the ebullating-bed pilot plant with two reactors (900 ml for each) in series. The flow diagram of the pilot plant is as shown in Fig. 1. The operation conditions are as listed in Table 2. The feedstock was Maya/Istmo VR(B) with 3.73° API, 22.59 wt.% CCR, 17.75 wt.% nC7 Insols, 4.5 wt.% S, 0.61 wt.% N, 84 wppm Ni and 418 wppm V, which is being actually processed at a commercial ebullating-bed unit. The ebullition of the AC catalyst was set up and adjusted by ebullating pump stroke according to the standard operation procedures and conditions of the pilot plant.

2.3.3. Aging test

Long term aging tests of the AC catalyst and the conventional Ni–Mo alumina catalyst were carried out at fixed-bed reactor (catalyst volume: 100 cc) at the conditions of 12 MPa, LHSV 0.5 h^{-1} and H_2/Oil 5500 SCF/bbl. The feedstocks properties for respective catalyst are as shown in Table 3. Product samples were collected at 12 h intervals for material balance and product analysis. The deactivation behavior of the catalyst in terms of conversion HDC, HDM and HDS was analyzed and compared. The catalyst bed temperature was raised stepwise from 673 K to the temperature at which the initial conversion becomes about 50% for respective catalyst and then the bed temperature kept

Table 3
Properties of feedstocks for aging test

Feedstock	Mixture of Maya VR/Other AR	Maya VR(B)
Catalyst	Extruded AC catalyst	Alumina catalyst
API gravity	4.14	1.96
CCR (wt.%)	22.66	25.04
Asphaltene (nC7 Insols) (wt.%)	20.57	22.59
S (wt.%)	5.01	5.88
N (wt.%)	0.608	N.A
Ni (wppm)	113	127.5
V (wppm)	550.5	582.8

Table 4
Pore structure of active carbon

	AC(A)	AC(B)	AC(C)
BET surface area (m^2/g)	794	556	832
Total pore volume (ml/g)	0.52	0.27	0.98
Mesopore volume (ml/g)	0.28	0.05	0.82
Average pore radius (nm)	1.3	1.0	2.3

constant to the end of run to observe the degradation of the catalyst activities.

3. Results

3.1. Preparation and evaluation of active carbon support

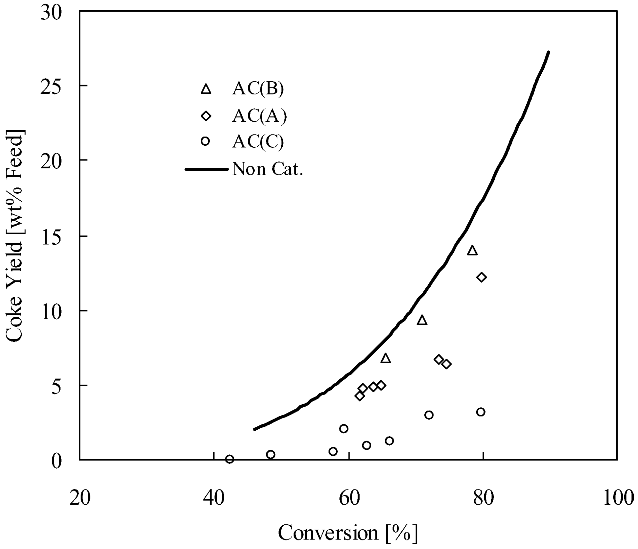
Three kinds of active carbon with different pore structures, such as AC(A), AC(B) and AC(C) were obtained as shown in Table 4. The total pore volume were in the order AC(B) < AC(A) < AC(C). The active carbon AC(B) developed only micropore (<2 nm) structure and the active carbon AC(C) mostly developed mesopore (2–50 nm) structure.

From the results of immersion tests of active carbons into vacuum residue, the deasphaltene rate was calculated as the reduction of asphaltene content in the vacuum residue. About 45 wt.% of adsorbed species on AC(C) with the largest pore volume was observed to be asphaltenes.

3.2. Fundamental studies of active carbon catalyst

3.2.1. Batch test by autoclave

The results of hydrocraking conversion and coke yield of AC(A), AC(B) and AC(C) in the form of the mixture with pyrite are as shown in Fig. 2. It was possible to attain higher conversion with least coke formation by the active carbon AC(C) with largest mesopore volume.

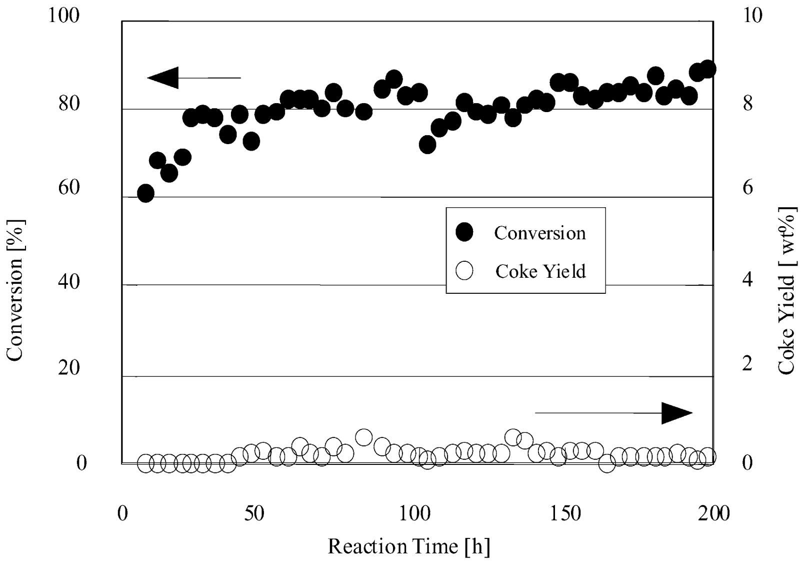


React. Temp.:688-708K, React. Press.:7MPa, React. Time:0.5-2h, Cat. Conc.: Mix-cat. (Pyrite 0.25wt% as Iron, AC 5wt%)

Fig. 2. Relationship between porosity of AC and coke yield.

3.2.2. Continuous test by CSTR

The results of hydrocracking of Middle Eastern VR(A) are as shown in Fig. 3. The catalyst activity was stable during the run in which the maximum conversion of 90% was achieved. The coke yields in the liquid product, which were measured with time on-stream at continuous operation, were in the range of 0.3–0.6% on vacuum residue feed throughout the run for 200 h. The rates of HDV (vanadium), HDNi



React. Temp.: 688-708K, React. Press.: 10MPa, LHSV: 0.1-0.4h^{-1}

Fig. 3. Conversion and coke yield with time-on-stream.

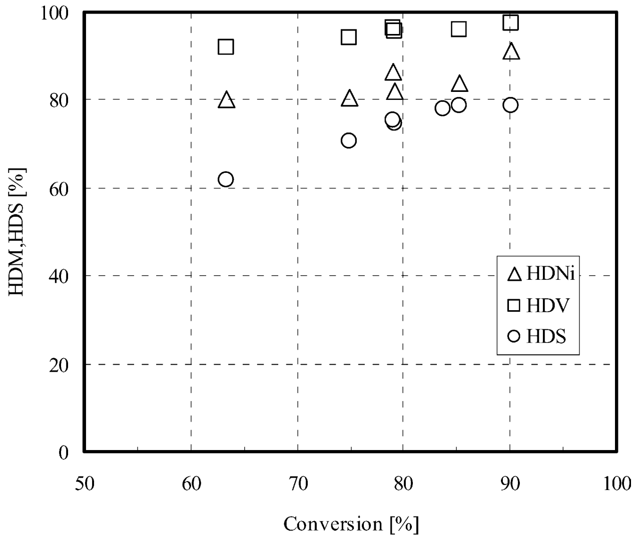


Fig. 4. HDM and HDS activities (Middle Eastern VR(A)).

(nickel) and HDS were plotted against the conversion as shown in Fig. 4. For such heavy oils as Maya VR(A) and Maya/Istmo VR(A), the catalyst also exhibited very high activities for removal of heavy metals HDM as shown in Fig. 5. The rate of HDS was allowable range for industrial use.

3.3. Evaluation of extruded active carbon catalyst

3.3.1. Fixed-bed test

Properties of the extruded Iron impregnated AC catalyst are as listed in Table 5. The extruded AC catalyst showed comparable activities to crushed granule AC catalyst, which has been used at the laboratory for fundamental studies, as shown in Table 6.

Table 5
Properties of Extruded Active Carbon Catalyst

Size (diameter × length)	1 × 3 to 1 × 6
True density (g/ml)	2.2
Bulk density (g/ml)	0.4
BET surface area (m^2/g)	1170
Total pore volume (ml/g)	0.68
Attrition loss (%) ASTM D4058	<1

Table 6
Comparison of performance of crushed and extruded active carbon catalysts

	Crushed	Extruded
Conversion (wt.%)	56	55
HDS (%)	43	40
HDV (%)	96	89
HDNi (%)	81	73
Sediment (%) IP375	<0.01	<0.01

3.3.2. Ebullating-bed pilot plant test

The ebullition of the extruded AC catalyst was traced by existing γ-ray density meter of the pilot plant. The hydrocracking operation was carried out for 500 h. The activities and performance of the extruded AC catalyst during the operation were observed as shown in Fig. 6.

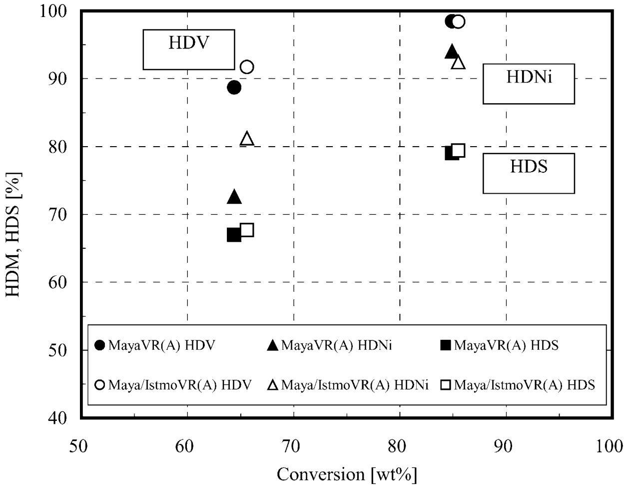


Fig. 5. HDS and HDM activities (Maya VR(A), Maya/Istmo VR(B)).

3.3.3. Aging test

The catalyst bed temperatures to obtain the conversion of 50% were 705 and 693 K for the extruded AC catalyst and conventional alumina catalyst, respectively. The HDC, HDM and HDS versus time-on-stream of each catalyst are as shown in Figs. 7 and 8. The metal uptake of the catalyst calculated by the data of HDM rates from analytical results of vanadium and nickel contents in liquid products is also plotted in Figs. 7 and 8. The HDC, HDM and HDS rates of respective catalyst at the initial and at the end of runs are as listed in Table 7.

4. Discussion

4.1. Preparation and evaluation of active carbon support

The increase of the total pore volume is attributed to the development of mesopore structure as shown in previous Table 4. For comparison of the deasphaltene ability of each AC samples, the deasphaltene rate per total pore volume of AC was calculated to compensate the total pore volume difference of each AC samples. The deasphaltene rate per total pore volume increased in the order AC(B) < AC(A) < AC(C) as shown in Fig. 9. It is noted that the active carbon, which developed mesopore structure, shows the adsorption selectivity to asphaltenes in vacuum residue.

4.2. Fundamental studies of active carbon catalyst

4.2.1. Batch test by autoclave

As shown in Fig. 2, such mesopore rich active carbon, which showed the affinity to heavy hydrocarbon compounds

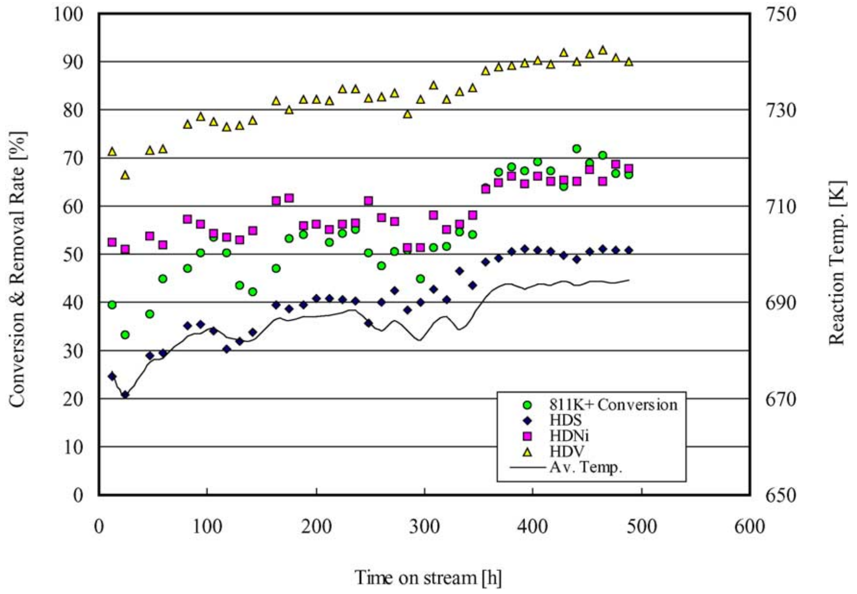


Fig. 6. Catalyst performance of extruded AC catalyst at ebullating-bed.

and adsorption selectivity to asphaltenes, exhibited better ability to restrict the coke formation during the hydrocracking reaction of vacuum residue. Resultantly it is conceivable that the mesopore of active carbon plays an important role for effective conversion of heavy hydrocarbon compounds into lighter fractions restricting carbon formation.

4.2.2. Continuous test by CSTR

The observed high activity of the AC catalyst for Middle Eastern VR(A) shown in Figs. 3 and 4 is assumed to be closely connected to the ability of the AC catalyst for the conversion of asphaltens in which such constituents as nickel, vanadium and sulfur are mostly concentrated. In the same manner, the AC catalyst is also effective for hydrocracking of such extra heavy oils as Maya VR(A) and Maya/Istmo VR(A) restricting coke formation and removing heavy metals as shown in Fig. 5. The AC catalyst seems to have the advantage of the conventional alumina catalyst, which suffers from degradation due to coke and metal deposition especially in processing extra heavy oils.

4.3. Evaluation of extruded active carbon catalyst

4.3.1. Fixed-bed test

Very high activity was also obtained for the extruded AC catalyst supporting the discussion in fundamental studies so

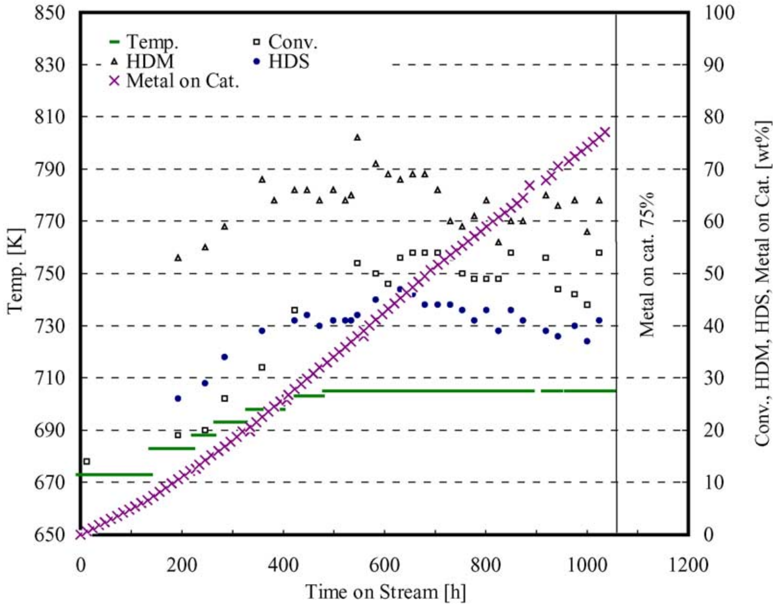


Fig. 7. Aging test of extruded AC catalyst.

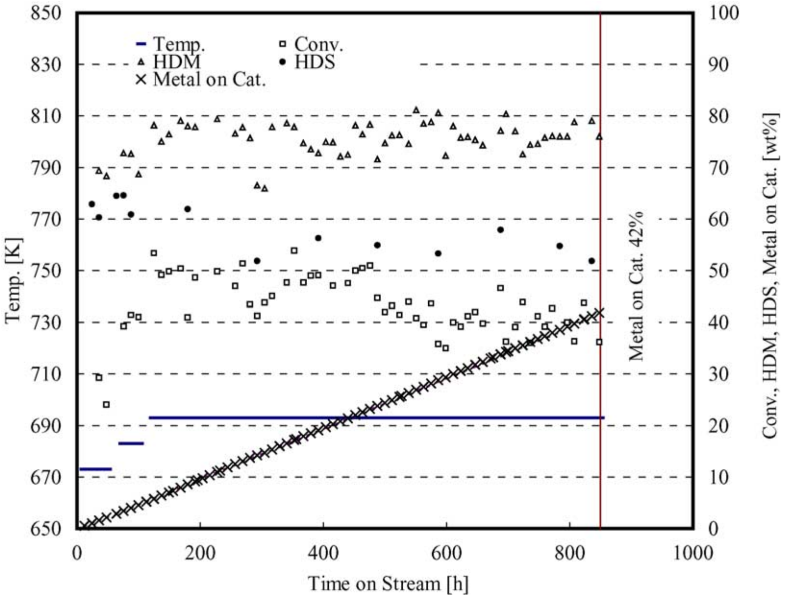


Fig. 8. Aging test of conventional alumina catalyst.

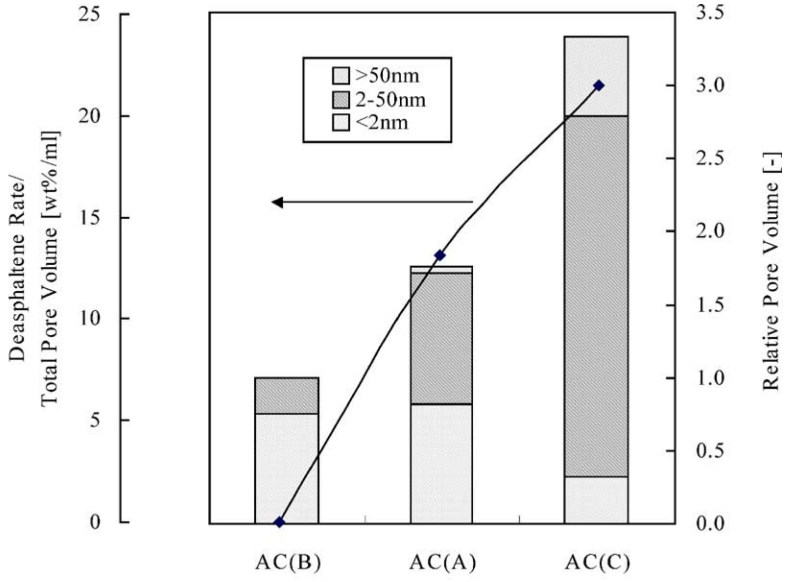
Table 7
Catalyst activities at aging test

Total time-on-stream (h)	Extruded AC catalyst 1050			Alumina catalyst 848		
	HDS	HDC	HDM	HDS	HDC	HDM
Rate at initial (%)	42	52	67	64	50	79
Rate at end of run (%)	40	50	64	52	39	77
Temperature	@ 705 K			@ 693 K		

far. As to know the advantage of the extruded AC catalyst to conventional alumina catalyst, the radial distribution of deposited metal across the extruded AC catalyst particle was analyzed. The profile of vanadium deposition is as shown in Fig. 10, which shows the distribution of vanadium to the inside of the particle meaning that the large molecules can penetrate into the center of the particle through large pores.

4.3.2. *Ebullating-bed pilot plant test*

The ebullition of the extruded AC catalyst was successfully traced and confirmed by γ-ray density meter.



Pore Dia. ; Macropore > 50nm, Mesopore 2-50nm, Micropore < 2nm

Fig. 9. Mesopore structure and adsorption selectivity to asphaltenes.

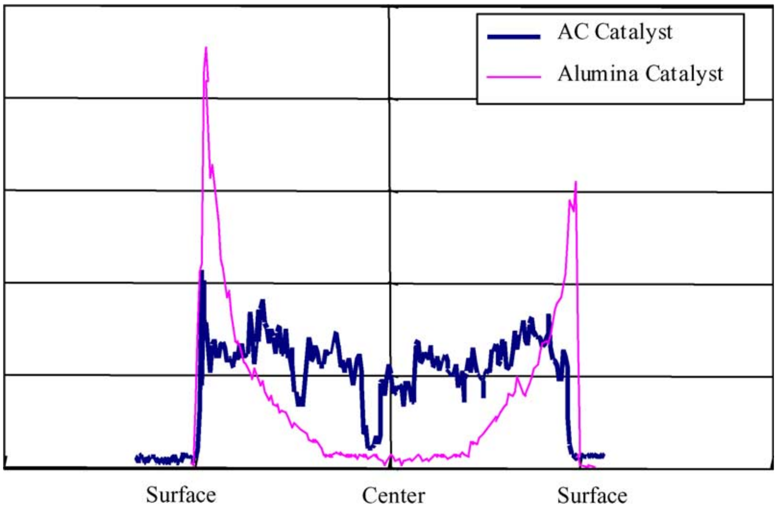


Fig. 10. Vanadium distribution on spent catalyst particle.

The extruded AC catalyst with lower density by about 25% than alumina catalyst was kept in stable ebullition without being carried out from the reactor. This means that the extruded AC catalyst is due possible to be used at the ebullating-bed unit.

The sediment against the conversion is plotted as in Fig. 11 together with the data of the equivalent commercial operation by conventional alumina catalyst for comparison. The sediment formation was considerably low than the conventional alumina data. It can be said that the conversion could be raised by 10 or more points than that of conventional alumina catalyst, if the maximum allowable limit of sediment formation is set at 0.9%. This enables the increased marginal gain in the distillable cracked product. If the conversion is set at the same level as the conventional alumina catalyst, the longer continuous operation time is expected due to lower sediment formation resulting in the reduction of related costs for turnaround and maintenance of the unit.

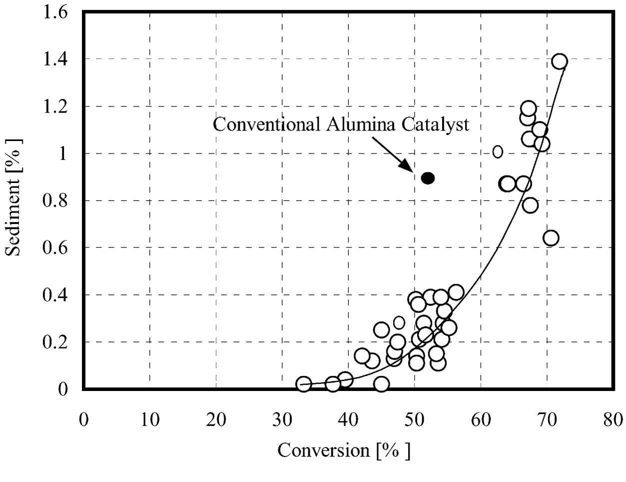


Fig. 11. Conversion and sediment.

4.3.3. *Aging test*

As shown in Fig. 7, the performance of the extruded AC catalyst was observed to be comparatively stable through the run. The performance of the conventional alumina catalyst, more specifically, the HDC and HDS rates were observed to decrease with the increase of time-on stream as shown in Fig. 8. This is clear to see the data shown in Table 7. The degradations of activities of HDC and HDS of the conventional alumina catalyst are greater than those of the extruded AC catalyst. The HDM rate of the conventional alumina catalyst was constant through the run in no relation to the degradation of HDC and HDS activities deferring from the discussion usually reported in other papers. The reason for this phenomenon observed for the alumina catalyst in this test is unexplainable. From the declining tendencies of the HDC and HDS activities, it is highly possible that the alumina catalyst will face the end of catalyst life in shorter time-on-stream than the extruded AC catalyst.

5. Conclusions

- The active carbon has the affinity to heavy hydrocarbon compounds and adsorption selectivity to asphaltenes, and exhibits better ability to restrict the coke formation during the hydrocracking reaction of VR.
- The mesopore of active carbon plays an important role for effective conversion of heavy hydrocarbon compounds into lighter fractions restricting carbon formation.
- The AC catalyst shows the high activities for the removal of such impurities as sulfur and heavy metals (nickel and

vanadium), which are mostly concentrated in the asphaltenes.
- The AC catalyst was confirmed to be very effective for the removal of heavy metals from Middle Eastern VR, Maya/Istmo VR and Maya VR.
- The ebullition of the extruded AC catalyst at the ebullating-bed pilot plant was successfully traced and confirmed by existing γ-ray density meter.
- The extruded AC catalyst showed stable performance with less sediment formation at an equivalent conversion by conventional alumina catalyst at commercial ebullating-bed unit.
- The degradation of the AC catalyst at the aging test was observed to be less than that of the conventional alumina catalyst.

Thus, the AC catalyst was confirmed to be effective and suitable for upgrading of heavy oil, especially such heavy oils as Maya, which contains much heavy metals.

The AC catalyst offers prominent application possibilities both in fixed-bed and ebullating-bed in combination with typical commercially available processes for synthetic crude production, upgraders with inline HDS and pretreators for hydrocracking of heavy oils.

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