[Regular Paper]

Hydrotreatment of Light Cycle Oil over Pt-Pd Supported Catalyst Combined with Ni-Mo Supported Catalyst

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Virgin light cycle oil (LCO) derived from the FCC process containing 6090 mass ppm sulfur and 76.1 mass% aromatics, and with cetane index of 26 was refined by hydrotreatment over Ni-Mo supported catalysts in a down flow fixed-bed reactor, and the resulting LCO was hydrotreated over Pt-Pd supported catalyst in a down flow fixed-bed reactor. Ni-Mo supported silica-alumina (Ni-Mo/SA) and Ni-Mo supported alumina containing USY zeolite (Ni-Mo/USY-Al₂O₃) were used for the first hydrotreatment reaction. The double layer system of Ni-Mo/SA and Ni-Mo/USY-Al₂O₃ showed slightly better nitrogen removal activity and cetane index improvement activity at the same sulfur removal activity than the single layer system of Ni-Mo/SA, so the double layer system of Ni-Mo/SA and Ni-Mo/USY-Al₂O₃ was used for the first hydrotreatment reaction. Hydrotreated LCO using the double layer system which contained 137 mass ppm sulfur and cetane index of 32 underwent hydrotreatment over Pt-Pd supported alumina containing USY zeolite (Pt-Pd/USY-Al₂O₃). The second hydrotreatment over Pt-Pd/USY-Al₂O₃ resulted in 5 mass ppm sulfur and cetane index of 47 at hydrogen pressure 4.9 MPa, LHSV 1.0 h⁻¹, hydrogen/oil ratio 400 N//l and reaction temperature 320°C, which confirmed the high hydrotreatment ability of Pt-Pd/USY-Al₂O₃. Catalytic life of Pt-Pd/USY-Al₂O₃ was tested for 266 days using first hydrotreated LCO containing 137 mass ppm sulfur and cetane index of 32. Throughout the life test, sulfur content were around 10 mass ppm and cetane index was 40. Under the same reaction conditions as the life test, another test for 42 days was carried out to examine coke deposition on Pt-Pd/USY-Al₂O₃. Coke deposition on the catalyst greatly increased towards the reactor outlet, mainly due to hydrogen reduction.

Keywords

Light cycle oil, Hydrotreatment, Platinum-Palladium catalyst, USY zeolite, Cetane index, Deep desulfurization

1. Introduction

Light cycle oil (LCO), which is a by-product from the fluid catalytic cracking reaction in oil refining, exhibits similar distillation properties to city diesel oil, but has lower quality in terms of sulfur content, cetane index and aromatics concentration. Therefore, LCO is too difficult to utilize for city diesel oil, except for blending in fuel oil and off-load diesel oil. Hydrotreatment of LCO over noble metal supported zeolite catalysts have been widely studied to reduce sulfur content, increase cetane index and reduce aromatics concentration^{1)~7)}. However, the activity of the noble metal catalyst usually deteriorates because of the low sulfur tolerance. Therefore, a two-stage process has been proposed, with pre-hydrotreatment of virgin LCO over base metal supported catalyst in the first stage, and

hydrotreatment of the resulting LCO over noble metal-supported catalyst in the second stage^{8)~10)}. Bimetallic noble metal-supported Y zeolite has been studied to enhance the sulfur tolerance of the hydrotreatment catalyst^{11)~13)}. We previously reported that Pt-Pd supported USY zeolite with high SiO₂/Al₂O₃ ratio exhibited high desulfurization and hydrogenation activity in the model reaction of 4,6-dimethyl-dibenzothiophene (4,6-DMDBT) hydrodesulfurization and tetralin hydrogenation¹⁴⁾. However, LCO hydrotreatment over noble metal-supported catalyst, especially in terms of catalyst life and coke formation, has not been thoroughly investigated.

In this study, we investigated the two-step hydrotreatment of LCO over NiO-MoO₃ supported catalysts and Pt-Pd supported catalyst to assess the catalytic activities, lifetime and coke formation on the Pt-Pd supported catalyst.

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2. Experiment

2.1. Materials

The composition of the virgin LCO is shown in **Table 1**. NiO-MoO₃ supported silica-alumina catalyst (Ni-Mo/SA) and ammonium Y type zeolite were obtained from Catalysts & Chemicals Ind. Co., Ltd., and the properties are shown in **Tables 2** and **3**.

2.2. Preparation of USY Zeolite

Ammonium Y zeolite with 65% ammonium ion (NH₄⁺) exchange rate was hydro-thermally treated at 660°C for 3 h using steam. The treated zeolite was added to ammonium sulfate aqueous solution 8 mass% and the mixture was kept at 90°C for 2 h to attain high

exchange of Na⁺ with NH₄⁺. Filtration and drying at 150°C for 24 h gave 95% NH₄⁺ exchanged zeolite. The resulting zeolite was treated at 700°C for 20 min with steam followed by addition to 25 mass% aqueous solution of sulfuric acid and stood at 70°C for 2 h. After filtration and drying at 150°C for 24 h, ultra stable Y zeolite (USY) with a SiO₂/Al₂O₃ ratio of 73 was obtained. The properties of USY are shown in **Table 4**.

2.3. Preparation of Ni-Mo/USY-Al₂O₃

Sodium aluminate aqueous solution (12 kg), 5 mass% concentration, was put into aluminum sulfuric acid aqueous solution (12 kg), 2.5 mass% concentration, and the mixture was stirred at 30°C for 10 min and then at 60°C for 3 h to obtain aluminum hydroxide. Ammonium aqueous solution (90 l, 0.3 mass%) was added and filtered. The resulting aluminum hydroxide was kneaded at 25°C for 30 min to reduce the moisture content to around 50 mass%. The resulting aluminum hydroxide (500 g dry base) and USY (500 g dry base) was kneaded at 25°C for 30 min. The kneaded product was then extruded to obtain 1/16 inch diameter carrier pellets followed by drying at 110°C for 16 h and calcining at 550°C for 3 h. The resulting carrier consisted of 50 mass% USY and 50 mass% Al₂O₃, and was named USY(50)-Al(50).

Aqueous solution (20 ml) of nickel carbonate (5.3 g) and molybdenum trioxide (21.5 g) was impregnated into USY(50)-Al(50) (50 g). The mixture was dried at 150°C for 3 h, and then calcined at 550°C for 3 h in air to obtain Ni-Mo/USY(50)-Al(50), consisting of 4.0 mass% NiO and 18.0 mass% MoO₃. The properties of Ni-Mo/USY(50)-Al(50) are listed in **Table 5**.

2.4. Preparation of Pt-Pd/USY-Al₂O₃

Sodium aluminate aqueous solution (12 kg), 5 mass% concentration, was added to aluminum sulfuric acid aqueous solution (12 kg), 2.5 mass% concentration, and the mixture was stirred at 30°C for 10 min

Table 1 Properties of Virgin LCO

Virgin LCO		
Density at 15°C	[g/cm ³]	0.9142
Sulfur	[mass ppm]	6090
Nitrogen	[mass ppm]	225
Cetane index	[—]	26
Total aromatics	[mass %]	76.1
Mono aromatics	[mass %]	32.4
Di ring aromatics	[mass %]	41.3
Tri ⁺ ring aromatics	[mass %]	2.4
Distillation		
Initial boiling point	[°C]	170
10 vol% fractionated temperature	[°C]	205
30 vol%/50 vol%	[°C]	227/247
70 vol%/90 vol%	[°C]	267/302

Table 2 Properties of NiO-MoO₃ Supported Silica-alumina Catalyst

MoO ₃ in catalyst	[mass %]	18.0
NiO in catalyst	[mass %]	4.0
SiO ₂ in carrier	[mass %]	11.0
Al ₂ O ₃ in carrier	[mass %]	89.0
Surface area	[m ² /g]	250
Pore volume	[ml/g]	0.46

Table 3 Properties of Ammonium Y Type Zeolite

Silica/alumina molar ratio	[—]	5.2
Surface area	[m ² /g]	720
Na ₂ O content	[mass %]	4.7
Ammonium exchange rate	[%]	65

Table 4 Properties of USY

SiO ₂ /Al ₂ O ₃ molar ratio	[—]	73
Surface area	[m ² /g]	728
Pore volume	[ml/g]	0.61
Na ₂ O content	[mass %]	0.04

Table 5 Properties of Ni-Mo/USY(50)-Al(50) and Pt-Pd/USY(70)-Al(30)

Catalyst type		Ni-Mo/USY(50)-Al(50)	Pt-Pd/USY(70)-Al(30)
Pore volume	[ml/g]	0.51	0.76
Surface area	[m ² /g]	530	321
USY in carrier	[mass %]	50	70
Al ₂ O ₃ in carrier	[mass %]	50	30
NiO in catalyst	[mass %]	4.0	—
MoO ₃ in catalyst	[mass %]	18.0	—
Pt in catalyst	[mass %]	—	0.38
Pd in catalyst	[mass %]	—	0.82

Fig. 1 Schematic Flow Diagram of the Down Flow Fixed Bed Bench Plant

and then at 60°C for 3 h to obtain aluminum hydroxide. Ammonium aqueous solution (90 l) 0.3 mass% was added and filtered. The resulting aluminum hydroxide was kneaded at 25°C for 30 min to reduce the moisture content to around 50 mass%. The resulting aluminum hydroxide (300 g dry base) and USY (700 g dry base) was kneaded at 25°C for 30 min. The kneaded product was then extruded to obtain 1/16 inch diameter carrier pellets followed by drying at 110°C for 16 h and calcining at 550°C for 3 h. The resulting carrier consisted of 70 mass% USY and 30 mass% Al_2O_3 , and was named USY(70)-Al(30).

Aqueous solution (30.5 ml) of $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ (1.30 g) and $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ (0.48 g) was impregnated into USY(70)-Al(30) (50 g). The mixture was dried at 150°C for 6 h, and then calcined at 300°C for 3 h in oxygen flow of 20 l/h to obtain Pt-Pd/USY(70)-Al(30) catalyst consisting of 0.38 mass% Pt and 0.82 mass% Pd. The properties of Pt-Pd/USY(70)-Al(30) are listed in Table 5.

2.5. Reactor

A fixed bed down flow reactor, 19.4 mm inside diameter, was used in the reaction flow scheme in Fig. 1. The pre-hydrotreatment and hydrotreatment were consecutively conducted in the same reactor.

2.6. Pre-hydrotreatment Reaction

Single layer system and double layer systems were used. Ni-Mo/SA (10 ml) was put in the reactor for the single layer system. Ni-Mo/SA and Ni-Mo/USY(50)-Al(50) (5 ml each) were positioned at the upper and lower parts of the reactor, respectively, for the double layer system. The catalyst was sulfurized as follows. Hydrogen containing 3 vol% hydrogen sulfide was supplied into the reactor at 40 Nl/h at 330°C for 10 h under atmospheric pressure. Then, the reactor was cooled down, and hydrogen was supplied into the reactor at 4.9 MPa and 9.8 MPa. Hydrogen flow started at 8 Nl/h followed by virgin LCO feeding at 20 ml/h, which corresponded to LHSV of 2.0 h^{-1} ; H_2 /oil volume

ratio in the flow was 400 Nl/l. The reactor temperature was controlled in the range from 280°C to 380°C during the pre-hydrotreatment reaction. Pre-hydrotreated product was collected in the container at room temperature and atmospheric pressure for analysis.

2.7. Hydrotreatment Reaction

Pt-Pd/USY(70)-Al(30) catalyst (20 ml) was put into the reactor, and then pre-hydrotreated product obtained from the double layer system was charged for hydrotreatment. The reactor was heated and kept at 300°C under H_2 flow of 8 Nl/h at atmospheric pressure for 3 h to reduce the Pt-Pd on the USY(70)-Al(30). The reactor was then cooled down to 240°C and reactor pressure was adjusted to 4.9 MPa with H_2 . The reaction was carried under H_2 flow of 8 Nl/h and pre-hydrotreated product at 9.8 MPa and 356°C feeding at 20 ml/h, which corresponded to LHSV of 1 h^{-1} ; H_2 /oil volume ratio in the flow was 400 Nl/l. The reactor temperature was controlled in the range from 280°C to 320°C during the hydrotreatment reaction. Hydrotreated LCO was collected in the container at room temperature and atmospheric pressure for analysis.

2.8. Lifetime Test

Two types of life test over Pt-Pd/USY(70)-Al(30) were started using pre-hydrotreated product. The long term test examined catalyst activity for 266 days and the short term test for 42 days investigated coke deposition on the catalyst. The reaction conditions were the same as for the hydrotreatment reaction in 2.7., and the reaction temperature was adjusted to obtain sulfur content of 10 mass ppm in the hydrotreated product.

2.9. Analyses

Sulfur content in oil was determined by X-ray fluorescence spectrometry, OXFORD MDX-1000, or UV fluorescence spectrometry, Mitsubishi Chemical, TS-100V. Aromatic compounds were analyzed by supercritical fluid chromatography, GILSON SFC-FID (SFC). Components in feed and product oil were classified as paraffins, mono-ring aromatics, di-ring aromatics, and triaromatics by comparison to the retention times of $n\text{-C}_{16}$ paraffin, toluene, tetralin, naphthalene, di-phenyl, phenanthrene, and anthracene on SFC chromatography as shown in Fig. 2. Coke on catalyst was determined by carbon analyzer, HORIBA EMIA-320V/FA.

3. Results and Discussion

3.1. Pre-hydrotreatment

The catalytic properties of Ni-Mo/SA and Ni-Mo/USY(50)-Al(50) in the pre-hydrotreatment of virgin LCO were investigated under reaction conditions of 9.8 MPa and 356°C as shown in Table 6. Pre-hydrotreated product obtained from the double layer system (LCO-1) showed lower nitrogen content of

Fig. 2 SFC-FID Chromatogram for Aromatic Compounds

Table 6 Properties of Pre-hydrotreated LCO

		Pre-hydrotreated product from single layer	Pre-hydrotreated product from double layer (LCO-1)
Density at 15°C	[g/cm ³]	0.8760	0.8732
Sulfur	[mass ppm]	137	137
Nitrogen	[mass ppm]	2	1
Cetane index	[—]	31	32
Distillation			
Initial boiling point	[°C]	174	161
10 vol% fractionated point	[°C]	201	197
30 vol%/50 vol%	[°C]	220/235	218/234
70 vol%/90 vol%	[°C]	253/287	252/287

Feed oil: Virgin LCO, LHSV: 2.0 h⁻¹, H₂/oil ratio: 400 N//l, Reaction temperature: 356°C, Reaction pressure: 9.8 MPa.

Feed oil: Virgin LCO, LHSV: 2.0 h⁻¹, H₂/oil ratio: 400 N//l, Catalyst: Double layer system of Ni-Mo/SA and Ni-Mo/USY(50)-Al(50).

Fig. 3 Aromatics Reduction and Cetane Index in Pre-hydrotreated LCO

1 mass ppm, higher cetane index of 32, and lower density of 0.8732 g/cm³, than product from the single layer system. Product quality did not show much difference, but was better from the double layer system than

from the single layer system, so the double layer system was utilized in the pre-hydrotreatment.

Changes in total aromatics reduction and cetane index with reaction temperature after pre-hydrotreatment are shown in Fig. 3. In the reaction at 4.9 MPa, total aromatics reduction reached the maximum of 11% at 356°C. Total aromatics reduction at 388°C is probably due to the thermodynamically predominant formation of aromatics at higher temperatures. In contrast, in the reaction at 9.8 MPa, total aromatics reduction increased with reaction temperature, and reached 27% at 388°C, possibly due to a shift of equilibrium caused by higher reaction pressure.

Cetane index could increase with decreasing total aromatics³⁾. However, no remarkable increase of cetane index was observed in the pre-hydrotreatment process, despite the increased total aromatics reduction rate even at 9.8 MPa reaction pressure. These results suggested that the predominant reaction forms alkyl tetralin, since the hydrogenation reaction from alkyl naphthalene to alkyl tetralin predominates in aromatics hydrogenation in pre-hydrotreatment, and these com-

Feed oil: Virgin LCO, LHSV: 2.0 h⁻¹, H₂/oil ratio: 400 N//l, Catalyst: Double layer system of Ni-Mo/SA and Ni-Mo/USY(50)-Al(50).

Fig. 4 Temperature Dependence of Sulfur Content in Pre-hydrotreated LCO

Feed oil: Pre-hydrotreated LCO-1, Reaction pressure: 4.9 MPa, LHSV: 1.0 h⁻¹, H₂/oil ratio: 400 N//l, Catalyst: Pt-Pd/USY(70)-Al(30).

Fig. 5 Aromatics Reduction and Cetane Index in Hydrotreated LCO

pounds show no wide difference in cetane index³⁾.

Changes in sulfur content with reaction temperature are shown in **Fig. 4**. The sulfur content in pre-hydrotreated product decreased with elevating reaction temperature; content of less than 10 mass ppm was attained by reaction at 388°C and 9.8 MPa. Pre-hydrotreatment at 350°C gave oil containing sulfur at less than 200 mass ppm, which is sufficient for supplying to the following hydrotreatment over Pt-Pd/USY(70)-Al(30) in terms of prevention of catalyst poisoning, as reported by our previous study¹⁴⁾.

3. 2. Hydrotreatment

Hydrotreatment was examined using pre-hydrotreated product LCO-1, obtained by pre-hydrotreatment at 9.8 MPa at 356°C over the double layer system.

Figure 5 shows the changes in total aromatics reduction and cetane index with reaction temperature in hydrotreatment. Total aromatics reduction increased with reaction temperature to a maximum of 95% in the hydrotreatment process. Cetane index increased with

◇ Catalyst: Double layer system of Ni-Mo/SA and Ni-Mo/USY(50)-Al(50), Feed oil: Virgin LCO, Reaction pressure: 9.8 MPa, LHSV: 2.0 h⁻¹, H₂/oil ratio : 400 N//l.

◆ Catalyst: Pt-Pd/USY(70)-Al(30), Feed oil: Pre-hydrotreated LCO-1, Reaction pressure: 4.9 MPa, LHSV: 1.0 h⁻¹, H₂/oil ratio: 400 N//l.

Fig. 6 Relationship between Aromatics Reduction Rate and Cetane Index

temperature to 42 and 47 at 300 and 320°C, respectively. Slight decrease of total aromatics reduction was observed by reaction temperature increase to 320°C from 300°C and cetane index degradation was expected, but the cetane index improved. These results suggested that saturated aromatics in hydrotreated LCO were increased by 320°C reaction, and the associated cetane index degradation was compensated by the improvement due to saturated aromatics with higher cetane index³⁾. These results showed that the present two-step hydrotreatment of LCO over Pt-Pd/USY(70)-Al(30) successively and efficiently improved the cetane index to over 40.

In the hydrotreatment reaction, increase of cetane index is attributable to efficient conversion of aromatics to saturated hydrocarbon. In fact, a linear relationship between cetane index and aromatic reduction rate was observed, as shown in **Fig. 6**. Therefore, Pt-Pd/USY(70)-Al(30) efficiently catalyzed the hydrogenation of aromatics to increase cetane index.

Figure 7 shows the sulfur content in hydrotreated LCO as a function of reaction temperature. A minimum sulfur content of 5 mass ppm in hydrotreated LCO was attained at 320°C. The efficient desulfurization probably depends on the high hydrogenation activity of Pt-Pd/USY(70)-Al(30).

3. 3. Catalyst Lifetime

Changes of sulfur content and cetane index with time in the catalyst lifetime test are shown in **Fig. 8**. The lifetime test was started using LCO-1, obtained by the pre-hydrotreatment at 9.8 MPa at 356°C over the dou-

Feed oil: Pre-hydrotreated LCO-1, LHSV: 1.0 h⁻¹, H₂/oil ratio: 400 N//l, Reaction pressure: 4.9 MPa, Catalyst: Pt-Pd/USY(70)-Al(30).

Fig. 7 Changes in Sulfur Content in Hydrotreated LCO with Reaction Temperature

Feed oil: Pre-hydrotreated LCO-1, Reaction pressure: 4.9 MPa, LHSV: 1.0 h⁻¹, H₂/oil ratio: 400 N//l, Catalyst: Pt-Pd/USY(70)-Al(30).

Fig. 8 Changes in Sulfur Content and Cetane Index in Hydrotreated LCO with Time

ble layer system. Throughout the lifetime test, sulfur content and cetane index were around 10 mass ppm and 40 for 266 days, respectively. In the process, reactor temperature was kept in the range from 280°C to 300°C. These results indicated that high desulfurization and cetane index improvement were successfully achieved by using stepwise hydrotreatment over Ni-Mo catalysts and Pt-Pd/USY(70)-Al(30) for 266 days. In the present hydrotreatment, the key process to obtain LCO with low sulfur content is desulfurization of the refractory sulfur compounds, such as 4,6-DMDBT. Effective catalytic hydrogenation of refractory sulfur compounds led to high desulfurization^{16),17)}. Therefore, the present catalyst system of Pt-Pd/USY(70)-Al(30) with higher hydrogenation activity is expected to be efficient for desulfurization. In addition, catalyst with higher hydrogenation activity is also expected to suppress coke formation on the catalyst to maintain catalytic activity for longer.

Figure 9 shows the coke deposition profile on the catalyst bed after 42 days in the life test. Coke deposition was much greater at the lower part of Pt-Pd/USY(70)-Al(30) in the reactor than at the upper part.

Feed oil: Pre-hydrotreated LCO-1, Reaction pressure: 4.9 MPa, LHSV: 1.0 h⁻¹, H₂/oil ratio: 400 N//l, Catalyst: Pt-Pd/USY(70)-Al(30).

Fig. 9 Changes in Coke Deposition on Pt-Pd/USY with Catalyst Bed Height

The high coke deposition at the lower part of the Pt-Pd/USY(70)-Al(30) bed was probably due to the decreased hydrogen concentration along the catalyst bed. However, another possibility was poly nuclear aromatics increase along the catalyst bed, probably produced by side reactions and polymerized to form the coke precursor during the longer residence time along the catalyst bed. These results suggested that a counter feed system, feed oil downward and hydrogen upward, will possibly improve catalyst activity and lifetime, because coke precursor formation in the lower bed is probably reduced by higher hydrogen concentration.

4. Conclusion

Two-step hydrotreatment of LCO over double-layered Ni-Mo supported catalyst followed by Pt-Pd/USY(70)-Al(30) was investigated. The first hydrotreatment, pre-hydrotreatment reduced the sulfur content in LCO from 6090 mass ppm to 137 mass ppm, and increased cetane index from 26 to 32, and successive hydrotreatment of pre-hydrotreated oil over Pt-Pd/USY(70)-Al(30) resulted in decrease of sulfur content to less than 10 mass ppm and reduction of aromatics fraction to increase cetane index to over 40. The catalytic activity for the hydrotreatment was maintained over 266 days. Coke deposition took place on the catalyst bed during the hydrotreatment, and increased with the feed flow direction. Therefore, a counter feed system, of feed oil downward and hydrogen upward, may reduce the coke deposition due to efficient hydrogenation of aromatics in the reactor and increase catalyst life.

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要 旨

Ni-Mo 担持触媒との組合せによる Pt-Pd 担持触媒での Light Cycle Oil の水素化精製

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硫黄濃度 6090 mass ppm, セタン指数 26 の Light Cycle Oil を Ni-Mo 担持触媒で一次水素化精製した後, Pt-Pd 担持触媒で二次水素化精製した。一次水素化精製反応にはシリカ-アルミナ担持 Ni-Mo 触媒 (Ni-Mo/SA) と USY ゼオライト-アルミナ担持 Ni-Mo 触媒 (Ni-Mo/USY-Al) を用いた。Ni-Mo/USY-Al との組合せは Ni-Mo/SA 単独に比べて, 脱窒素活性やセタン指数などがわずかに優れていることから一次水素化精製触媒として Ni-Mo/SA と Ni-Mo/USY-Al との組合せを選択した。この組合

せで得られた硫黄濃度 137 mass ppm, セタン指数 32 の一次水素化精製油を Pt-Pd 担持 USY ゼオライト-アルミナ触媒 (Pt-Pd/USY-Al) で二次水素化精製し, 硫黄濃度 5 mass ppm, セタン指数 47 の二次水素化精製油を得て Pt-Pd/USY-Al の高度な水素化精製活性を確認した。上述の一次水素化精製油を用いて Pt-Pd/USY-Al 単独の寿命試験を実施し, 266 日の期間にわたり約 10 mass ppm の硫黄濃度と約 40 のセタン指数を得ることができた。

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