Residual Oil Cracking with Hydrogen Generation

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The cracking of residual oils with simultaneous hydrogen generation has been carried out. In this process, the by-product coke deposited on the surface of the catalyst is partially oxidized in the regenerator with the formation of carbon monoxide, and the heat of reaction generated is utilized for cracking of the feed. Carbon monoxide works as a reducing agent for converting triiron tetraoxide (Fe_3O_4) in the catalyst to ferrous oxide (FeO), which in turn, is converted to Fe_3O_4 by its reacting with steam to generate hydrogen. A large amount of hydrogen can be produced from the process without coke formation. The amount of hydrogen production is large enough to desulfurize the product distillates produced from the process. Feasibility of the process for upgrading residual oils has been confirmed by the results of 0.6 BPD- and 250 BPD- pilot plants.

1. Introduction

It is difficult to predict the future of the petroleum refining industry under the current unstable circumstances. However, the fact must be recognized that demands for lighter products are increasing and that crude oils are getting heavier. Such circumstances will obviously bring about a glut of residual oils, which need to be converted into lighter, more valuable products at reasonable costs. Efforts are being made to meet the need.

This paper discusses the cracking of residual oils with simultaneous hydrogen generation. The basic research on the process was carried out by Nippon Mining Co. and the process further developed jointly by researchers from Nippon Mining Co., Hitachi Ltd., and Kashima Oil Co. serving as members of the Research Association for Residual Oil Processing (RAROP).

2. Cracking of Residual Oils over an Iron Catalyst

Iron is a well known catalyst for hydrocarbon dehydrogenation,¹⁾ carbon gasification,²⁾ coal liquefaction,³⁾ the Fischer-Tropsch reaction,⁴⁾ ammonia synthesis,⁵⁾ and others.⁶⁾ In these reactions, iron acts mainly as a dehydrogenation catalyst or a redox agent.

Cracking of residual oils over nickel oxide ore has been studied, and the ore was found to be an effective catalyst.⁷⁾⁻¹⁰⁾ A lower yield of heavy fraction boiling at temperatures above 343°C and a

higher coke yield were obtained over laterite catalyst A in comparison with other catalysts,¹¹⁾ though iron oxide ore showed low activity for cracking of residual oils.^{12),13)} This is probably because laterite A not only contains a large amount of nickel and iron, both of which accelerate dehydrogenation and coke formation, but it also has a larger specific surface area than other catalysts. **Table 1** lists the properties of laterite catalysts.

Laterite is a red soil of weathered rock and is widely distributed in the tropical and subtropical zones. The supply of laterite is said to be inexhaustible, and it can probably be used in the future. From the viewpoint of commercialization, it has the advantage of yielding smaller amounts of heavy fractions because of the lower amount of recycle oil involved. Although high coke production that results in lower oil yields is generally considered a disadvantage, high coke production can be utilized for high hydrogen generation in the process combining residual oil cracking and hydrogen generation. This process will be discussed subsequently. The mechanical strength of a catalyst is one of the important characteristics when the catalyst is used in fluidized bed reactors. The higher the calcination temperature, the higher the attrition resistance of the catalyst. Effects of calcination temperature of nickel oxide ore on cracking of residual oils and on mechanical strengths were reported.¹⁴⁾ In some experiments, laterite was calcined at 1,100–1,200 °C though its activity approached that of thermal cracking at such high temperatures.

Table 1 Composition and Properties of Catalysts

	Fe (wt%)	Ni (wt%)	MgO (wt%)	SiO ₂ (wt%)	Al ₂ O ₃ (wt%)	S.A. ^{a)} (m ² /g)
Laterite catalyst A	57.9	1.23	0.76	2.44	2.83	10.6
Laterite catalyst B	56.6	1.16	0.88	2.77	6.74	2.0
Laterite catalyst C	50.2	1.1	0.5	1.8	2.4	0.5
Laterite catalyst D	44.2	1.89	7.5	10.0	5.7	0.3

a) Specific surface area

Changes in the properties and yields of recycle oil through a series of repeated cracking over laterite catalyst B have been studied.¹⁵⁾ Most of the heavy metals and asphalten decreased in the first repeated crackings of the series, and the amount of cracked products decreased with repetition due to the increase in the aromaticity of the recycle oil.

3. Hydrogen Generation by the Reaction of Reduced Iron Oxide with Steam

Regeneration efficiency is also one of the important characteristics of a catalyst in cracking. The combustion rate of coke on the laterite catalyst A was investigated in a fixed bed reactor, and, as shown in **Fig. 1**, most of the coke on the catalyst was consumed during heating of the catalyst bed in a flow of nitrogen gas prior to the introduction of combustion air. For comparison, the combustion curve of fluid coke is shown in dashes in **Fig. 1**. The iron oxide in the laterite catalyst seemed to be readily reducible by coke.

When coke-deposited laterite catalyst C was subjected to reduction, the percent reduction of iron oxide was found to increase with increasing amount of coke on the catalyst, as shown in **Fig. 2**. Results of X-ray diffraction for laterite catalyst C and those of gas analysis show that iron oxide in the catalyst is reduced to liberate carbon monoxide and dioxide.¹⁶⁾ The percent reduction of the catalyst streaming out of the regenerator was calculated from the following equation:

$$R(\%) = \Delta R + R(\text{Fe}_3\text{O}_4)$$

$$\Delta R(\%) = \frac{[\text{CO}] + 2[\text{CO}_2] + 2\{[\text{O}_2]_{\text{out}} - [\text{O}_2]_{\text{in}}\}}{1.5N_{\text{Fe}}} \times 100$$

where R : percent reduction of the catalyst ($R=0$ for Fe_2O_3 and $R=100$ for Fe),

$R(\text{Fe}_3\text{O}_4)$: percent reduction of $\text{Fe}_3\text{O}_4=11.1$

R : difference between percent reductions of the catalyst at the regenerator inlet and outlet, respectively,

$[\text{CO}]$: amount of CO in the regenerator outlet gas, (g-mol/hr)

$[\text{CO}_2]$: amount of CO_2 in the regenerator outlet gas, (g-mol/hr)

Fig. 1 Conversion of Coke on Laterite Catalyst

Fig. 2 Relationship between Amount of Coke on Catalyst and Percent Reduction of Iron Oxide

$[\text{O}_2]_{\text{out}}$: amount of O_2 in the regenerator outlet gas, (g-mol/hr)

$[\text{O}_2]_{\text{in}}$: amount of O_2 in the regenerator inlet gas, (g-mol/hr), and

N_{Fe} : amount of iron in the catalyst fed to the regenerator, (g-mol/hr).

Hydrogen was generated by steam reacting with ferrous oxide produced by the reduction of the catalyst. As **Fig. 3** shows, the amount of hydrogen increases with increasing percent reduction of the iron oxide.

Burning coke on the catalyst to supply the heat for residual oil cracking is necessary. Therefore,

Fig. 3 Generated Hydrogen vs. Percent Reduction of Iron Oxide

Fig. 4 Effect of O_2/C on Total Reaction Heat and Percent Reduction of Iron Oxide

the conditions for heat generation by partial oxidation of coke and for reducing the iron oxide in the catalyst were investigated.

Major reactions at the partial oxidation stage were as follows:

Figure 4 shows the relationship between the percent reduction of catalyst C and the ratio of oxygen in the inlet gas to carbon deposited on the catalyst (O_2/C). The relationship between the total heat of reactions, 1—4, and O_2/C is also shown in **Fig. 4**. As this figure indicates, O_2/C can regulate both the total heat of reaction and percent reduction of the catalyst. It was found using a fixed bed reactor that the higher the molar ratio of oxygen to carbon,

1: after cracking, 2: after regeneration, 3: after hydrogen generation

○: Fe_3O_4 , △: FeO

Fig. 5 X-ray Diffraction Patterns of the Catalyst at Various Reaction Stages

the lower the reduction of iron oxide, and the greater the heat evolved. The most favorable molar ratio appears to be 0.3—0.4, because, in this range, the heat evolved in the regenerator corresponds to the heat required for cracking the residual oil.

4. Reduction and Oxidation of Iron Oxide in a Fluidized Bed

A coke-deposited catalyst was prepared by cracking Kuwait vacuum residual oil over laterite D. The iron oxide in the coke-deposited catalyst was reduced by partial oxidation of the coke. Hydrogen was generated by reaction of the reduced iron oxide with steam. These operations were carried out in fluidized bed reactors.

Figure 5 shows X-ray diffraction patterns of catalyst C at various reaction stages. The change in the crystal structure of the iron oxide is similar to that observed in the fixed bed reactor¹¹, that is, ferric oxide (Fe_2O_3) changes to triiron tetraoxide (Fe_3O_4) during cracking, and part of the triiron tetraoxide is reduced in the regenerator to ferrous oxide (FeO) which is then oxidized to triiron tetraoxide in the hydrogen generator. As shown in **Fig. 5**, the crystal structure of the iron oxide changes between FeO and Fe_3O_4 . In the steam-iron process developed at the Institute of Gas Technology (IGT), part of the iron oxide is reduced to metallic iron.^{17,18} However, sticking (or bogging) of the particles in the fluidized bed occurs more readily in this case^{19,20} although the amount of hydrogen

generated by the reaction of metallic iron with steam is larger than that generated by the reaction of FeO with steam. Furthermore, the catalyst is assumed to be more easily pulverized because of the large difference in the specific volumes of Fe and Fe₃O₄.²¹⁾

5. Behavior of Sulfur²²⁾

The behavior of sulfur in the process is assumed as shown in Fig. 6. In the cracker, most of the sulfur contained in the feed oil was transferred to the cracked oil (560°C+) and coke. The sulfur content of the cracked oil (560°C+) was almost the same as that of the feedstock.

The coke-deposited catalyst was charged continuously into the regenerator and then into the hydrogen generator. The concentration of sulfur in the gas from the regenerator was found to be so low that the gas emitted into the atmosphere will not cause serious air pollution problems, even without desulfurization. Concerning the composition of the sulfur compounds, it is considered that, when the sulfur in the coke is oxidized at the bottom of the regenerator, sulfur dioxide is first formed. Passing through the reactor in bubbles, the sulfur dioxide reacts with hydrogen or carbon monoxide to form hydrogen sulfide or carbonyl sulfide, respectively, which in turn reacts with iron oxide to form iron sulfide.^{23),24)}

The catalyst containing ferrous oxide (FeO), tri-iron tetraoxide (Fe₃O₄), iron sulfide (FeS), and coke was charged to the hydrogen generator through the regenerator and reacted with steam at 750°C to generate hydrogen.

Iron sulfide is partially desulfurized by reacting with steam in the hydrogen generator. Desulfurization of iron sulfide is thought to be controlled by the equilibrium between the following reactions:²⁵⁾

It is also evident from calculations that the more FeO is fed to the hydrogen generator, the lower becomes the present desulfurization of FeS.

6. Process Involving Desulfurization of Iron Sulfide by Roasting

When a sulfur-containing residual oil is cracked over a catalyst containing iron, and the coke on the catalyst is burned reductively, the iron oxide in the catalyst is sulfided into iron sulfide. This iron sulfide must be desulfurized if the catalyst is to be used repeatedly. One of the desulfurizing techniques is to react the iron sulfide with steam to remove the sulfur as hydrogen sulfide. Another technique is to roast the iron sulfide to remove the sulfur as sulfur dioxide. When a residual oil of such low sulfur content as Taching vacuum oil or desulfurized residual oil is used as feedstock, the iron sulfide is preferably desulfurized with steam, and the sulfur recovered as H₂S. When a residual oil with a high sulfur content is used as feedstock, the sulfur will likely be accumulated in the catalyst if it is desulfurized with steam. In such a case, the removal of sulfur as SO₂ by roasting the

Fig. 6 Schematic Behavior of Sulfur

Fig. 7 Hydrogen Concentration in Product Gas from Cracker, Amount of Hydrogen Generated, and CO/CO₂ Molar Ratio in Product Gas from Regenerator during 10-Day Run

iron sulfide is preferred. With the latter technique, the major reactions involved are as follows:

In the cracker:

In the regenerator:

In the roaster:

7. Small Scale Pilot Plant Operation ^{26),27)}

Feasibility of our process for upgrading residual oils has been confirmed using a pilot plant of 4 kg/hr (0.6 BPD) capacity. The cracker, the regenerator, and the roaster are made of type 304 stainless steel, and they are heated with electric furnaces. Sizes of the individual units are shown in **Table 2**. The composition and properties of the catalyst used are shown in **Table 3**.

Figure 7 shows the changes during a continuous

Table 2 Sizes and Operating Conditions of Pilot Plant

	Cracker	Regener- ator	Roaster
Sizes:			
Inner-diameter (mm)	127	151	102
Height (mm)	1,600	1,800	1,900
Height of fluidized bed (mm)	500	500	600
Operating conditions:			
Reaction temperature (°C)	525-545	780-830	750-810
Fluidizing gas	steam + N ₂	air + N ₂	air + N ₂

Table 3 Composition and Properties of Catalyst

Composition (wt%):			
Fe ₂ O ₃	82.1	SiO ₂	2.7
NiO	1.5	Al ₂ O ₃	6.6
MgO	0.8		
Properties:			
Average particle diameter	0.18 mm		
Angle of repose	35°		
Bulk density	1.73 g/mL		
Specific surface area	2 m ² /g

Fig. 8 Attrition Resistance of Catalyst vs. Days on Stream

ten-day run in the hydrogen concentration of the product gas from the cracker, in the amount of hydrogen generated, and in the CO/CO₂ molar ratio of the product gas from the regenerator. The higher the CO/CO₂ ratio was, the greater the amount of hydrogen generated. That is, increasing the reduction atmosphere inside the regenerator increased hydrogen generation, probably, because of the increased percent reduction of the catalyst. No catalyst deterioration was observed (**Fig. 8**) although the curve did fluctuate somewhat due to the

Fig. 9 Effect of Excess Air Coefficient on Percent Combustion of Sulfur and Carbon in Roaster of the Pilot Plant

varying operating conditions.

The amount of hydrogen generated was 180 NI- H_2 /kg-feed oil by reacting ferrous oxide with steam and was 30 NI- H_2 /kg-feed oil by dehydrogenation of the feed oil.

Desulfurization of FeS was conducted, and the percent combustion of carbon was compared with the percent combustion of sulfur by varying the excess air coefficient at temperatures from 750 to 810°C. **Figure 9** shows the relationship between the excess air coefficient and the percent combustion of carbon and that of sulfur. Obviously, sulfur is more readily oxidized than carbon, especially at lower levels of excess air coefficient.

Roasting iron sulfide without coke is a well-known process for sulfuric acid production.^{28)~30)} In the present process, however, coke coexists with iron sulfide. It is preferable to minimize coke consumption during roasting because the coke acts as an effective reductant of iron oxide.

8. Large Scale Pilot Plant Operation

Commercial feasibility of this process was confirmed in 1983 by operating a large scale pilot plant (250 BPD) built in the Mizushima Refinery of Nippon Mining Company, Japan in 1981.

In fluidized bed engineering, bubbles in the fluidized bed grow with increasing reactor diameter, and their growth decreases contact efficiency.^{31)~33)} Some efforts have been made to prevent the decrease in contact efficiency.^{34),35)} In the scaling-up of a plant, it must be taken into account that the rate constant is reduced by decrease in contact efficiency between the reactant and catalyst particles

Fig. 10 Flow Diagram of Large Scale Pilot Plant

Table 4 Sizes and Operating Conditions of Large Scale Pilot Plant

	Cracker	Regener- ator	Roaster
Sizes:			
Diameter (m)	0.82	1.60	0.56
Height (m)	15.9	17.0	10.4
Operating conditions:			
Pressure (kg/cm ²)	2.3-3.5	2.3-3.5	2.3-3.5
Temperature (°C)	500-550	780-850	600-800
Feed rate (BPD)	150-250	—	—

in the fluidized bed.^{36)~38)}

Figure 10 is a process flow diagram of the plant.³⁹⁾ Sizes and operating conditions of the individual units of the plant are shown in **Table 4**.⁴⁰⁾ The catalyst containing iron oxide was circulated between cracker and regenerator, and a small amount of the catalyst was circulated between regenerator and roaster to keep the sulfur content of the catalyst at a constant level.

At the beginning of the large-scale-pilot plant operation, large vertical forces in the fluidized bed were observed. These forces damaged the immersed tubes and their support system in the bed. The designer should be aware of the magnitude and frequency of the forces caused by buffeting action of bubbles,^{41),42)} especially in the case of coarse particles with high specific gravity.⁴³⁾ These forces were eliminated only after careful designing of the fluidized bed reactor, the bed height, the distribution of bubbles, and the particle size of the catalyst.^{34),40)}

After the problem of forces had been overcome, a number of operations totalling about 2,400 hours

Fig. 11 Amount of Hydrogen Generated in Cracker

Table 5 Product Yield Obtained with Large Scale Pilot Plant

Feedstock: Arabian light vacuum residue	
Specific gravity (15/4°C)	1.021
Viscosity at 120°C (cSt)	410
Sulfur (wt%)	4.2
Conradson carbon residue (wt%)	21.6
Reaction conditions:	
Cracking temperature (°C)	514
Regeneration Temperature (°C)	830
Roasting temperature (°C)	750
Pressure (kg/cm²)	2.0
Yield (vol%):	
C ₂ -	9.0*
C ₃	15.2
C ₄	2.4
C ₅ -180°C	5.2
180-230°C	8.2
230-360°C	14.2
360-510°C	28.2
total	82.4
Hydrogen (Nm³/kl-feed)	185
Note: * Fuel oil equivalent	

Table 6 Properties of Cracked Oil Before and After Hydrotreating

Kerosene:		
	cracked oil	
	before	after
Reaction	neutral	neutral
Flash point (°C)	63	61
95% Fraction (°C)	259.5	261.5
Sulfur (wt%)	1.85	0.0093
Smoke point (mm)	14	21
Copper corrosion	1	1a
Color	—	—
Diesel oil:		
	cracked oil	
	before	after
Reaction	neutral	neutral
Flash point (°C)	126	97
90% Fraction (°C)	320.5	319.5
Pour point (°C)	-15.0	-10.0
Cetane no.	—	—
Cetane index	39.1	51.0
Viscosity at 30°C (cSt)	5.55	4.93
Sulfur (wt%)	3.63	0.63

were conducted. Typical test results are shown in **Tables 5** and **6**.⁴⁴⁾ **Figure 11** illustrates the amount of hydrogen generated in the cracker. The large-scale-pilot plant showed excellent stability.

Efforts to improve catalyst activity were made also in the plant; and hydrogen generation amounting to about 185 Nm³/kl-feed oil was estimated. It was found that a large amount of hydrogen could be generated from the process without coke production and that the amount of hydrogen generated was sufficient to desulfurize the product distillates.

Concentrations of SO_x and NO_x were below 100 ppm and 20 ppm, respectively. It was also noted that flue gas from the process contained such small amounts of SO_x and NO_x that, even without desulfurization and/or denitrogenation, it caused no pollution problems.

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要 旨

水素発生を伴う重質油分解

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重質油分解プロセスにおいては副生するコークの処理方法が問題となるが、本研究は酸化鉄の酸化還元を利用して副生コークとスチームから水素を発生させる工程を加味した重質油分解プロセスの開発について検討したものであり、その主な成果は次のとおりである。

触媒としてラテライト鉱石を用いて減圧残油の分解を行い、触媒上にコークを付着させた後、このコークを 850°C で部分酸化すると、触媒中に含まれる四三酸化鉄 (Fe_3O_4) が還元されて酸化第一鉄 (FeO) に変化した。還元された酸化鉄にスチームを接触させると水素を発生し、酸化第一鉄は四三酸化鉄に酸化されることがわかった (Fig. 5)。また、酸化鉄の還元率および再生塔における発熱量は送入酸素と触媒上コークの比 (O_2/C) により制御できることがわかった (Fig. 4)。

Fig. 6 は本プロセスにおける硫黄の挙動を概念的に表したものである。分解反応後の触媒を再生塔で部分酸化反応に供するとコーク中の硫黄分がガス化し、即座に触媒中に FeS として捕捉されるが、生成した FeS は水素発生塔でスチームにより脱硫される。そのため再生塔廃ガス中の硫黄分は 100 ppm 以下となる。また、空気比が低いため NO_x の発生は見られない。

大慶の減圧残油あるいは脱硫した残油のように硫黄分の低い原料の場合はこの方式でも触媒中の硫黄分はバランスするが、中東系の減圧残油を脱硫せずにフィードする場合は、触媒中に硫黄分が蓄積することがある。

高硫黄原料油を処理するときの反応は以下ようになる。

分解塔において、

再生塔において、

ばい焼塔において、

このプロセスの工業化について検討するため、0.6 BPD の 3 塔循環流動層パイロットプラントの運転を行った。運転条件を Table 2 に、使用した触媒の性状を Table 3 に示す。Fig. 7 の 10 日間の連続運転状況結果から、再生塔の CO/CO_2 比が高いほど水素発生量が多いこと、約 200 $\text{Nm}^3/\text{kg-feed oil}$ の水素がこのプロセスで得られることがわかった。コーク存在下で硫化鉄のばい焼を行うと、炭素より硫黄の方が酸化されやすいことが見出された。

1981 年に 250 BPD の大型パイロットプラント (Fig. 10) を日本鉱業(株)水島製油所に建設し、総計約 2,400 時間の運転を行い、1983 年にその運転を終了した。運転当初は流動層内の推力発生等のトラブルを経験したが、流動層の設計、流動層高、気泡径、粒子径等の改良により解決した。水素化精製前後の生成油性状例を Tables 5 と 6 に、水素発生状況を Fig. 11 に示す。水素発生量約 185 $\text{Nm}^3/\text{kg-feed oil}$ が得られる見通しを得たが、これはこのプロセスで得られる留出油を水素化精製するに十分な量である。再生塔廃ガス中の SO_x および NO_x 濃度は、それぞれ 100 ppm および 20 ppm 以下であり、脱硫設備なしでも無公害であることが判明した。

Keywords

Cracking, Fluidized bed, Hydrogen generation, Iron oxide, Laterite, Residual oil