Residual Oil Cracking with Generation of Hydrogen (Part 2)[†]

Reduction and Oxidation of Iron Oxide in Fluidized Bed

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Fluidized-bed experiments have been carried out to investigate whether the process proposed in one of the previous papers is feasible for commercial operation. The results obtained are as follows: (1) the reactions required for this process can be induced under the reaction conditions usually employed in fluidized bed reactors, (2) the degree of reduction of the iron oxide obtained with a fluidized bed is nearly equal to that obtained with a fixed bed, (3) the amount of hydrogen generated does not vary greatly with repeated series of reactions; moreover the properties of the catalyst do not change significantly, (4) the amount of hydrogen generated is about 210 Nm³/k-l-vacuum residual oil. This amount is about twice the amount of hydrogen required for desulfurization of the cracked oil obtained from the present process.

1. Introduction

In recent years, residual oil cracking has become one of the most important problems facing the petroleum industry. Generally, large amounts of hydrogen are required to produce distillates from residual oils. Hydrocracking calls for much hydrogen, and the distillates produced by thermal cracking or catalytic cracking have to be hydrodesulfurized. Production of hydrogen will, therefore, be a major challenge in the future.

The authors have investigated cracking of residual oils with simultaneous hydrogen generation in which iron oxide in the catalyst is reduced by coke, and hydrogen is generated by reaction of steam with ferrous oxide in the catalyst. In one of the previous papers¹⁾, a new process of residual oil cracking was proposed. In this paper, the investigation using a fluidized-bed reactor, on the reduction, of iron oxide in the catalyst to generate hydrogen is presented.

2. Experimental

2.1 Feedstock

Kuwait vacuum residual oil was used as feedstock, and its properties are shown in **Table 1**.

2.2 Catalyst

A spherical catalyst prepared from laterite ore was used as a catalyst after being calcined at

Table 1 Properties of Feedstock

Specific Gravity (15/4°C)	1.0497
Conradson Carbon Residue (wt%)	17.5
Asphaltene (wt%)	6.8
C (wt%)	84.2
H (wt%)	10.6
S (wt%)	4.96
N (wt%)	0.4
V (ppm)	101
Ni (ppm)	30

Table 2 Composition and Properties of Catalyst

Composition	
Fe ₂ O ₃	63.3 (wt%)
NiO	2.4
MgO	7.5
SiO ₂	10.0
Al ₂ O ₃	5.7
Properties	
Average Particle Diameter (mm)	0.218
Bulk Density (g/ml)	1.52
Specific Surface Area (m ² /g)	0.3

1,200°C. The composition and properties of the catalyst are shown in **Table 2**.

2.3 Method of Experiments

The apparatus used for cracking of the vacuum residual oil is shown in **Fig. 1**. The cracker (6) made of type 304 stainless steel was 102 mm in inner-diameter and 1,050 mm in length. The height of the fluidized bed was 400 mm. The catalyst was charged from the catalyst hopper (7) to the cracker through a quartz tube (8) at a constant flow rate by regulating the nitrogen flow rate, and it was discharged into the catalyst pot (9). Steam was used as a fluidizing gas. The residual oil was atomized with steam and fed through a spray nozzle (5) to the bottom of the cracker.

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Fig. 1 Flow Diagram of Experimental Apparatus for Cracking Residual Oil

The superficial gas velocity in the cracker was 24 cm/s at the cracking temperature of 540°C.

The apparatus for reduction of iron oxide in the catalyst and for generation of hydrogen is shown in **Fig. 2**. The regenerator (4), made of type 304 stainless steel was 66 mm in diameter and 1,200 mm in length and the fluidized bed was 450 mm in height. The size of the hydrogen gen-

Fig. 2 Flow Diagram of Experimental Apparatus for Reduction of Catalyst and Hydrogen Generation

Table 3 Operating Conditions of Fluidized Bed Reactors

	Cracker	Regenerator	Hydrogen Generator
Reaction Temperature (°C)	540	850	750
Weight of Catalyst (kg)	2.6	1.4	1.4
Catalyst Residence Time (min)	17	14	14
Feed Rate of Vacuum Residual Oil (kg/hr)	3.0	—	—
Feed Rate of Steam (kg/hr)	1.9	—	0.5
Feed Rate of Air (Nm ³ /hr)	—	0.6	—

erator (12) was the same as that of the regenerator which was connected to the hydrogen generator with a catalyst transfer tube (10). The coke-deposited catalyst was charged from the catalyst hopper (5) into the regenerator through a quartz tube (6) at a constant flow rate and was transferred to the hydrogen generator (12) through the catalyst transfer tube (10), thence discharged into the catalyst pot (13). Air and steam were used as fluidizing gases for the regenerator and the hydrogen generator, respectively. The product gas was cooled with a cooler (8) and the flow rate was measured with a gas meter (9). The composition of the gas was analyzed by gas chromatography. Operating conditions of the cracker, the regenerator, and the hydrogen generator are shown in **Table 3**.

2.4 Analyses

Percent carbon deposited on the catalyst was measured with a carbon analyzer (Kokusai Electric Co. "Coulomatic C").

The method of analyzing the product gases generated in the regenerator and in the hydrogen generator was the same as previously described¹⁾.

The measurement of bulk density of the catalyst was made according to JIS K 6721. Attrition resistance of the catalyst was measured by the method described in the previous paper²⁾.

2.5 Definition

Percent reduction, was calculated on the catalyst from the regenerator by the following equations:

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

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

where

R : percent reduction of the catalyst, ($R=0$ for Fe_2O_3)

$R_{\text{Fe}_3\text{O}_4}$: percent reduction of $\text{Fe}_3\text{O}_4 = 11.1$

ΔR : difference in percent reduction between the catalysts at the inlet and at the outlet of the regenerator

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

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

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

$[O_2]_{in}$: amount of O_2 in reactant gas, (g-mol/hr)
 N_{Fe} : amount of iron in the catalyst fed to the regenerator, (g-atom/hr)

3. Results and Discussion

3.1 Cracking of Residual Oil

Kuwait vacuum residual oil was cracked in the cracker under the operating conditions shown in **Table 3**. Typical yields of gas, oil, and coke in once-through operation are listed in **Table 4**. The yield pattern obtained over the laterite ore catalyst is similar to that obtained over the nickel oxide ore catalyst^{3),4)}. When the high boiling fraction of the product oil was recycled to the cracker, coke yields were about 25 wt% from the pilot plant data obtained over the nickel oxide ore catalyst⁴⁾.

3.2 Reduction of Iron Oxide

The coke-deposited catalyst accumulated in the catalyst pot in **Fig. 1** was charged into the regenerator in **Fig. 2**, and partial oxidation of coke was carried out under the operating conditions shown in **Table 3** in order to investigate the reduction of iron oxide in the catalyst.

Figure 3 shows the effect of the molar ratio of oxygen to carbon fed into the regenerator on reduction of iron oxide. The molar ratio of oxygen to carbon was found to affect the reduction of iron oxide. In the previous paper¹⁾, it was

Table 4 Yields of Products Obtained by Once-through Cracking of Feedstock

Gas (wt%)	8
Oil (wt%)	78
Coke (wt%)	14

Fig. 3 Relationship between Percent Reduction of Catalyst and Molar Ratio of Oxygen to Carbon Fed into Regenerator

found with a fixed bed reactor that the higher the molar ratio of oxygen to carbon was, the lower the reduction of iron oxide became, and the greater the heat evolved. The most favorable molar ratio appears to be 0.3—0.4 because the heat evolved in the regenerator in this molar ratio range corresponds to the heat required for cracking of residual oil. The same tendency was observed with the fluidized bed reactor.

The molar ratio of CO_2 to CO in the product gas streaming out of the regenerator is plotted against percent reduction of iron oxide in **Fig. 4**.

The ferric oxide (Fe_2O_3) in the catalyst was reduced to triiron tetraoxide (Fe_3O_4) during the feed oil cracking reaction¹⁾. The carbon contained in the coke on the catalyst was partially oxidized to carbon monoxide and dioxide in the regenerator, and the triiron tetraoxide in the coke-deposited catalyst was presumably reduced to ferrous oxide (FeO) according to the following equations^{5)~7)}:

Figure 5 shows the iron-oxygen-carbon equilibrium⁸⁾. The solid line in **Fig. 4** shows the relationship between molar ratio of CO_2 to CO and percent reduction of iron oxide at $850^\circ C$ obtained from **Fig. 5**. The following relationships can be deduced from these figures:

- 1) Fe_3O_4 ($R=11\%$) is stable above 77% of CO_2 concentration in the CO_2 - CO gas mixture (**Fig. 5**) at $850^\circ C$, or in the range of $CO_2/CO > 3.3$ (**Fig. 4**),
- 2) At 77% of CO_2 concentration in the CO_2 -

Fig. 4 Relationship between CO_2/CO in Product Gas from Regenerator and Percent Reduction of the Catalyst at $850^\circ C$

Fig. 5 Fe-O-C Equilibrium⁸⁾

CO gas mixture (**Fig. 5**), or at $\text{CO}_2/\text{CO}=3.3$ (**Fig. 4**), iron oxide exists as Fe_{1-y}O ($0.11 \leq y \leq 0.25$) (between $\text{Fe}_{0.89}\text{O}$ and Fe_3O_4) (**Fig. 5**), or $11\% \leq R \leq 25\%$ (**Fig. 4**),

3) Iron oxide is reduced from $\text{Fe}_{0.89}\text{O}$ to FeO with decrease in CO_2 concentration in the CO_2 — CO gas mixture from 77% to 33% (**Fig. 5**), or R increases from 25% to 33% with decrease in CO_2/CO from 3.3 to 0.5 (**Fig. 4**),

4) A mixture of FeO and Fe ($33\% \leq R \leq 100\%$) is coexisting at CO_2 concentration of 33% in the CO_2 — CO gas mixture (**Fig. 5**) or at $\text{CO}_2/\text{CO}=0.5$ (**Fig. 4**),

5) Fe ($R=100\%$) is stable at CO_2 concentration below 33% in the CO_2 — CO gas mixture (**Fig. 5**), or in the range of $\text{CO}_2/\text{CO} \leq 0.5$ (**Fig. 4**).

The data shown in **Fig. 4** are found to lie on the solid line (equilibrium curve).

3.3 Hydrogen Generation

The reduced catalyst containing ferrous oxide (FeO) was transferred continuously to the hydrogen generator from the regenerator shown in **Fig. 2**, and hydrogen was generated according to Eq. (4)

The relationship between the amount of hydrogen generated in the hydrogen generator and the $\text{H}_2\text{O}/\text{C}$ molar ratio, and that between hydrogen concentration in the product gas from the hydrogen generator excluding hydrogen sulfide and the $\text{H}_2\text{O}/\text{C}$ molar ratio are shown in **Fig. 6**, where the denominator C in the $\text{H}_2\text{O}/\text{C}$ molar ratio shows the amount of carbon fed to the regenerator and the numerator of the $\text{H}_2\text{O}/\text{C}$ molar ratio shows the amount of steam introduced to the hydrogen

Fig. 6 Relationships between Hydrogen Generated and $\text{H}_2\text{O}/\text{C}$ Molar Ratio and between Hydrogen Concentration and $\text{H}_2\text{O}/\text{C}$ Molar Ratio

generator.

The higher the $\text{H}_2\text{O}/\text{C}$ molar ratio becomes, the greater the hydrogen generation is as shown in **Fig. 6**. The highest concentration of hydrogen, however, is approximately 90%. The remainder of the product gas contains carbon dioxide, carbon monoxide, methane, and hydrogen sulfide.

Hydrogen is generated by the reaction of ferrous oxide with steam as shown above. The ferrous oxide is produced by the reaction of iron oxide with carbon monoxide converted from coke (Eqs. (1)~(3)). Accordingly, hydrogen can be said to be obtained from the coke and steam.

With increase in the $\text{H}_2\text{O}/\text{C}$ molar ratio, steam conversion decreases as shown in **Fig. 7** though the amount of hydrogen generated increases as seen in **Fig. 6**. Therefore, from the standpoint of economy there is an optimum $\text{H}_2\text{O}/\text{C}$ molar ratio.

3.4 Change in Crystal Structure of Iron Oxide

The results of X-ray diffraction analyses of the catalysts taken out of the cracker, the regenerator, and the hydrogen generator are shown in **Fig. 8**. Change in the crystal structure of the iron oxide

Fig. 7 Steam Conversion vs. $\text{H}_2\text{O}/\text{C}$

Fig. 8 X-Ray Diffraction Patterns of the Catalyst at Various Reaction Stages

is similar to that observed with the fixed bed reactor¹⁾, that is, ferric oxide (Fe_2O_3) changes to triiron tetraoxide (Fe_3O_4) during the cracking reaction, and part of the triiron tetraoxide is reduced to ferrous oxide (FeO) in the regenerator. The ferrous oxide is oxidized to triiron tetraoxide in the hydrogen generator. However, part of the ferrous oxide remained unchanged in the hydrogen generator because the residence time of the catalyst in the hydrogen generator was short (14 min) compared with that in the previous experiment (60 min).

3.5 Changes in the Activity and Physical Properties of the Catalyst through Repeated Reactions

In order to investigate the durability of the catalyst, a series of reactions (cracking, partial oxidation, and hydrogen generation) was repeated five times.

The carbon dioxide/carbon monoxide molar ratio in the product gas from the regenerator and the

Fig. 9 Changes in Bulk Density with Cycle Number

Fig. 10 Changes in Attrition Resistance with Cycle Number

amount of hydrogen generated in the hydrogen generator at each series of reactions are shown in **Table 5** together with the reaction conditions involved. The amount of hydrogen generated, which indicates the activity of the catalyst, did not differ greatly from series to series. The differences in the amounts of hydrogen generated (**Table 5**) and bulk density (**Fig. 9**) are small because the catalyst used was previously calcined at $1,200^\circ\text{C}$ which is higher than the reaction temperature. The results

Table 5 CO_2/CO and Hydrogen Generated in Repeated Series of Reactions

Cycle Number	1	2	3	4	5
Temperature of the Regenerator ($^\circ\text{C}$)	840	845	840	845	820
Catalyst Circulation Rate (kg/hr)	4.1	3.4	3.7	5.9	5.2
Coke on Catalyst (wt%)	5.5	6.7	6.2	3.9	4.5
O_2/C Molar Ratio	0.31	0.30	0.31	0.30	0.30
Temperature of the Hydrogen Generator ($^\circ\text{C}$)	740	730	745	730	700
Steam Fed to the Hydrogen Generator (kg/hr)	0.42	0.42	0.54	0.42	0.54
CO_2/CO in Product Gas (mol/mol)	0.48	0.44	0.54	0.55	0.42
Hydrogen Generated (Nl/hr)	126	104	110	104	118
Hydrogen Generated ($\text{Nm}^3/\text{kl-feed oil}$)	230	200	210	210	200

of attrition resistance shown in **Fig. 10** increased with repeated series of reactions, probably because the coke on the catalyst helped to enhance the attrition resistance.

3.6 Amount of Hydrogen Generated

The amount of hydrogen generated was calculated to be about 210 Nm³/kl-vacuum residual oil as shown in **Table 5** assuming that the coke yield is 25% (see **3.1**). This amount of hydrogen is about twice the amount required for desulfurization of the cracked oil⁹⁾ obtained from the present process.

4. Conclusion

Fluidized-bed experiments have been carried out to investigate whether the process proposed in one of the previous papers is feasible for commercial operation.

The yield pattern obtained over the laterite ore catalyst is similar to that obtained over the nickel oxide ore catalyst.

The degree of reduction of iron oxide obtained with a fluidized bed is nearly equal to that obtained with a fixed bed. The relationship between molar ratio of CO₂ to CO and percent reduction of iron oxide at 850°C agreed with the equilibrium curve.

With increase in the H₂O/C molar ratio, steam conversion decreases though the amount of hydrogen generated increases. Ferrous oxide is oxidized to triiron tetraoxide to generate hydrogen. However, part of the ferrous oxide remained unchanged in the hydrogen generator because of the shortness of residence time of the catalyst.

In order to investigate the durability of the catalyst, a series of reactions (cracking, partial oxidation, and hydrogen generation) has been repeated five times. The amount of hydrogen generated did not vary greatly with repeated series

of reactions and no significant change in the properties of the catalyst was observed.

The reactions required for this process can be induced under the reaction conditions usually employed in fluidized bed reactors.

The amount of hydrogen generated was estimated to be about 210 Nm³/kl-vacuum residual oil. This amount of hydrogen is about twice the amount required for desulfurization of the cracked oil obtained from the present process.

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要 旨

水素発生を伴う重質油分解(第2報)
流動層における酸化鉄の還元と酸化

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前報¹⁾で、触媒中の酸化鉄の還元および酸化を媒介とした水素発生を伴う重質油分解プロセスを提案した。このプロセスが工業化可能か否かについて検討するために流動層実験を行った。

Table 2 に示す組成を持つラテライト触媒上でクウェート減圧残油の分解を行い **Table 4** に示す収率を得た。この収率は酸化ニッケル鉱石上で得られた結果^{2),4)} と類似である。

再生塔入口の酸素と炭素のモル比に対する酸化鉄の還元率を **Fig. 3** に示すが、この図から流動層と固定層ではほとんど差がないことがわかる。また、再生塔出口ガス中の CO_2/CO 比と酸化鉄の還元率との関係は、**Fig. 4** に見られるように平衡曲線とよく一致している。

$\text{H}_2\text{O}/\text{C}$ モル比が増加すると水素発生量は増加するが、スチーム転化率は減少する (**Figs. 6, 7**)。酸化第一鉄はスチームに

よって酸化されて四三酸化鉄になり水素を発生するが、触媒滞留時間が短かったため、一部の酸化第一鉄が未反応のまま残っていた (**Fig. 8**)。

触媒の耐久性について検討するため、分解—再生—水素発生の一連の反応を5回繰り返したが、水素発生量の変化はほとんど無く (**Table 5**)、触媒のかさ比重も一定であった (**Fig. 9**)。 **Fig. 10** に見られるように、反応繰り返しにより触媒強度の向上が認められている。

以上の検討から、このプロセスに要求される反応は、流動層反応器で通常用いられる反応条件下で十分に進行することが明らかである。

水素発生量は約 $210 \text{ Nm}^3/\text{kl}$ -減圧残油と推定され (**Table 5**)、この水素量は本プロセス自体から得られる分解油の脱硫に要する量の約2倍である。

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