Residual Oil Cracking with Generation of Hydrogen (Part 4)

Proposal for a New Cracking Process with Desulfurization of Iron Sulfide by Roasting

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A sulfur-containing residual oil has been cracked in a fluidized bed of an iron-containing catalyst with hydrogen generation of 180 NI-H₂/kg-feed oil by reaction of ferrous oxide with steam and of 30 NI-H₂/kg-feed oil by dehydrogenation of the feed oil. The iron sulfide formed in the catalyst during partial oxidation of coke has been desulfurized by roasting with air in a fluidized bed roaster. The desulfurization reaction has been found to be fast enough to attain equilibrium during roasting. Based on these results, a new cracking process has been proposed. It consists of cracking sulfur-containing residual oil, generation of hydrogen, partial oxidation of coke on the catalyst, fixation of gaseous sulfur compounds in the catalyst, and roasting of the iron sulfide.

1. Introduction

When a sulfur-containing residual oil is cracked over a catalyst containing iron, the iron oxide in the catalyst is sulfided to iron sulfide as previously reported¹⁾. It is necessary that this iron sulfide be desulfurized for repeated use of the catalyst for cracking. One of the desulfurizing techniques is to treat the iron sulfide with steam¹⁾ to remove the sulfur as hydrogen sulfide. Another technique is to roast the iron sulfide to remove the sulfur as sulfur dioxide.

We have made studies of the latter technique and have proposed a new residual oil cracking process.

2. Experimental

2.1 Feedstock

Vacuum residual oil was used as feedstock. The properties are shown in **Table 1**.

2.2 Catalyst

The properties and composition of the catalyst used are shown in **Table 2**.

Table 1 Properties of Feedstock

Specific Gravity (15/4°C)	1.0412
Conradson Carbon Residue (wt%)	24.2
Sulfur (wt%)	5.62
V (ppm)	130
Ni (ppm)	30

Table 2 Composition and Properties of Catalyst

Composition	
Fe ₂ O ₃	82.1 (wt%)
NiO	1.5
MgO	0.8
SiO ₂	2.7
Al ₂ O ₃	6.6
Properties	
Average Particle Diameter (mm)	0.18
Angle of Repose	35°
Bulk Density (g/ml)	1.73
Specific Surface Area (m ² /g)	2

2.3 Method of Experiment

The experimental apparatus for cracking of residual oil with generation of hydrogen is shown in **Fig. 1**. Its feed capacity is 4 kg/hr. The three reactors (cracker, regenerator, and roaster) are made of type 304 stainless steel and heated with electric furnaces. Sizes of the reactors are shown in **Table 3**. The catalyst was circulated between cracker (1) and regenerator (2). The catalyst was continuously transferred from the regenerator (2) to the catalyst pot (6) with a rotary feeder (5) and it was periodically transferred to the catalyst hopper (7), from which the catalyst was supplied

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Fig. 1 Flow Diagram of Experimental Apparatus

Table 3 Sizes and Operating Conditions of the Reactors

	Cracker	Regenerator	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 or N ₂	air+N ₂	air+N ₂
Superficial Velocity (cm/s)	23—25	36—40	30—37
Catalyst Circulation Rate (kg/hr)	←15—23→		
Feed Rate of Vacuum Residual Oil (kg/hr)	1.8—2.4	—	—
Feed Rate of Steam (kg/hr)	1.2—3.0	—	—
Feed Rate of Air (m ³ /hr)	—	1.5—2.0	2.0—2.6

to the roaster (3). The catalyst discharged from the roaster (3) was accumulated in the catalyst pot (8) and transferred to the catalyst hopper (4) to supply the regenerator.

The residual oil was fed to the bottom of the cracker together with an atomizing and fluidizing gas. The cracked gas and oil were discharged from the cracker, and they were quenched in the quencher (9). The cracked gas was separated from the oil and water in the oil trap (10) and its flow rate was measured with the gas meter (12). Partial pressure of steam in the gas from the cracker was calculated from the amount of water separated.

The product gases from the regenerator and the roaster were cooled in the coolers (14), and their flow rates were measured with respective gas meters

(12). The composition of the gases was analyzed by gas chromatography. The operating conditions of the reactors are shown in **Table 3**.

2.4 Definition

The excess air coefficient is expressed by the following equation:

Excess air coefficient
= $\frac{\text{Amount of air fed to the roaster}}{\text{Amount of combustion air theoretically required for the following reactions}}$
 $C + O_2 \longrightarrow CO_2$
 $S + O_2 \longrightarrow SO_2$
 $3FeS + 5O_2 \longrightarrow 3SO_2 + Fe_3O_4$

2.5 Analyses

The amount of carbon deposited on the catalyst was measured with a carbon analyzer (Kokusai Electric Co. "Coulomatic C"). The content of

Table 4 Analytical Conditions of Gas Chromatography

Gases	Gas Chromatograph	Packing	Detector
Hydrocarbons	HITACHI 063	activated alumina TR	FID
CH ₄ , H ₂	Shimadzu GC-2C	active carbon	TCD
CO ₂ , H ₂ S	HITACHI K-23	Porapak Q	TCD
CO ₂ , H ₂ S, SO ₂	HITACHI 163	Porapak Q	FPD
CH ₄ , CO ₂	Shimadzu 3BT	active carbon	TCD
N ₂ , H ₂ , O ₂ , CH ₄ , CO	Shimadzu 3BT	molecular sieve 5A	TCD

sulfur in the coke-deposited catalyst was measured according to JIS K 2541.

The composition of product gases generated in the three reactors was analyzed by gas chromatography. **Table 4** lists the analytical conditions.

The attrition resistance of the catalyst was determined by the method described in a previous paper²⁾.

3. Results and Discussion

3.1 Cracking of Residual Oil

Once-through cracking of the feed oil was conducted using steam as the atomizing and fluidizing gas. Typical yields of gas, oil, and coke obtained over the catalyst in the cracker are shown in **Table 5**.

3.2 Hydrogen Generation by Dehydrogenation of Residual Oil

Cracking of residual oil was carried out using nitrogen instead of steam as the atomizing and fluidizing gas under the operating conditions shown in **Table 3**. The composition of the product gas is shown in **Table 6**. The amount of generated hydrogen was 29.4% of the product gas and 30 NI/kg-feed oil. This hydrogen was apparently generated by dehydrogenation of the feed oil.

3.3 Hydrogen Generation by Reaction of Ferrous Oxide with Steam

The residual oil was cracked using steam as the atomizing and fluidizing gas under the operating conditions shown in **Table 3**. The composition of the product gas is shown in **Table 6**. The amount of hydrogen generated was 69.4% by volume of the product gas and 210 NI/kg-feed oil. This hydrogen was apparently generated by both the reaction of ferrous oxide with steam and the dehydrogenation of residual oil. Steam reforming of hydrocarbons is not thought of as taking place at such a low cracking temperature³⁾. Therefore, the difference between 210 and 30 (=180 NI/kg-feed oil) must be the amount of hydrogen generated by the reaction of ferrous oxide with steam (H_s).

The coke-deposited catalyst was transferred from the cracker to the regenerator, and partial oxidation of coke was carried out at 800°C. The triiron tetraoxide in the catalyst was simultaneously reduced to ferrous oxide. A typical composition of the gas from the regenerator is given in **Table 7**.

Figure 2 shows the relationship between H_s and CO_2/CO molar ratio in the product gas from the regenerator. The lower the CO_2/CO ratio was,

Table 5 Yields of Cracked Products

Gas (wt%)	8
Oil (wt%)	79
IBP–180°C	6
180–560°C	30
560°C+	43
Coke (wt%)	14

Table 6 Composition of Cracked Gas

Fluidizing Gas	H ₂ O	N ₂
H ₂ (vol%)	69.4	29.4
CO	0	0
CO ₂	1.2	0.2
H ₂ S	1.0	0.2
CH ₄	11.7	27.0
C ₂ hydrocarbons	8.8	21.8
C ₃ hydrocarbons	5.4	13.1
C ₄ hydrocarbons	2.1	6.8
C ₅ hydrocarbons	0.4	1.5
H ₂ /CH ₄	5.9	1.1
Hydrogen Yield (NI/kg-feed oil)	210	30

Table 7 Typical Composition of Gas from Regenerator

CO	16.8 (vol%)
CO ₂	17.6
N ₂	61.5
CH ₄	0.3
H ₂	3.8
H ₂ S	47 (ppm)
COS	4 (ppm)
SO ₂	134 (ppm)

Fig. 2 Hydrogen Generated by Reaction of H₂O with FeO in Cracker vs. CO_2/CO Molar Ratio in the Product Gas from Regenerator

the higher the amount of hydrogen generated; that is, if the atmosphere inside the regenerator becomes more reducing, H_s increases, probably because the percent reduction of the catalyst increases. The decrease in the O_2/C molar ratio produces a reducing atmosphere in the regenerator (wherein the CO_2/CO ratio decreases), as shown in **Fig. 3**, resulting in an increase in H_s .

Figure 4 shows the changes in the hydrogen

Fig. 3 CO_2/CO Molar Ratio in Product Gas from Regenerator vs. Molar Ratio of O_2 in Air fed to Regenerator and C in Coke fed to Regenerator

concentration of the product gas from the cracker, the amount of hydrogen generated, and the CO/CO_2 molar ratio in the product gas from the regenerator during a continuous ten-day-run. The amount of hydrogen generated is affected by partial pressure of steam. No catalyst deterioration is observed; the curve did fluctuate somewhat, however, due to the variation in the operating conditions.

3.4 Sulfur Distribution in Cracked Products

The sulfur distribution in the cracked products is shown in Table 8. The sulfur distributed to the coke and catalyst is oxidized to sulfur dioxide in the roaster, while the sulfur in the oil and gas is converted to hydrogen sulfide in the hydrosulfurizer. Sulfur is recovered as molten sulfur

Table 8 Sulfur Distribution in Cracked Products

Gas (wt%)	9
Oil (wt%)	59
Coke (wt%)	32
Catalyst (wt%)	
Total	100

more easily from hydrogen sulfide than from sulfur dioxide. Therefore, the more sulfur distributed to gas and oil, the easier its recovery. Table 8 shows that fairly large amounts of sulfur are distributed to gas and oil.

Figure 5 shows the relationship between $\text{H}_2\text{S}/\text{H}_2$ and $\text{H}_2\text{O}/\text{H}_2$ in the product gas from the cracker. It can be seen that partial pressure of hydrogen sulfide increases with increase in partial pressure of steam; that is, the sulfur distributed to the gas increases with increase in partial pressure of steam in the product gas. The relationship between $\text{H}_2\text{S}/\text{H}_2$ and $\text{H}_2\text{O}/\text{H}_2$ agrees well with the equilibrium line⁴⁾ obtained from the following equation:

$$\log (p_{\text{H}_2\text{O}}/p_{\text{H}_2}) = 3/4 \log (p_{\text{H}_2\text{S}}/p_{\text{H}_2}) - 1/4 \log K_T$$
where

$p_{\text{H}_2\text{O}}$, p_{H_2} , $p_{\text{H}_2\text{S}}$: partial pressures of H_2O , H_2 , and H_2S , respectively

K_T : equilibrium constant of the reaction
 $3\text{FeS} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 3\text{H}_2\text{S} + \text{H}_2$

3.5 Desulfurization of FeS

Desulfurization of FeS was conducted under the operating conditions shown in Table 3. Percent combustion of carbon was compared with percent combustion of sulfur by varying the excess air coefficient at 750–810°C. Figure 6 shows the relationship between excess air coefficient and percent combustion of carbon and percent combustion

Fig. 4 Hydrogen Concentration in Product Gas from Cracker, Amount of Hydrogen Generated, and CO/CO_2 Molar Ratio in Product Gas from Regenerator during 10-Day-Run

— equilibrium line obtained from
 $\log (p_{\text{H}_2\text{O}}/p_{\text{H}_2}) = 3/4 \log (p_{\text{H}_2\text{S}}/p_{\text{H}_2}) - 1/4 \log K_T$
 Fig. 5 Relationship between H_2S , H_2 , and H_2O in Product Gas from Cracker

of sulfur. It is found that sulfur is oxidized more easily than carbon, especially at low excess air coefficients.

Roasting of iron sulfide without coke is a well-known process for sulfuric acid production^{5)~8)}. In the present process, coke coexists with iron sulfide. It is preferable to minimize the consumption of coke during roasting because coke acts as an effective reductant of iron oxide.

Figure 7 shows the results of X-ray diffraction analyses of the catalyst before and after desulfurization. It can be seen in this figure that FeS is converted to Fe_3O_4 sufficiently and that the iron is not further oxidized beyond the Fe_3O_4 level.

Attrition resistance of the catalyst is plotted

Sulfur content in catalyst fed to the roaster :
 4.5—5.5wt%
 Carbon content in catalyst fed to the roaster :
 2.2—4.5wt%
 Reaction temperature : 750—810°C

Fig. 6 Effect of Excess Air Coefficient on Percent Combustion of Carbon and Sulfur in Roaster

against process time in **Fig. 8**, which indicated that it did not change during the run.

Composition of the product gas from the roaster is compared in **Table 9** with the equilibrium values calculated by Yazawa's method⁹⁾. The good agreement between them indicates that desulfurization reaction is fast enough to attain equilibrium during roasting in the roaster.

3.6 Cracking Process for Residual Oil of High Sulfur Content

The above observations permit us to deduce the

Fig. 7 X-ray Diffraction Pattern of Catalyst before and after Desulfurization

Fig. 8 Attrition Resistance of Catalyst vs. Process Time

Table 9 Composition of Gas from Roaster (750°C)

	Observed	Equilibrium
N ₂	85.7	85.6
CO ₂	5.2	4.3
SO ₂	7.3	9.1
H ₂ O	1.0	0.87
S ₂	—	0.17
H ₂ S	trace	0.010
CO	0	0.010
COS	0	0.002
H ₂	0.05	0.002
O ₂	0.67	10 ⁻¹⁴
CH ₄	0	10 ⁻¹⁸

following processes for residual oil cracking with generation of hydrogen.

(1) In the cracker, the vacuum residual oil is cracked over the catalyst containing iron oxide, and hydrogen is simultaneously generated by the reaction of ferrous oxide with steam.

(2) In the regenerator, the coke deposited on the catalyst is partially oxidized, and triiron tetraoxide (Fe₃O₄) is reduced to ferrous oxide (FeO). The sulfur dioxide produced by partial oxidation of coke is fixed into the catalyst.

(3) In the roaster, the sulfur fixed in the catalyst is desulfurized by roasting with air.

4. Conclusion

A sulfur-containing residual oil has been cracked

in a fluidized bed of a catalyst containing iron. The iron sulfide formed in the catalyst during partial oxidation of coke has been desulfurized by roasting with air. The results obtained are as follows:

1) The amount of hydrogen generated was 30 NI/kg-feed oil during the cracking of residual oil using nitrogen as the atomizing and fluidizing gas, however, it was 210 NI/kg-feed oil when steam was used as the atomizing and fluidizing gas. The difference is the amount of hydrogen generated by the reaction of ferrous oxide with steam.

2) It can be seen that partial pressure of hydrogen sulfide in the product gas from the cracker increases with increase in the partial pressure of steam. The relationship between H₂S/H₂ and H₂O/H₂ agrees well with the equilibrium line obtained from the following equation:

log (p_{H₂O}/p_{H₂}) = 3/4 log (p_{H₂S}/p_{H₂}) - 1/4 log K_T
(3FeS + 4H₂O = Fe₃O₄ + 3H₂S + H₂)

3) It has been found that sulfur is oxidized more readily than carbon, especially at low excess air coefficients. The desulfurization reaction is fast enough to attain equilibrium during roasting in the roaster.

4) The above observations permit us to deduce the following processes for residual oil cracking with generation of hydrogen:

In the cracker, the vacuum residual oil is cracked over the catalyst containing iron oxide, and hydrogen is simultaneously generated by the reaction of ferrous oxide with steam.

In the regenerator, the coke deposited on the catalyst is partially oxidized, and triiron tetraoxide is reduced to ferrous oxide. The sulfur dioxide produced by partial oxidation of coke is fixed in the catalyst.

In the roaster, the sulfur fixed in the catalyst is desulfurized by roasting with air.

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要 旨

水素発生を伴う重質油分解 (第4報) 焙焼による硫化鉄の脱硫を含む新しい分解プロセスの提案

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硫黄分の多い重質油を鉄含有触媒上で分解すると、触媒中に硫化鉄が蓄積することは前報^{1),2)}で報告した。ここでは硫化鉄の脱硫手段として空気による焙焼を含む重質油分解プロセスについての検討結果を報告する。

分解塔の中では水素発生と重質油分解が主な反応であるが、水素発生は重質油分解時に起こる脱水素反応によるものと酸化第一鉄とスチームの反応によるものとが考えられる。そこで、流動化ガスの種類を変えて、それぞれの反応による水素発生量を求めたところ、**Table 6**に見られるように、脱水素反応による水素発生量が 30 Nl/kg-原料油、酸化第一鉄とスチームの

反応による水素発生量が 180 Nl/kg-原料油と推定された。

再生塔に供給する コークと 流動化空気の比 (O_2/C) を変えることにより再生塔内の雰囲気をも **Fig. 3** に示すように制御して、再生塔出口ガス中の CO_2/CO 比と分解塔における酸化第一鉄とスチームの反応に基づく水素発生量の関係を求めたところ、**Fig. 2** に見られるようによい相関が得られた。

焙焼塔では、**Fig. 6** に示すように硫化鉄は焙焼によって容易に脱硫され、反応条件を選択することによってある程度コークの燃焼を抑制することが可能であることが判明した。

これらの実験結果に基づいて、含硫黄重質油の分解、水素発生、触媒上コークの部分酸化、ガス状硫黄化合物の触媒への固定、そして硫化鉄の焙焼から成る新しい分解プロセスを提案した。

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