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Hydro-Cracking of Gas Oil, I.

By

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The term "Hydro-Cracking" is used to describe a method of cracking in which mineral oil is decomposed in the presence of high pressure hydrogen. The hydro-cracked gasoline is reputed to be of superior quality as compared with ordinary cracked gasoline.

There are very few reports on the hydro-cracking of petroleum products, though many have been published on destructive hydrogenation of coal tars.

The author has formerly dealt with vapor phase cracking of gas oil[1] and in the present paper, the thermal reactions of the same gas oil under high hydrogen pressure is discussed.

This series of experiments was conducted as the preliminary test for continuous hydro-cracking experiments to determine the reaction conditions of the latter.

SAMPLE AND CATALYST.

Sample. Siragiku gas oil (Ogura Oil Co.) was used as the sample. Its properties are shown in the following table.

Table 1. Properties of the sample.

Specific gravity $D_{15}^{15} = 0.8218$

Distillation test (100 c.c.)

I. B. P.	148.0°C.	55%	256.5°C.
5%	193.0	60	259.0
10	209.0	65	262.0
15	220.0	70	264.0
20	227.0	75	267.0
25	233.5	80	270.0
30	239.0	85	274.0
35	243.5	90	278.0
40	247.0	95	385.5
45	250.5	D.P.	289.0
50	253.5		

(Mean boiling point 248.6°C.)

1) H. Ohtuka, J. Soc. Chem Ind. Japan, **37**, 420, 1934; **38**, 742, 1935; **39**, 790, 1936.

Component hydrocarbons (in % by wight)	
Unsaturated hydrocarbons	0%
Aromatic hydrocarbons	23%
Naphthene hydrocarbons	13%
Paraffin hydrocarbons	64%
After washing with 99% H_2SO_4	
Aniline point	83°C.
Specific gravity (D_{15}^{15})	0.8069

Catalyst. Ammoniumthiomolybdate on pumice stone was used as the catalyst. Ammoniacal solution of ammonium molybdate containing 1 kg of this reagent was first saturated with hydrogen sulfide. 1 kg of bean-size pumice stone was then added to the sulfurized solution and impregnated with the thiomolybdate by evaporating the solution with constant stirring.

METHOD OF EXPERIMENT.

Apparatus. A rotating autoclave was employed. This was made of Cr-Ni-steel (18 : 8), and its capacity was 4,960 c.c. The details of this autoclave were described by S. Utida[2].

Procedure. The sample and catalyst were weighed into the autoclave, and then hydrogen was admitted until the required initial pressure was reached. The volume of compressed hydrogen was corrected at N.T.P. and its weight was shown in % by weight in proportion to the sample.

Rotating the autoclave, the charge was heated to the desired reaction temperature, and kept at that temperature for the duration of reaction time and then cooled. The temperature and pressure were recorded at regular intervals during the reaction.

After the autoclave was cooled to room temperature, the gaseous product was released through a gas washer containing KOH solution, U-tubes filled with $CaCl_2$, soda-lime and active charcoal, and a gas meter. The produced gas was analysed by means of the Hempel apparatus. The liquid product was weighed out of the autoclave and examined.

Analysis of Oily Product.

The oily product was fractionated into four portions, i.e., initial boiling point ~ 97°C., 97 ~ 120°C., 120 ~ 200°C. and 200°C. over, and each fraction was analysed into component hydrocarbons by the method as following.

I. Analysis of the fractions below 200°C.

Specific gravity of each sample is measured and recorded. One vol. of each sample is washed with two vols. of 87% H_2SO_4 for 15 min. Weight decrease by this treatment is regarded as "unsaturated hydrocarbons." The recovered oil is washed again with three vols. of 99% H_2SO_4 for 30 min. Weight decrease by the second acid treatment is regarded as "aromatic hydrocarbons." "Paraffins"

2) S. Utida, Report of Imperial Fuel Research Institute, Japan, No. 18.

and "naphthenes" of the aromatic free oil are calculated from the aniline point data.

II. Analysis of the fraction above 200°C.

Unsaturated and aromatic hydrocarbons are determined as described above. Naphthene content is calculated from Griffith's formula as following.

$$\text{Weight } \% \text{ of naphthene} = \{100 \cdot S_{P+N} - S_P(100-N)\} / S_{P+N}$$

Where,

$100-N$: Vol. % of paraffins in the aromatic free sample.
N: Vol. % of naphthenes in the same sample.
S_P: Mean specific gravity of paraffins in the fraction.
S_{P+N}: Specific gravity of the sample.

EXPERIMENTAL RESULTS.

Table 2. Reaction Conditions.

Exp. No.	A—9	A—10	A—11	A—12	A—13*
Sample (g.)	250	250	250	250	250
Catalyst (g.)	25	25	25	25	25
H_2 compressed (Wt. %)	8.2	8.3	8.3	8.3	16.6
Init. press. (atm.)	51	52	52	52	106
Init. press. (°C.)	13	14	14	13	16
React. press. (atm.)	141	123	150	153	—
End press. (atm.)	44	50	37	48	—
End press. (°C.)	14	15	15	13	—
React. temp. (°C.)	450	400	500	550	—
React. time (min.)	62	64	62	60	—

Remarks: *Exp. No. A—13 was started under ca. 100 atm. of initial hydrogen pressure. But the experiment could not be finished owing to extraordinary pressure increase near the reaction temperature.

Table 3. Yields of Produced Oil. (in wt. %)

Exp. No.	A—9		A—10		A—11		A—12	
React. temp. (°C.)	450		400		500		550	
Yield of total produced oil (%)	68.6		97.1		43.9		27.8	
I.B.P. ~ 97°C. (%)	12.4	39.7	0.9	9.1	12.4	30.5	7.2	11.5
97 ~ 120°C. (%)	6.9		0.6		3.9		1.3	
120 ~ 200°C. (%)	20.4		7.6		14.2		3.0	
200°C. over (%)	21.4		84.4		9.3		16.3*	
Residue (%)	3.9		0.9		1.4		—	
Loss (%)	3.6		2.7		2.7		—	
D.P. (°C.)	265		299		283		—	

Remarks: *The liquid product at 550°C. contained an appreciable amount of carboid and deposited naphthalene in the course of distillation.

Table 4. Specific Gravities of Produced Oil. (D_{15}^{15})

Exp. No.	A—9	A—10	A—11	A—12
React. temp. (°C.)	450	400	500	550
I.B.P. ~ 97°C.	0.6838	0.7233	0.7552	0.8612
97 ~ 120°C.	0.7368	0.7496	0.8364	0.8950
120 ~ 200°C.	0.8004	0.7906	0.8928	0.8964
200°C. over	0.8752	0.9209	0.9812	—
Mean sp. gr.	0.782	0.750	0.808	0.872

Table 5. Volatilities of Produced Gasoline.

Exp. No.	A—9	A—10	A—11	A—12
React. temp. (°C.)	450	400	500	550
I. B. P. (°C.)	31.5	62.0	31.5	69.1
I.B.P. ~ 97°C. (%)	33.6	11.1	44.1	63.5
97 ~ 120°C. (%)	17.4	7.4	12.9	10.8
120 ~ 200°C. (%)	49.0	81.5	43.0	25.7

Table 6. Composition of Produced Gasoline. (Wt. %)

Exp. No.		A—9	A—10	A—11	A—12
React. temp. (°C.)		450	400	500	550
I.B.P. ~ 97°C.	Unsat. hydrocarbons (%)	15	—	3	—
	Arom. ,,	0	—	49	—
	Naph. ,,	34	—	44	—
	Para. ,,	51	—	4	—
	After washing with 99% H_2SO_4 — Aniline pt. (°C.)	58.0	—	40.0	—
	After washing with 99% H_2SO_4 — Sp. gr. (D_{15}^{15})	0.6848	—	0.7262	—
97 ~ 120°C.	Unsat. hydrocarbons (%)	5	—	2	—
	Arom. ,,	17	—	70	—
	Naph. ,,	38	—	28	—
	Para. ,,	40	—	0	—
	After washing with 99% H_2SO_4 — Aniline pt. (°C.)	58.0	—	43.0	—
	After washing with 99% H_2SO_4 — Sp. gr. (D_{15}^{15})	0.7240	—	0.7599	—
120 ~ 200°C.	Unsat. hydrocarbons (%)	1	4	3	—
	Arom. ,,	66	20	85	—
	Naph. ,,	26	32	12	—
	Para. ,,	7	44	0	—
	After washing with 99% H_2SO_4 — Aniline pt. (°C.)	61.0	67.5	54.0	—
	After washing with 99% H_2SO_4 — Sp. gr. (D_{15}^{15})	0.7677	0.7766	0.7877	—

Table 7. Composition of the Fraction above 200°C. (Wt. %)

Exp. No.	A—9	A—10	A—11	A—12
React. temp. (°C.)	450	400	500	550
Unsat. hydrocarbons (%)	0	12	8	—
Arom. ,,	56	16	77	—
Naph. ,,	18	31	0	—
Para. ,,	26	41	15	—
After washing with 99% H_2SO_4 — Aniline pt. (°C.)	72.0	81.5	91.0	—
After washing with 99% H_2SO_4 — Sp. gr. (D_{15}^{15})	0.8284	0.8001	0.8086	—

Table 8. Distribution of Unsaturated Hydrocarbons in the Produced Oil. (Wt. of each fraction = 100%)

Exp. No.	A—9	A—10	A—11	A—12
React. temp. (°C.)	450	400	500	550
I.B.P. ~ 97°C. (%)	15	—	3	—
97 ~ 120°C. (%)	5	—	2	—
120 ~ 200°C.	1	4	3	—
200°C. over (%)	0	12	8	—

Table 9. Distribution of Aromatic Hydrocarbons in the Produced Oil. (Wt. of each fraction = 100%)

Exp. No.	A—9	A—10	A—11	A—12
React. temp. (°C.)	450	400	500	550
I.B.P. ~ 97°C. (%)	0	—	49	—
97 ~ 120°C. (%)	17	—	70	—
120 ~ 200°C. (%)	66	20	85	—
200°C. over (%)	56	16	77	—

Table 10. Distribution of Naphthene Hydrocarbons in the Produced Oil. (Wt. of each fraction = 100%)

Exp. No.	A—9	A—10	A—11	A—12
React. temp. (°C.)	450	400	500	550
I.B.P. ~ 97°C. (%)	34	—	44	—
97 ~ 120°C. (%)	38	—	28	—
120 ~ 200°C. (%)	26	32	12	—
200°C. over (%)	18	31	0	—

Table 11. Distribution of Paraffin Hydrocarbons in the Produced Oil. (Wt. of each fraction = 100%)

Exp. No.	A—9	A—10	A—11	A—12
React. temp. (°C.)	450	400	500	550
I.B.P. ~ 97°C. (%)	51	—	4	—
97 ~ 120°C. (%)	40	—	0	—
120 ~ 200°C. (%)	7	44	0	—
200°C. over (%)	26	41	15	—

Table 12. Produced Gas. (in wt. %)

Exp. No.	A—9	A—10	A—11	A—12
React. temp. (°C.)	450	400	500	550
Vol. of produced gas (l./100 g. sample)	10.78	11.77	9.86	19.77
Sp. gr. of produced gas (g./l.)	0.80	0.78	0.78	0.88
Wt. increase of active charcoal (%)	17.13	0.16	36.00	26.72
Amount of total produced gas (%)	25.75	9.33	43.68	44.15

Table 13. Amount of Produced Methane. (Wt. %)

Exp. No.	A—9	A—10	A—11	A—12
React. temp. (°C.)	450	400	500	550
Amount of methane (%)	6.59	6.41	6.02	11.72
Vol. % of methane in the produced gas	88.10	94.35	94.62	82.99
Vol. of produced methane (l./100g. sample)	9 22	8.97	8.42	16.39

Table 14. Consumption of H_2. (Wt. %)

Exp. No.	A—9	A—10	A—11	A—12
React. temp. (°C.)	450	400	500	550
H_2 consumed (%)	3.52	3.28	3.80	0.77

Table 15. Material Balance.

Exp. No.	A—9	A—10	A—11	A—12
React. temp.	450	400	500	550
Sample (g.)	250	250	250	250
Sample (%)	92.4	92.3	92.3	92.3
Compressed H_2 (g.)	20.4	20.8	20.8	20.8
Compressed H_2 (%)	7.6	7.7	7.7	7.7
Produced oil (g.)	172.0	242.5	109.6	69.4
Produced oil (%)	63.61	89.55	40.48	25.63
Produced gas (g.)	21.4	18.5	17.3	43.6
Produced gas (%)	7.91	6.83	6.39	16.10
Wt. increase of active charcoal (g.)	42.8	0.4	90.0	66.8
Wt. increase of active charcoal (%)	15.83	0.15	33.23	24.67
Unreacted H_2 (g.)	11.6	12.6	11.3	19.1
Unreacted H_2 (%)	4.29	4.65	4.17	7.05
Produced water (g.)	2.1	1.8	2.5	2.4
Produced water (%)	0.78	0.66	0.92	0.89
Loss (%)	7.58	−1.84	14.81	25.66

OBSERVATIONS ON THE RESULTS.

The conditions which govern the hydro-cracking reactions are hydrogen pressure, reaction temperature, reaction time, nature of catalyst and properties of sample. In this series of experiments, only the effect of reaction temperature was observed.

1. The yield of liquid products was highest at 400 deg. C. and lowest at 550 deg. C. But the maximum yield of hydro-cracked gasoline was obtained at 450 deg. C.

Decomposition of sample gas oil occurred only slightly at 400 deg. C. and excessively at 550 deg. C. The optimum temperature for obtaining a good yield of hydro-cracked gasoline was 450 deg. C. under our experimental conditions.

2. The hydro-cracked gasoline mainly consisted of naphthene, paraffin and aromatic hydrocarbons. The unsaturated hydrocarbon content was small in all

cases. The content of aromatics increased rapidly with temperature. On the contrary, the content of naphthenes slowly and that of paraffins rapidly decreased with temperature.

3. At temperatures between 400 deg. C. and 500 deg. C., the hydrogen consumption was almost constant (3~4 wt. % to the sample). But at 550 deg. C. the apparent consumption of hydrogen was very small owing to the hydrogen evolution due to dehydrogenation reactions which occurred predominantly at this temperature.

4. The amount of gas evolution was also almost constant between 400 deg. and 500 deg. C., while it increased considerably at 550 deg. C. The principal component of the evolved gas was naturally methane, which always accompanied a small amount of higher paraffin gases.

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