Catalytic Partial Oxidation of Hydrocarbons at High Temperature*

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Summary: Partial oxidation of hydrocarbons at high temperature has been investigated by use of nickel catalysts. Two types of catalysts containing 5% of NiO were used: one of these catalysts was supported with high alumina carrier (catalyst I) and another was supported with dolomite-alumina carrier (catalyst II.) The hydrocarbons used were paraffins, naphthenes and aromatics. To decide the optimum condition of partial oxidation, the steam reaction and the oxygen reaction were examined by use of C₆ hydrocarbons at first. The amounts of steam which gave good results in steam reaction were in the ratio of steam/feed=1. Oxygen reaction was hardly affected by the amounts of air added. LHSV for hydrocarbons should be less than 1 in both reaction. Catalyst I was more effective than catalyst II and was hardly affected by temperature. The fission of C-H bond was promoted by catalyst I, and the cracking of C-C bond was promoted by catalyst II.

The order of reactivity in paraffins and naphthenes increased with the number of carbon when treated with catalyst II, but decreased with the carbon number when catalyst I was used. The same tendency of reactivity in aromatics was obtained for both catalysts and the order of reactivity increased with the carbon number in the side chain. The tendency of reactivity in oxygen reaction agreed with that of steam reaction. From the results, the oxygen reaction process was assumed as follows: at the initial stage, partial combustion of hydrocarbons took place, and the steam and the carbon dioxide produced at initial stage reached with the fragments of hydrocarbon cracked at the second stage whose reaction was slow.

(The standard free energy change of partial oxidation was calculated and the results of the experiments are discussed.)

Introduction

The researches on production of synthesis gas, hydrogen, and city gas from petroleum have become active recently, and a part of these studies has been applied industrially. The catalytic gasification of petroleum fraction from methane to heavy oil has been investigated in our laboratory¹⁻⁴⁾. The principal reactions of the gasification are classified into the hydrocarbon-steam reaction and hydrocarbon-oxygen reaction. These reactions are finally represented by the following equations;

Steam reaction

Oxygen reaction

Equations (1), (3) are reactions for obtaining synthesis gas, and equation (2) represents the reaction to produce hydrogen. Reactions (1), (2) are remarkably endothermic, while (3) is exothermic. It seems that actual reactions are not simple as shown in (1), (3), and that the reactions which are presented finally by (1), (3) are obtained through complex process. Although the partial oxidation of hydrocarbon has been studied by use of lower hydrocarbons⁵⁻⁸⁾ and explained by Ger-

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Fig. 1 Apparatus

hold,⁹⁾ *et al*, these processes of reactions (1), (2), (3) have not been illustrated sufficiently. Especially, the partial oxidation of liquid hydrocarbons has not been studied fundamentally.

In order to illustrate these points, hydrocarbon-steam reaction and hydrocarbon-oxygen reaction at high temperature have been investigated by use of catalysts; i.e. the optimum conditions of reaction (1), (3) were determined by using C₆ hydrocarbons and then under the condition the partial oxidation of hydrocarbons was examined. From the experimental results, the tendency in reactivity of each series of hydrocarbons and the difference in the selection of catalysts against samples were obtained. Catalytic action and the process of reactions (1), (3) are discussed.

Experiment

The experimental apparatus is shown in Fig. 1. After the preheater (B) and reactor (A) were heated to the desired temperature, hydrocarbons and steam were automatically charged from (C) in the steam reaction. In the case of oxygen reaction, constant ratio of oxygen (or air) to feed was charged by using the (H₃) and (W). The gas produced was accumulated in the gas holder (H₁, H₂). Gaseous products were analyzed by gas chromatography and absorption method (Hempel's apparatus).

The hydrocarbons used in the experiment were paraffins, naphthenes and aromatics as shown in Table 1. Two types of nickel catalysts containing NiO 5% were used. One

Table 1 Hydrocarbons

Series	Hydrocarbons	d_4^{20}	n_D^{20}
Paraffins	<i>n</i> -Hexane	0.6612	1.3802
	<i>n</i> -Heptane	0.6839	1.3876
	<i>i</i> -Octane	0.7019	1.3912
	Cetane	0.8090	1.4590
Naphthenes	Cyclohexane	0.7789	1.4258
	Methyl-Cyclohexane	0.7700	1.4225
	Decaline	0.8993	1.4822
Aromatics	Benzene	0.8783	1.4996
	Toluene	0.8767	1.4949
	Xylene	0.8648	1.4950
	Ethylbenzene	0.8676	1.4948
	<i>i</i> -Propyl-Benzene	0.8632	1.4914
	Dodecyl-Benzene	0.8726	1.4889

of these catalysts was supported with high alumina carrier (catalyst I) and another was supported with dolomite-alumina carrier (catalyst II). These were the typical industrial catalysts which were reported in our previous papers.²⁾ Catalyst I was effective for the reforming of the gaseous hydrocarbons and catalyst II was suitable to reform heavy oil. The results of X-ray refraction method showed that the greater parts of catalyst I consisted of α -alumina. The greater parts of carrier of the catalyst II consisted of periclase and the rest were gelinite, etc . . .

The results of experiments were represented by using the amounts of make gas, the volume ratio of gas produced to theoretical gas yield, and conversion (observed $\text{CO} + \text{H}_2$ /theoretical $\text{CO} + \text{H}_2$). These values were almost in proportion.

Experimental Results

Hydrocarbon-Steam Reaction

The effects of temperature, steam/feeds ratio and LHSV have been studied by using C_6 hydrocarbons to determine the optimum condition in the steam reaction.

(1) C_6 Hydrocarbon-Steam Reaction

Effect of Temperature. Fig. 2 shows the effects of temperature for the amounts of make gas and conversion. The volume of gas produced and conversion increased with temperature. The carbon dioxide and lower hydrocarbons as CH_4 in gaseous products decreased

Fig. 2 Effect of Temperature
Catalyst I, LHSV=1, steam/feeds (cc/cc)=1

with the rise in temperature. The contact temperature in steam reaction should be at least above 800°C.

Effect of Steam/Feed Ratio: The results of benzene-steam reaction are shown in Fig. 3 as an example of the effect by steam/hydrocarbon ratio. In any temperature, the maximum value of conversion was obtained when the steam/feed ratio (cc/cc) was 1, and the amount of gas produced became maximum at this point. CO_2 and H_2 in gaseous products

Fig. 3 Effect of Steam/Feeds Ratio
Catalyst II, LHSV=3, benzene

increased, and CO decreased with the ratio of steam to hydrocarbon. It was known that there was the same tendency in the steam reaction of either C₆ hydrocarbons beside benzene. The optimum value of steam to hydrocarbon agreed with the mol ratio of theoretical equation (1).

Effect of LHSV: The effect of LHSV for hydrocarbon is shown in Fig. 4. The greater the LHSV for feed, the smaller the amount of gas produced and decrease in conversion rate. The carbon balance decreased with the reduction of conversion and the volume of make gas. Carbon dioxide and lower hydrocarbons as CH₄ in gaseous products increased with LHSV. From Fig. 4, it was known that LHSV of hydrocarbon should be less than 1 at least.

(2) Hydrocarbon-Steam Reaction

From the above results, the hydrocarbon-steam reaction has been studied by using the condition as follows, LHSV for feed was set at 1, preheater temperature to 400°C, contact temperature in the range between 800 to 1000°C and the ratio of steam to hydrocarbons in accordance to the mol ratio of equation (1). Fig. 5,6,7 show the volume ratio of make gas/theoretical gas, and composition of gaseous products is represented in Table 2.

The ratio of the gas produced/theoretical gas increased with rise in temperature. The conversion and carbon balance increased in proportion to the ratio of gas produced to theoretical gas. Catalyst I was superior to catalyst

Fig. 4 Effects of LHSV
Catalyst 1, steam/feeds (cc/cc)=1

II. The amounts of carbon dioxide and lower hydrocarbon as methane in gaseous products increased at lower temperature, but decreased at higher temperature. The volume of lower hydrocarbons in make gas was slightly more when catalyst II was used.

The tendency of reactivity in hydrocarbon-steam reaction was as follows; the reactivity

Fig. 5 Effect of Temperature

Fig. 6 Effect of Temperature

of paraffin and naphthene hydrocarbons decreased with the number of carbon or the increment of the complication of structure when treated with catalyst I, and increased when catalyst II was used. However, the same tendency of the reactivity in aromatics was

Fig. 7 Effect of Temperature

obtained for both catalysts and the reactivity increased with carbon number in the side chain.

Hydrocarbon-Oxygen (Air) Reaction

In order to decide the optimum condition for the hydrocarbon-oxygen (air) reaction, the effects of temperature, the volume of air and LHSV were studied by using C_6 hydrocarbons as in the steam reaction.

(1) C_6 Hydrocarbon-Oxygen Reaction

Effects of Temperature: The effect of temperature is shown in Fig. 8. The conversion increased with temperature. The amounts of make gas and carbon balance increased with the conversion. Catalyst I was more effective than catalyst II, and was hardly affected by temperature.

Effect of Air: The danger of explosion and the nitrogen content in gas produced were increased when the large amount of air was used. It has been also reported that the kerosene-air reaction was hardly affected by the amounts of air from 0.7 to 1.71/cc oil.¹⁾ Thus, 30~50% of theoretical volume of air were used for the experiments. The result are shown in Table 3.

The amount of gas produced, conversion, and carbon balance increased slightly with the volume of air added. The same results were obtained when treated under other conditions and no notable change was recognized in oxy-

Table 2 Composition of Gaseous Products
LHSV=1.0, Preheater Temperature 400°C

Hydrocarbons	Catalyst	Temp. (°C)	Composition of Gaseous Products (mol/mol)			
			CO ₂	C _m H _n	CO	H ₂
Hexane	I	800	0.63	1.15	2.26	7.58
		900	0.32	0.96	3.22	8.46
		1000	0.36	1.13	4.22	8.60
	II	800	0.21	2.98	0.12	0.90
		900	0.36	2.65	0.60	2.06
		1000	0.45	2.54	1.05	4.27
Cyclohexane	I	800	0.36	1.10	2.05	6.65
		900	0.61	1.36	3.15	8.21
		1000	0.34	0.68	4.02	8.52
	II	800	0.27	1.82	0.41	1.47
		900	0.83	2.36	0.87	3.16
		1000	0.60	2.13	1.36	3.51
Benzene	I	800	0.45	0.42	1.81	3.92
		900	0.84	0.33	2.67	5.04
		1000	0.32	0.31	2.91	5.27
	II	900	0.46	0.19	0.32	1.56
		1000	0.51	0.27	0.72	2.15

Fig. 8 Effect of Temperature
LHSV 1, air 40% of theoretical value
gen reaction. When 50% of theoretical volume
was used, the explosion took place frequently.
Effect of LHSV: The effect of LHSV is
shown in Fig. 9. The greater the LHSV for

feed, the smaller the amount of gas produced. The conversion and carbon balance decreased with reducing the amount of make gas. The quality of make gas deteriorated with LHSV. LHSV for hydrocarbons should be less than 1 as in steam reaction.

(2) Hydrocarbon-Oxygen Reaction

From the preceding results, the partial air oxidation of hydrocarbons has been investigated by using the following condition; LHSV of feeds was 1, preheater temperature was 400°C, reactor temperature was in the range of 800°C to 950°C and the amount of air added was 40% of the theoretical value.

The effects of temperature are shown in Fig. 10, 11, 12 and the composition of gaseous products are represented in Table 4.

The volume ratio of gas produced to theoretical gas, conversion, and carbon balance increased with temperature. As in the case of steam reaction, the effect of temperature on catalyst I was less than on catalyst II, which was inferior to catalyst I. Carbon dioxide and lower hydrocarbons as methane in gaseous products decreased with rising temperature. The amounts of lower hydrocarbons in make gas

Table 3 Effect of Air added
Temperature 850°C, LHSV=1.0

Hydrocarbons	Catalyst	Air added (%)	Gas produced (cc/cc feed)	Composition of Gaseous Products (mol/mol)				Conversion (%)	Carbon Balance (%)
				CO ₂	C _m H _n	CO	H ₂		
Hexane	I	30	1220	0.17	0.74	1.92	3.72	43.4	59.6
		40	1270	0.11	1.17	2.19	4.00	47.5	67.0
		50	1340	0.22	1.38	2.57	3.67	48.0	83.0
	II	30	1090	0.20	1.75	1.45	2.43	30.2	65.4
		40	1170	0.19	2.08	1.56	3.16	36.3	72.5
		50	1270	0.12	2.32	1.81	4.09	45.4	64.5
Cyclohexane	I	30	1310	0.14	1.04	1.63	3.40	41.9	52.7
		40	1520	0.17	1.14	1.73	3.57	44.1	57.7
		50	1610	0.22	0.82	2.91	3.33	51.9	70.5
	II	30	1120	0.17	1.72	1.11	2.56	30.6	63.5
		40	1230	0.25	1.60	1.53	3.03	38.0	64.6
		50	1430	0.24	1.42	2.14	3.23	44.8	71.6
Benzene	I	30	930	0.28	0.33	1.28	1.78	34.0	41.6
		40	1140	0.21	0.25	1.85	1.43	36.4	68.5
		50	1290	0.36	0.31	2.24	1.87	45.8	56.1
	II	30	590	0.48	0.35	0.75	0.74	16.6	36.8
		40	620	0.75	0.40	0.71	0.60	14.6	38.9
		50	900	0.68	0.30	1.47	0.99	27.4	37.8

Fig. 9 Effect of LHSV

were slightly more when treated with catalyst II.

The difference in tendency of oxygen reactions on both catalysts was as follows; when catalyst I was used, the reactivity of paraffins decreased with the number of carbon, and in

naphthenes cyclohexane, which had the simplest structure, was cracked most easily. When treated with catalyst II, the reactivities of paraffins and naphthenes increased with the carbon number or the increment in complication of structure. However, the same tendency of the reactivity in aromatics was obtained for both catalysts, and the reactivity increased with the carbon number in the side chain.

Discussion

Difference of Catalytic Action

As described in above section, remarkable difference was recognized between the action of both catalysts in partial oxidation of hydrocarbons. In order to illustrate this point, the hydrocarbons were cracked by using catalyst at high temperature. The results are shown in Table 5.

The extent of cracking of paraffins and naphthenes decreased with the increment of complication in structure when treated with catalyst I, and increased when catalyst II was used. The extent of cracking on aromatics increased for both catalysts with carbon number in the side chain. When catalyst I was used, the hydrogen was produced in large quantities and the amount of methane in make gas was little. On the other hand, for cata-

Table 4 Composition of Gaseous Products
 LHSV=1.0, Preheater Temperature 400°C

Hydrocarbons	Catalyst	Temp. (°C)	Composition of Gaseous Products (mol/mol)			
			CO ₂	C _m H _n	CO	H ₂
Hexane	I	800	0.25	1.75	1.97	3.74
		850	0.15	1.53	2.44	3.98
		900	0.24	1.58	2.53	3.90
		950	0.17	1.60	2.70	4.36
	II	800	0.33	2.51	1.07	1.39
		850	0.30	2.34	1.51	2.41
Cyclohexane	I	800	0.19	1.35	2.31	3.82
		850	0.16	1.10	2.38	3.94
		900	0.15	1.26	2.57	4.13
		950	0.09	0.97	2.45	4.34
	II	800	0.37	1.79	1.02	1.51
		850	0.36	1.63	1.74	2.71
Benzene	I	800	0.53	1.76	1.57	1.60
		850	0.27	0.30	1.81	1.66
		900	0.28	0.58	1.95	1.85
		950	0.19	0.55	2.12	1.89
	II	800	0.86	0.30	0.41	0.57
		850	0.48	0.28	1.56	1.35
		900	0.27	0.46	2.04	1.43
		950	0.26	0.79	2.12	1.76

Fig. 10 Effect of Temperature

Fig. 11 Effect of Temperature

lyst II, methane and hydrogen were produced in same proportion. The mol ratio of hydrogen to methane on catalyst I was larger than

1, and on the catalyst II was equal to 1 approximately. Carbon balance on catalyst I was smaller than on catalyst II. From the above

Fig. 12 Effect of Temperature

results, the catalytic action of both catalysts were presumed as follows; catalyst I was more effective for the fission of C-H bond than for the cracking of C-C bond, and catalyst II promoted the fission of C-H bond and also the demethylation which was the cracking of C-C bond in wide sense. The mol ratio of H_2/CH_4 was very small when catalyst I was used for cetane. It seems that this resulted from the character of catalyst I which promoted the cracking of C-C bond with the fission of C-H bond when the straight chain of paraffins was above certain length.

Comparison between Steam Reaction and Oxygen Reaction

The summary of the tendency in partial oxidation of hydrocarbons is represented in Table 6.

In the paraffins and naphthenes, the tendency of the results of reaction of catalyst I was in the reverse order to that of catalyst II. The same tendency in aromatics was obtained for both catalysts. The tendency in steam reaction agreed with that of oxygen reaction. The results of the Table 6 supported the experience as follows; that is, the catalyst on alumina carrier was effective for the reforming of the gaseous hydrocarbons as methane and LPG, and the catalyst on dolomite-alumina carrier was suitable to reform the heavy oil.

The process of the steam reaction of catalyst I was assumed as follows from the composition of reaction products and the experimental results

in the former section; the dehydrogenation occurred remarkably, and the materials as coke and the radicals which were formed by the fission of C-H reacted with steam to produce carbon monoxide and hydrogen. On the catalyst II, the steam reaction was thought to start by cracking of C-C bond from the results in the former section.

It seemed that the agreement of the tendencies in steam reaction and oxygen reaction were due to the following reason; in oxygen reaction the perfect combustion of hydrocarbons took place partially at the first step, and the steam and carbon dioxide produced, reacted with hydrocarbons at the next stage which decided the rate of the whole reaction. It has been also reported that the lower hydrocarbons-oxygen reaction were exothermic at the first step and then it changed into the endothermic reaction in the second step.³⁾ From these reports and the results in methane-oxygen reaction which were obtained by Mungen,¹⁰⁾ the partial air oxidation of hydrocarbons was started by the perfect combustion which produced steam and carbon dioxide as shown in formula (4).

These combustion products reacted with the feed and the cracked fragments (radicals) of hydrocarbons to produce hydrogen and carbon monoxide as represented in (5), (6).

The sum of (4), (5), (6) agreed with (3).

As the rate of combustion reaction (4) was very fast and the rates of reaction (5), (6) were slow in comparison with (4), it is believed that the tendency in partial air oxidation agrees with that of steam reaction.

In paraffins, the results for both catalysts showed the reverse tendency. This resulted from the following reason. As shown in Table 5, the quantity of hydrogen in make gas is large and the carbon balance poor when catalyst I was used. This denotes considerable dehydrogenation took place and increase in the formation of materials as coke; i.e. catalyst I had the specific character to promote the

Table 5 Catalytic Cracking at High Temperature
Temperature 900°C, LHSV for Feed=1.0

Catalyst	Hydrocarbons	Gas produced (cc/cc feed)	Composition of Gas produced (vol %)					Carbon Balance (%)	H ₂ /CH ₄ (mol/mol)
			CO ₂	C _m H _n	CO	CH ₄	H ₂		
Catalyst I	<i>n</i> -Hexane	935	0.1	2.0	4.2	15.8	77.8	22.2	4.9
	<i>n</i> -Heptane	956	0.4	1.4	3.9	16.8	77.2	22.2	4.6
	<i>i</i> -Octane	880	0.2	0.5	3.3	17.9	77.0	18.5	4.3
	Cetane	640	0.2	8.6	4.7	46.5	3.93	36.8	0.9
	Cyclohexane	1050	0.3	5.7	3.9	17.3	72.6	29.7	4.2
	Methyl-cyclohexane	946	0.1	0.6	2.7	17.4	79.1	14.9	4.5
	Decaline	922	0.0	2.3	2.3	18.7	76.7	16.9	4.1
	Toluene	659	0.1	1.2	3.3	12.7	82.4	7.6	6.4
	Xylenes	693	0.4	1.2	2.8	20.0	75.5	12.9	3.8
	Ethylbenzene	694	0.1	1.9	3.5	15.8	78.3	11.7	4.9
	<i>i</i> -Propyl-benzene	706	0.3	2.5	3.1	22.4	71.3	16.6	3.2
	Dodecyl-benzene	884	0.0	1.7	2.5	20.8	74.8	17.4	3.6
Catalyst II	<i>n</i> -Hexane	675	0.2	9.2	2.9	47.2	40.5	46.9	0.9
	<i>n</i> -Heptane	676	0.3	9.2	0.6	44.2	45.5	41.8	1.0
	<i>i</i> -Octane	707	0.0	8.0	3.7	38.3	49.7	39.1	1.3
	Cetane	746	0.0	6.4	1.5	43.5	48.5	35.9	1.1
	Cyclohexane	800	0.2	8.6	5.0	40.1	45.5	42.1	1.1
	Methyl-cyclohexane	705	0.3	8.0	4.2	43.1	44.4	30.1	1.0
	Decaline	681	0.3	4.8	3.3	41.1	50.3	26.0	1.0
	Ethylbenzene	469	0.3	4.0	3.5	37.2	54.9	19.9	1.5
	<i>i</i> -Propyl-benzen	647	0.0	2.5	5.6	38.1	53.5	26.1	1.4
	Dodecyl-benzene	808	0.0	5.5	8.7	40.1	45.6	35.2	1.1

Table 6 Tendency in Partial Oxidation of Hydrocarbons

Type of Reaction	Series	Non Catalytic	Catalyst I	Catalyst II
Steam Reaction	Paraffins		C ₆ >C ₇>C ₁₆	C ₆ <C ₇ <.....<C ₁₆
	Naphthenes		C ₆ >C ₇ >C ₁₀	C ₆ <.....<C ₁₀
	Aromatics		C ₆ <C ₇ <C ₈ <.....	C ₆ <C ₇ <C ₈ <.....
Oxygen Reaction	Paraffins	C ₆ <.....<C ₁₆	C ₆ >C ₇ >.....>C ₁₆	C ₆ <C ₇ <.....
	Naphthenes	C ₆ >C ₇	C ₆ >C ₇	C ₆ <C ₇
	Aromatics	C ₆ <C ₇ <C ₈	C ₆ <C ₇ <C ₈ <.....	C ₆ <C ₇ <C ₈ <.....

fission of C-H bond. Therefore, it is believed that C_mH_n in (5), (6) contained materials which were similar to carbeneous matters dehydrogenated and that this process took place easily when lower hydrocarbons were used. When catalyst II was used, the volume of hydrogen in gas produced was small, and carbon balance and the quantity of lower hydrocarbons were large as shown in Table 5. It seems that this resulted from the character of catalyst II to promote the cracking of C-C bond and that radicals were easily formed on catalyst II. In addition, reaction (5), (6) proceeded more easily when C_mH_n in equation (5), (6) were not hydrocarbons but radicals. Therefore, it was thought that the partial oxidation on catalyst II was carried out advantageously on the long chain hydrocarbons which formed the radicals more easily than lower hydrocarbons, and that the results for both catalysts showed the reverse tendency as above mentioned.

Standard Free Energy Change of Partial Oxidation.

It was very difficult to discuss the partial oxidation of liquid hydrocarbons from the standpoint of kinetics because the reaction products were distributed widely. The presump-

tion for partial oxidation process was attempted by calculating the standard free energy change of reaction. The standard free energy was easily calculated from the specific heat of reactants, the enthalpy and entropy change of the given reaction. However, as the formula of specific heat for hydrocarbons was limited, the value of free energy change were calculated by Thomas' method¹¹⁾ which combined the equation for the free energy of formation of the compounds.

(1) Standard Free Energy of Steam Reaction

The values of standard free energy change (ΔF°) of hydrocarbons-steam reaction are shown in Table 7.¹²⁾

From this table, it was known that the value of $-\Delta F^\circ$ of paraffins were almost equal to that of naphthenes and the possibility of steam reaction increased with temperature, for the $-\Delta F^\circ$ increased with rising temperature. It seems from the data of $-\Delta F^\circ$ of each reaction that the possibility of aromatics-steam reaction was smaller than that of paraffins and naphthenes.

The value of $-\Delta F^\circ$ in paraffins increased with the molecular weight, and the $-\Delta F^\circ$ of branched structure was larger than that of normal structure if the carbon number was equal. These tendencies were similar to the

Table 7 Standard Free Energy of Steam Reaction
 $C_mH_n + mH_2O = mCO + (m + n/2)H_2$

Hydrocarbons	$\Delta F^\circ = a + bT$ cal/mol			$-\Delta F^\circ$ Kcal/carbon atom				
	a	b	$\Delta F^\circ = 0$ (°K)	900°K	1000°K	1100°K	1200°K	1300°K
<i>n</i> -Hexane	242902	-357.98	678.5	13.21	19.18	25.15	31.11	37.08
<i>n</i> -Heptane	279419	-415.31	672.7	13.48	19.41	25.35	31.28	37.21
<i>n</i> -Octane	319646	-477.54	669.3	13.78	19.70	25.71	31.68	37.64
<i>i</i> -Octane	323286	-494.54	653.7	15.23	21.41	27.59	33.77	39.95
<i>n</i> -Cetane	626686	-954.08	656.8	14.50	20.46	26.43	32.39	38.35
Cyclohexane	231702	-347.48	666.8	13.50	19.30	25.09	30.88	36.67
Methyl-cyclohexane	271989	-404.41	672.5	13.14	18.92	24.69	30.47	36.25
Benzene	179092	-252.84	708.3	8.08	12.29	16.51	20.72	24.93
Toluene	220646	-310.36	710.9	8.38	12.82	17.25	21.68	26.12
<i>m</i> -Xylene	260806	-369.34	706.1	8.95	13.57	18.18	22.60	27.42
Ethylbenzen	258640	-369.25	700.4	9.21	13.83	18.44	23.06	27.67
<i>i</i> -Propyl-benzene	300263	-429.87	698.4	9.62	14.40	19.17	23.95	28.70

experimental results in steam reaction. However, the tendency in experiments on catalyst I was in contrast to that in theoretical results. It was thought that this was caused by the difference of catalytic action as described in the former section.

The value of $-\Delta F^\circ$ of cyclohexane was slightly larger than that of methylcyclohexane, and the methyl group in side chain reduced the possibility of naphthene-steam reaction. This tendency agreed with the results on catalyst I, but was in contrast to the results obtained by use of catalyst II.

In aromatics, the possibility of steam reaction increased with carbon number in the side chain, and this tendency agreed with the experimental results. It was thought that the difference between the tendency in aromatics and in naphthenes was caused by the specific character of ring which combined with side chain. However, this point has not been illustrated sufficiently for lack of data in naphthenes.

(2) Standard Free Energy of Oxygen Reaction

It was more difficult than in steam reaction to discuss by means of kinetics the results of oxygen reaction which contained combustion, and thus the assumption for the possibility of

reaction was tried by use of $-\Delta F^\circ$ as shown in preceding section. The standard free energy change of hydrocarbon-oxygen reaction is shown in Table 8.

From Table 8, it was known that the value of $-\Delta F^\circ$ and the possibility of oxygen reaction increased with temperature. The value of $-\Delta F^\circ$ of paraffins increased with the carbon number, and if the number of carbon was equal, $-\Delta F^\circ$ of isoparaffin was larger than that of normal. The methyl group in the side chain of naphthene reduced the value of $-\Delta F^\circ$, and in aromatics, the possibility of oxygen reaction increased with the carbon number in the side chain. The conversion increased with that in $-\Delta F^\circ$ except the paraffins on catalyst I.

The equilibrium constant ($\log Kp$) of steam reaction and oxygen reaction were calculated by equation $\Delta F^\circ = -RT \ln Kp = -4.575 T \log Kp$. The values of $\log Kp$ were very large and thus, it was thought that the partial oxidation proceeded to the right side of reaction (1), (3). The tendency of the $\log Kp$ in steam reaction was contrary to oxygen reaction; $\log Kp$ of the latter decreased and $\log Kp$ of the former increased with temperature.¹²⁾¹³⁾ However, the experimental results conformed little to equilibrium values.

Table 8 Standard Free Energy of Oxygen Reaction
 $C_m H_n + m/2 O_2 = mCO + n/2 H_2$

Hydrocarbons	$\Delta F^\circ = a + bT$ cal/mol		$-\Delta F^\circ$ Kcal/carbon atom				
	a	b	900°K	1000°K	1100°K	1200°K	1300°K
<i>n</i> -Hexane	-110936	-280.34	60.54	65.21	69.89	74.56	79.23
<i>n</i> -Heptane	-133392	-324.73	60.81	65.45	70.09	74.72	79.36
<i>n</i> -Octane	-152138	-374.02	61.09	65.77	70.46	75.12	79.80
<i>i</i> -Octane	-148498	-391.02	62.55	67.44	72.33	77.22	82.10
<i>n</i> -Cetane	-316882	-747.04	61.83	66.50	71.16	75.86	80.50
Cyclohexane	-122136	-269.84	60.83	65.83	69.38	74.32	78.82
Methyl-cyclohexane	-140822	-313.83	60.47	64.95	69.43	73.92	78.40
Benzene	-174746	-175.20	55.40	58.32	61.24	64.16	67.80
Toluene	-192165	-219.78	55.71	58.95	61.99	65.13	68.27
<i>m</i> -xylene	-210978	-265.82	56.28	59.60	62.92	66.25	69.57
Ethylbenzene	-213144	-265.73	56.54	59.86	63.18	66.50	69.82
<i>i</i> -Propyl-benzen	-232678	-315.12	57.37	60.87	64.37	67.87	71.37

Conclusion

The following conclusion has been derived from the above results.

(1) The partial oxidation of hydrocarbons was promoted by using the Nickel catalysts; amount of make gas and conversion were increased with the rise in contact temperature. The catalyst I supported with high alumina carrier was more active than catalyst II supported with dolomite-alumina carrier. The activity of catalyst I was hardly affected by temperature.

(2) In the steam reaction, the optimum ratio of steam to feeds was 1 (cc/cc). The oxygen-hydrocarbon reaction was hardly affected by the amounts of air added.

(3) In either of steam or oxygen reaction, good results were obtained when the LHSV of hydrocarbons were smaller—at least $LHSV < 1$.

(4) Catalyst I promoted the breaking of C-H bond and Catalyst II promoted the fission of C-C bond.

(5) When catalyst I was used, the reactivity of the paraffin and naphthene hydrocarbons decreased with the number of carbon but increased when treated with catalyst II. In the aromatic hydrocarbons, the same tendency was obtained for the both catalysts. These reactivity increased with the carbon number in the side chain.

(6) The tendency of reactivities of hydrocarbons in oxygen-reaction agreed with that in steam reaction. From the results, the reaction process of oxygen reaction was presumed as follows; the combustion took place partially at the first step, and steam and carbon dioxide were produced. At the second stage which was the rate determining step, these steam and carbon dioxide reacted with the fragments of hydrocarbons cracked.

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