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Author(s)	Fujikawa, Masahisa; Kugo, Masao
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Refining of Benzene by Catalytic Cracking

Masahisa FUJIKAWA and Masao KUGO

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Preface

As a method of benzene refining, a catalytic cracking to remove paraffin hydrocarbons in benzene was carried out. The industrial catalytic cracking of paraffin hydrocarbons has been done since many years ago, but the thermal behaviour of hydrocarbons of small amounts contained in benzene apparently have not been studied in detail. In the application of this method the desulphutizing also could be expected.

I. Experimental

The paraffin hydrocarbon in benzene is expected to be almost heptane; the sample such as pure benzene No. 1 used in this experiment also contains a small amount of n-heptane. N-hexane, however, was used as a paraffin hydrocarbon being added to the sample benzene, because as well known the thermal decomposition of n-hexane is more difficult than that of n-heptane. The n-hexane used here of which specific gravity and refractive index are 0.6864 and 1.3863 respectively, contained n-heptane and some others as shown in Fig. 1.

The apparatus is a flow system as in Fig. 2 and the length and diameter of reactor which is packed with catalyst are 1000 and 20 mm, respectively. The reduction of catalyst was carried out in the reactor under hydrogen of

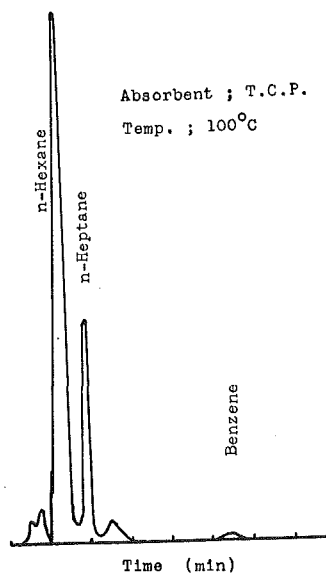


Fig. 1. Gaschromatograph of n-Hexane used

10 atm. The gas which was sampled after the trap cooled with ice and salt, was analysed with the hempel method as well as the gaschromatography.

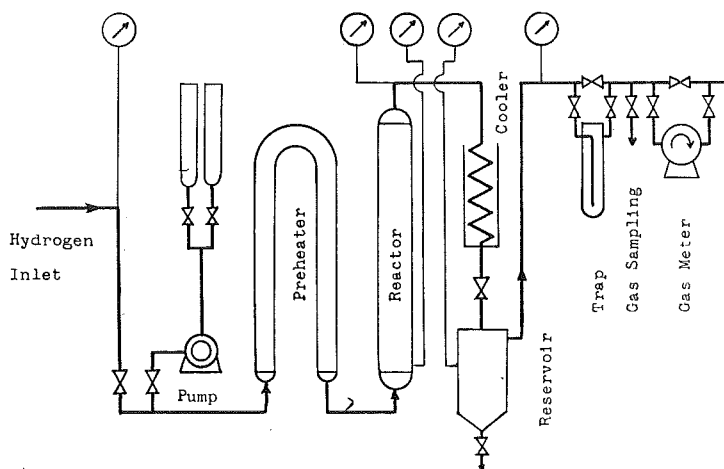


Fig. 2. Experimental Apparatus

II Results

The n-Hexane was alone craked at 500, 575 and 600°C under 10 atm passing through the reactor packed with 41 g of alumina-silica (F.C.C.) catalyst at rate of 35 g/g-hr.

TABLE 1. Results of Cracking of n-Hexane

Temp. (°C)	Liquid Space Velocity	Percentage of Decomposition (%)	V/F' (sec)	Volume of Gas Product (l/hr)	K (l/sec)
550	0.871	22.5	84.8	2.49	0.0031
575	0.848	54.2	84.5	6.74	0.0092
600	0.826	65.6	84.1	11.90	0.0127

V : Reactor Volume Packed with Catalyst

F' : Volume of Oil Vapor at Reaction Temperature

K : Rate Constant

These results are shown in Table 1 as well as Fig. 3¹⁾. In general the decomposition of paraffin hydrocarbons is of a first order reaction; its rate equation is as follows;

$$\ln \frac{100}{100-X} = K\theta \quad (1)$$

where X : percentage of decomposition (%)
 θ : reaction time (sec)
 K : rate coefficient

Then the sample benzene added with 10% of hexane was decomposed at 550 up to 625°C under 5 to 15 atm while changing the amount of catalyst at constant rate of oil feed (SV; 1~3.3 g/g·hr). These results are shown in Table 2.

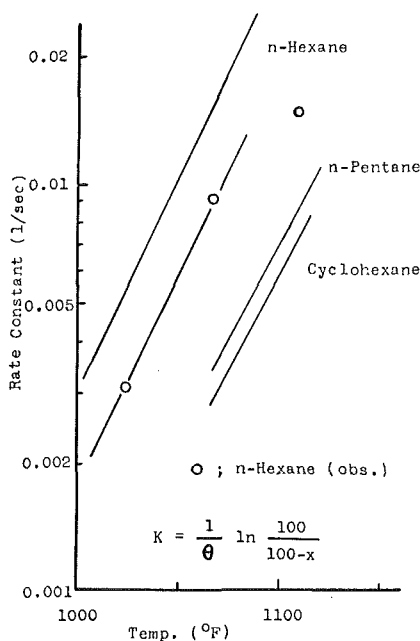


Fig. 3. Rate Constant of Cracking

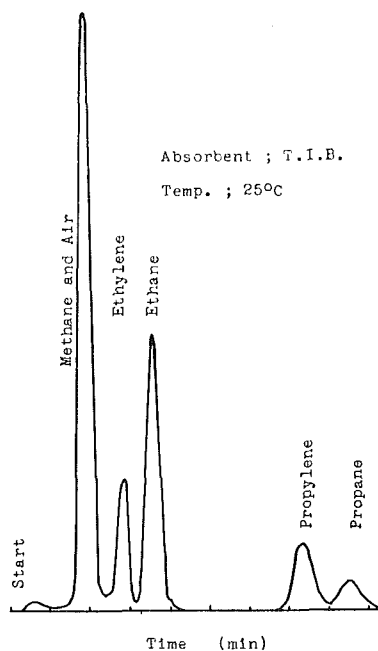


Fig. 4. Gaschromatograph of Cracked Gas

The results obtained by another silicagel catalyst contaminated with chrome (H. F. catalyst) in which the size is 4 to 6 mesh and 6 to 8 mesh, are denoted in Table 3. The activity of this silicagel catalyst was less than that of alumina-silica catalyst. The composition of gas produced when the alumina-silica catalyst was used, is shown in Table 4; the gas is almost hydrogen and methane. As an example of gaschromatograph of cracked gas shows in Fig. 4, the heavy hydrocarbon gas is composed of ethane, ethylene, propane and propylene. The liquid caught in the cold trap was recognized as unreacted benzene by the gaschromatography, except that a small quantity of toluene as well as ethylbenzene are found at the reaction temperature of over 600°C. As shown by

TABLE 2. Results of Catalytic Cracking of Benzene added with 10% n-Hexane

Temp. (°C)	Pressure (kg/cm ²)	Wt. of Catalyst (g)	Liquid Space Velocity	Refractive Index of Liquid Product (20°C)	Specific Gravity of Liquid Product (20°C)	Percentage of Decompo- sition (%)	Rate Constant K
625	5	41.0	1.047	1.4934	0.8706	58.3	0.546
		20.0	2.150	1.4920	0.8682	47.6	
		13.0	3.180	1.4916	0.8675	44.5	
	10	41.0	0.997	1.4966	0.8761	82.5	1.165
		41.0	1.090	1.4957	0.8745	75.2	
		25.0	1.624	1.4959	0.8749	76.8	
	15	30.0	1.470	1.4969	0.8766	84.7	1.700
		20.0	2.122	1.4956	0.8742	74.6	
		25.0	1.650	1.4966	0.8761	82.2	
600	5	13.0	3.180	1.4899	0.8649	31.9	0.409
		20.0	1.852	1.4898	0.8645	31.0	
		25.0	1.630	1.4906	0.8660	37.6	
	10	30.0	1.295	1.4941	0.8720	63.7	0.723
		41.0	1.070	1.4944	0.8722	65.3	
		25.0	1.520	1.4939	0.8713	61.6	
	15	13.0	3.126	1.4902	0.8652	34.0	0.784
		41.0	1.05	1.4944	0.8723	65.7	
		13.0	3.49	1.4939	0.8715	62.1	
575	5	41.0	1.043	1.4887	0.8638	23.0	0.104
		30.0	1.460	1.4888	0.8630	24.2	
		25.0	1.745	1.4884	0.8623	20.8	
	10	41.0	1.070	1.4908	0.8662	39.1	0.273
		25.0	1.770	1.4894	0.8639	28.1	
		20.0	2.243	1.4896	0.8642	29.8	
	15	30.0	1.405	1.4896	0.8643	29.8	0.415
		41.0	1.063	1.4916	0.8676	44.8	
		30.0	1.471	1.4929	0.8697	54.4	
550	5	20.0	2.083	1.4909	0.8630	39.4	0.056
		25.0	1.722	1.4909	0.8630	39.4	
		30.0	1.405	1.4896	0.8643	29.8	
	10	41.0	1.039	1.4880	0.8616	18.2	0.082
		30.0	1.433	1.4882	0.8619	18.8	
		20.0	2.219	1.4876	0.8610	15.0	
	15	41.0	1.070	1.4893	0.8638	27.4	0.169
		25.0	1.532	1.4882	0.8620	19.7	
		20.0	2.222	1.4885	0.8625	21.7	

TABLE 3 (a). Results by Silica-chrome Catalyst (4~6 mesh)

Temp. (°C)	Pressure (kg/cm ²)	Wt. of Catalyst (g).	Liquid Space Velocity	Refractive Index of Liquid Product (20°C)	Specific Gravity of Liquid Product (20°C)	Percentage of Decomposition (%)
600	5	41.0	1.090	1.4922	0.8637	20.15
	10	41.0	1.020	1.4941	0.8680	43.20
	15	41.0	1.129	1.4957	0.8704	59.00
600	5	30.0	1.433	1.4921	0.8644	19.75
	10	30.0	1.353	1.4944	0.8690	43.25
	15	30.0	1.350	1.4945	0.8693	60.30
600	5	20.0	2.030	1.4918	0.8639	17.70
	10	20.0	2.082	1.4950	0.8696	41.50
	15	20.0	1.886	1.4962	0.8721	57.64
600	5	13.0	3.245	1.4918	0.8642	16.60
	10	13.0	3.238	1.4938	0.8673	36.00
	15	13.0	3.380	1.4959	0.8706	47.58
550	10	41.0	1.110	1.4907	0.8623	10.00
	10	30.0	1.500	1.4907	0.8623	9.35
	10	20.0	2.150	1.4906	0.8616	6.20
	10	13.0	3.204	1.4904	0.8611	3.10

TABLE 3 (b). Results by Silica-Chrome Catalyst (6~8 mesh)

Temp. (°C)	Pressure (kg/cm ²)	Wt. of Catalyst (g)	Liquid Space Velocity	Refractive Index of Liquid Product (20°C)	Specific Gravity of Liquid Product (20°C)	Percentage of Decomposition (%)
600	10	41.0	1.070	1.4925	0.8691	45.20
	10	30.0	1.433	1.4924	0.8680	42.30
	10	20.0	2.150	1.4918	0.8679	36.50
	10	10.0	3.312	1.4903	0.8653	23.40

the relation between decomposition percentage and reaction time (W/F , where W is weight of catalyst and F is weight of oil feed g/hr) in Fig. 5, the decomposition percentage is not zero at zero of the reaction time. This result seems to be due to a catalytic action of the reactor wall as well as a purely thermal reaction. To confirm this, some experiments without catalyst were carried out. The results obtained without catalyst are nearly the same with the values extrapolated up to zero of the reaction time in Fig. 5. Hence the

TABLE 4. Analysis of Cracked Gas

Pressure (kg/cm ²)	Temp. (°C)	Liquid Space Velocity	Hydrogen (%)	Methane (%)	Heavy Hydro- carbon Gas (%)
5	625	1.395	42.20	49.22	8.58
	600	1.414	47.00	43.90	9.10
	625	3.260	48.40	44.00	7.60
	600	3.175	50.40	38.00	11.60
	625	1.090	48.73	46.00	5.27
10	625	1.519	55.75	37.40	6.85
	575	1.405	47.98	40.20	11.82
	600	3.126	25.18	58.20	16.62
	625	0.997	24.20	64.30	11.50
	600	1.070	25.12	58.10	16.78
15	625	3.195	32.60	59.20	8.20
	600	3.490	34.47	55.80	14.73
	625	1.650	35.58	61.30	3.12
	575	3.540	30.79	53.41	15.80

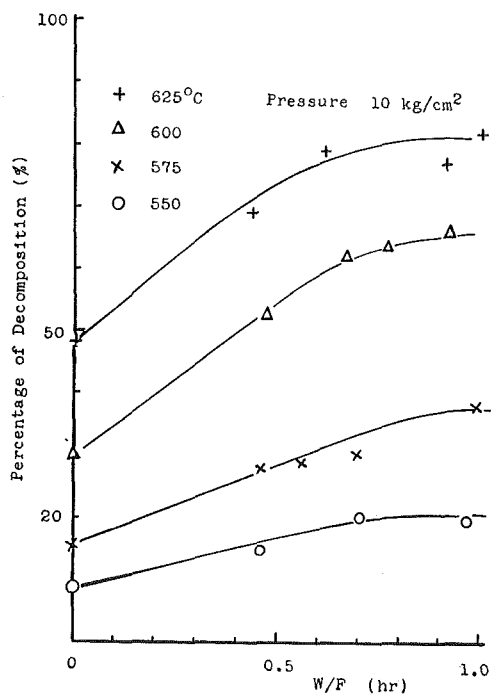


Fig. 5. Percentage of Decomposition vs. Reaction Time

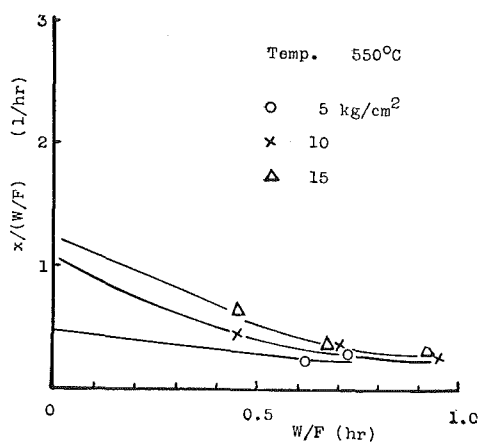


Fig. 6 (a). Rate vs. Reaction Time

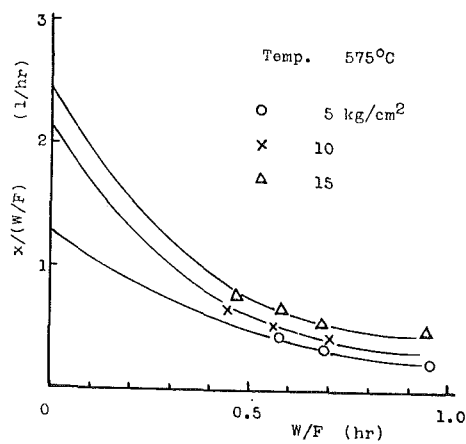


Fig. 6 (b). Rate vs. Reaction Time

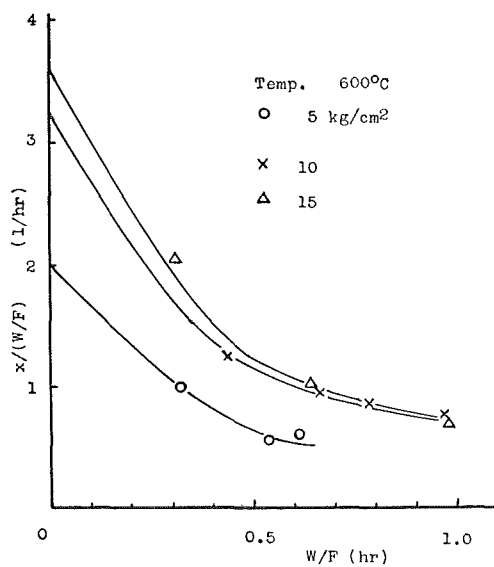


Fig. 6 (c). Rate vs. Reaction Time

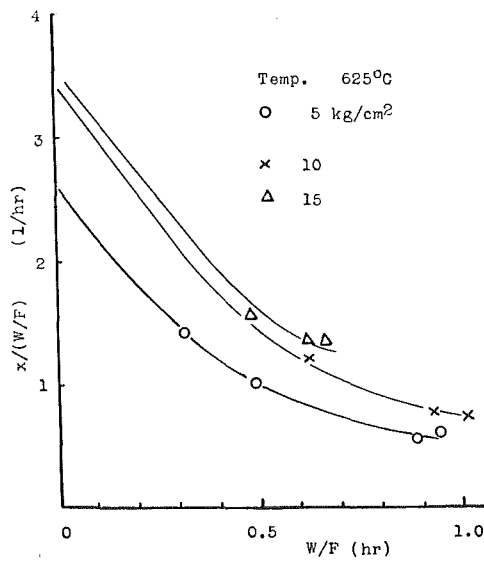


Fig. 6 (d). Rate vs. Reaction Time

difference between the values observed and those at zero of W/F was used to analyse the mechanism of reaction.

To decide the rate determining step of the reaction, it is one of the necessary way to obtain the relation between the pressure and the initial rate of reaction (r_0) obtained by the value of $X/(W/F)$ at zero of (W/F) as in Fig. 6. According to the results shown in Fig. 7 the rate determining step of this reaction is considered to be of surface reaction controlling of first-order reaction²⁾.

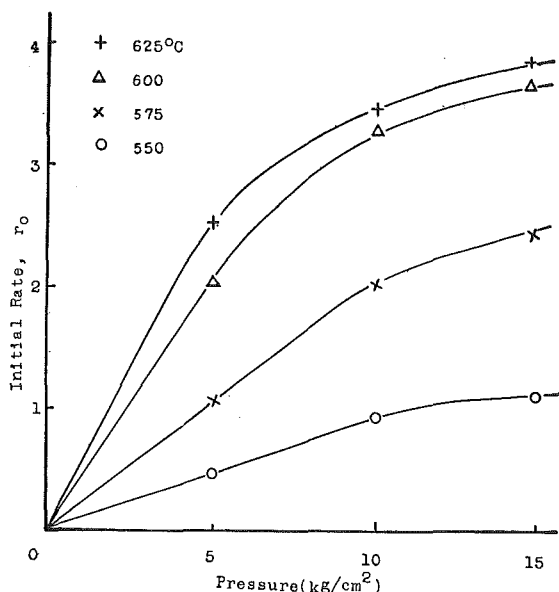


Fig. 7. Initial Rate vs. Pressure

The percentage of undecomposition which was calculated based upon the residual concentration in case of non catalyst as the initial concentration has a straight-line relation in semi-log scale to the reaction time as in Fig. 8. The rate constant could be calculated by the slope of line as denoted in Table 2; the activation energy calculated was 42 kcal/mol.

TABLE 5. Results by Cracking of Benzene added with 2% n-Hexane

Pressure (kg/cm ²)	10	10	10	10	10	10	10	10
Temp. °C	625	600	625	600	625	600	625	600
Reaction Time	0.915	0.915	0.705	0.690	0.462	0.440	0.315	0.315
Percentage of Decomposition	82.80	85.42	98.00	63.40	98.00	68.45	66.05	36.70

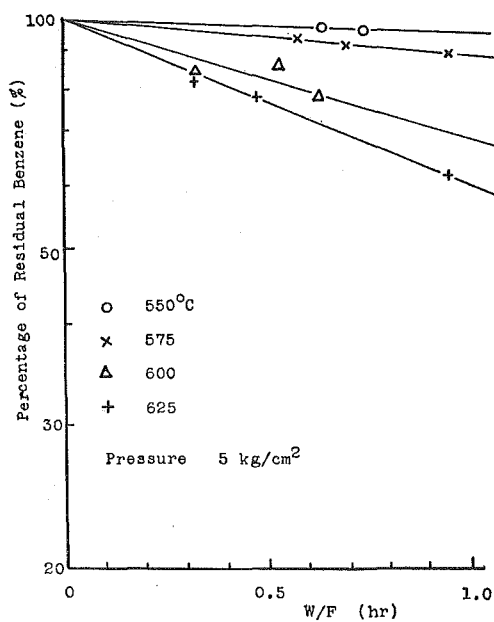


Fig. 8 (a). Percentage of Residual Benzene

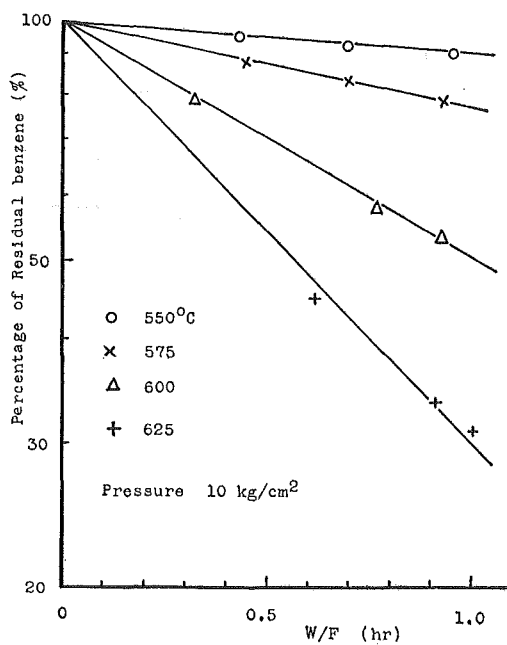


Fig. 8 (b). Percentage of Residual Benzene vs. Reaction Time

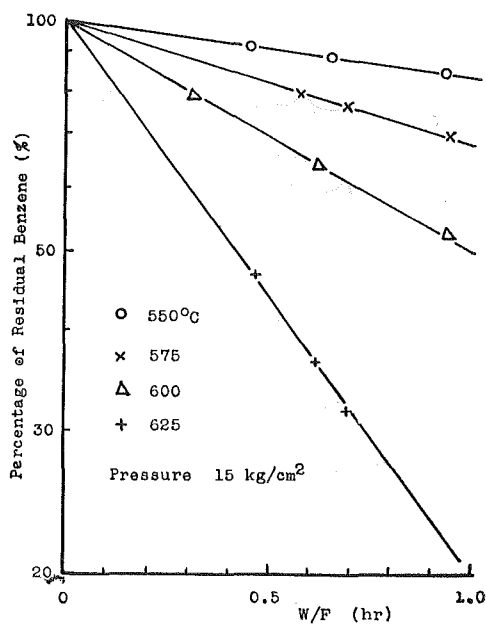


Fig. 8 (c). Percentage of Residual Benzene vs. Reaction Time

Besides owing to the line being straight in Fig. 8, the back mixing in the reactor is considered not to have occurred. In Table 5 there are the results obtained by the sample added with 2% of n-hexane.

An example of the gaschromatograph of benzene produced are illustrated in Fig. 9, where n-heptane contained in the sample benzene was almost decomposed to produce benzene of 99.8%. The calculations mentioned above are based upon the rate of liquid feed (F), but the reaction is of vapor phase. Therefore the values calculated based on the vapor volume in the reactor

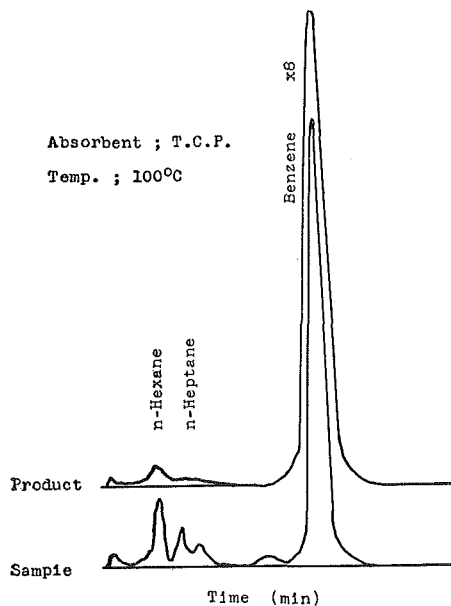


Fig. 9. Gaschromatographs of Sample added with 2% n-Hexane and Product

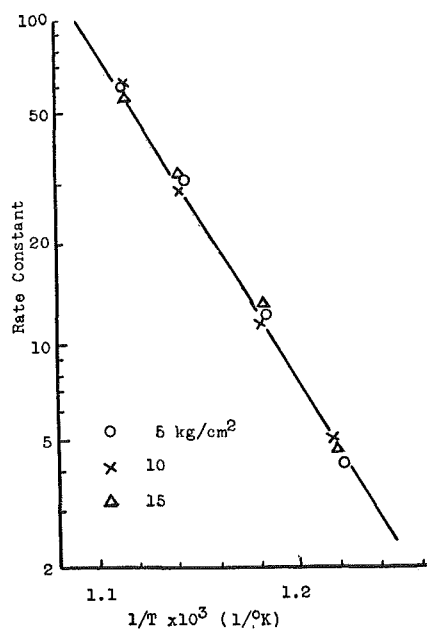


Fig. 10. Rate Constant vs. Reaction Temp. Calculated as Vapor in Reactor

estimated by applying the compressibility of benzene vapor are shown in Fig. 10 where no effect of working pressure is observed; there is only one line on which all points are situated.

Experiments under the pressure of hydrogen, were also carried out expecting to prolong the catalyst life due to the decreasing of carbon deposit on catalyst, and to desulphurize (Table 6).

As a method of analysing sulphur the lamp method was used where to prevent soot formation the heating of a sample on a water bath and the passing of primary air through the sample oil were practised.

TABLE 6. Results obtained by Cracking under Pressure of Hydrogen

Temp. (°C)	Reaction Time (hr)	Volume of Hydrogen (l/hr)	Percentage of Decomposition (%)	Hydrogen /Sample Oil (mol ratio)	Rate Constant
550	0.944	32.0	44.5	2.62	0.10
	0.675	28.4	27.5	2.33	
	0.500	26.9	32.1	2.25	
575	0.671	34.5	43.5	2.82	0.26
	0.529	26.9	47.5	2.25	
	0.322	32.3	34.3	2.65	
600	0.650	38.2	61.8	3.12	0.50
	0.480	30.6	56.8	2.51	
	0.322	28.4	53.8	2.33	
625	0.714	38.1	88.6	3.10	1.07
	0.500	33.0	82.4	2.71	
	0.300	30.6	65.2	2.51	

TABLE 7. Desulphurizing Results

	Total Sulphur (%)	Desulphurizing (%)
Sample Benzene	0.012	—
Cracked Benzene under 5 atm	0.0069	42.5
10 atm	0.0061	49.0
15 atm	0.0059	52.6

TABLE 8. Carbon Deposit on Catalyst

	Wt. of Feeded Oil (g)	Wt. of Catalyst (g)	Wt. of Carbon Deposit (g)
Cracking under no Hydrogen	511	41.0	6.0
	498	30.0	5.5
	477	20.0	5.0
	581	13.0	5.0
Cracking under Pressure of Hydrogen	600	41.0	0.7
	410	30.0	0.2
	540	20.0	0.5
	440	13.0	0.3

(Pressure; 15 kg/cm², Temp.; 550~625°C)

The result of desulphurization are denoted in Table 7 where 50% of sulphur contained in sample benzene are removed under 15 atm of hydrogen.

As shown in Table 8, the carbon deposit on the catalyst also decreases as much as one tenth to one twentieth of that in case of no hydrogen.

It could be concluded by means of no difference of the rate constant and of the activation energy such as 48 kcal/mol that there is no difference of the reaction kinetics between the reactions with or without the pressure of hydrogen.

Summary

As a process to refine the benzene, the catalytic cracking of benzene added with n-hexane was carried out on the catalysts such as alumina-silica (F. C. C.) as well as silica-chrome (H. F.) to remove the paraffin hydrocarbons contained in benzene as a most impurity.

The results obtained are as follows;

1. The decomposition percentage of paraffin hydrocarbons contained in benzen is 82 to 85 on the silica-alumina catalyst at 625°C and 1~1.6 of S, V (as liquid) under 10~15 atm; this percentage is higher than that of silicagel catalyst such as 65.

2. The rate determining step of this reaction is considered as of surface reaction controlling of the first-order. There is no difference of reaction kinetics between both reactions with and without the pressure of hydrogen.

3. The activation energy based upon the liquid feed was 42 kcal/mol and that obtained as the vapor calculated by applying the compressibility of benzene vapor was 48 kcal/mol, where the effect of reaction pressure on the rate constant diminished so that the values of rate constant of all pressures were on the same line.

4. By the application of the pressure of hydrogen the deposit of carbon on the catalyst decreased as much as one tenth to one twentieth of those under no hydrogen, and the desulphurizing also occurred so remarkably as 50% of total sulphur in pure benzene No. 1.

5. The gaseous products were almost hydrogen and methane with the small quantities of ethane, ethylene, propane and propylene. When the reaction temperature was over 600°C, there was a little amount of toluene as well as ethylbenzene in the liquid product.

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- 1) Kisemo Hayashi: "The Chemistry", **13**, No. 5, 16 (1958).
- 2) O. A. Hougen: "Reaction Kinetics in Chemical Engineering", Chem. Eng. Prog., Monog. Series, No. 1, 42 (1953); Z. Elektrochem., **57**, 481 (1953).