

RESTRICTED

ENCLOSURE (B)

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THE THERMAL CRACKING OF PHENOL
UNDER HIGH PRESSURE HYDROGEN

Reference NavTechJap Document No. ND. 26-0008.6 ATIS No. 4579

by

NAVAL ENGINEER
T. OGAWA

Research Period: 1928-1929

Translation Prepared by Chem. Eng. Lt. Cndr. K. MITSUI
and Reviewed with him by the U. S. Naval Technical Mission to Japan.

December 1945

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SUMMARY

Phenol was heated to 450-500°C under high pressure of hydrogen, and a 20-60% yield of benzene was obtained.

The conversion of phenol to benzene was proved to be a simple dehydration reaction which was prompted by increasing temperature and reaction time.

I. INTRODUCTION

This investigation of the thermal cracking of phenol, in the presence of high pressure hydrogen, was related to the utilization of high and low-temperature tars as paste oils; in the hydrogenation of coal, particularly to determine the necessity for specifications on tarry acids and asphaltenes contained in such tars.

Up to this time, many studies had been made on the thermal cracking or hydrogenation of phenol in the presence of various catalysts, but little work had been done on the conversion in the presence of high pressure hydrogen in the absence of catalysts.

Therefore this investigation was particularly concerned with conversion of phenol under the latter conditions.

The key research personnel working on the project were:

Naval Eng. T. OGAWA
Naval Assist. Eng. I. TAKAHASHI

II. DETAILED DESCRIPTIONA. Preparation of Sample

Commercial phenol was heated 2-3 hours with lead oxide, and distilled to yield a pure material with boiling point, 180°C, and melting point, 41°C.

In these experiments, 100 grams of the sample were put into a 2 liter rotating-type autoclave, and the air was displaced by hydrogen. Hydrogen pressure was increased to 100 atmospheres and the autoclave was heated to the desired reaction temperature.

B. Experiment I

No change of pressure was observed after the sample was heated 2 hours at a temperature of 475°C, and according to the analysis, nothing but hydrogen was found in the gas in the autoclave after the reaction.

The total liquid product (96.2gm) was fractionated into the following out:

Water	3.0 gm
75-83°C Fraction	7.6 gm
160-185°C Fraction	79.0 gm

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Only a trace of residue over 200°C was obtained. No crystalline materials were present in this residue. The 75-85°C cut was redistilled, and the physical properties of each fraction determined, with the following results shown in Table I(B)1.

Fraction 2 (in Table I(B)1) was treated with a 50-50 mixed acid (H₂SO₄ and HNO₃). Examination of the physical constants of the nitrated product showed that it was practically pure nitrobenzene. It was, therefore, concluded that Fraction 2 was chiefly composed of benzene.

Fraction 1 was investigated by the same method and it was found that it consisted largely of benzene and a small amount of lower boiling compounds.

A large part of the 160-185°C reaction product was composed of crystals with 40°C mp., insoluble in NaOH solution, and which was proved to be phenol by the color reaction with FeCl₃.

C. Experiment II

When the autoclave was heated three hours at 500°C, the pressure decreased slightly, the difference of the pressure before and after reaction amounting to 10 atmospheres (S.T.P.).

The gas remaining in the autoclave after reaction contained 95.7% hydrogen and 4.3% (n=1.2) saturated hydrocarbons. From these results, the quantity of hydrogen converted into reaction product was calculated to be 1.2 mol percent of the original H₂, and that, converted into gaseous hydrocarbons was 0.45 mol percent. The liquid product (84 gm) was fractionated as follows:

50-160°C Fraction	39.3 gm
160-190°C Fraction	34.9 gm
Residue	0.4 gm
Water	8.2 gm

The 50-160°C fraction was redistilled and the specific gravity and the refractive index of each cut was measured as shown in Table II(B)1.

By physical constants, it was concluded that fraction 1 (in Table II(B)1) was chiefly composed of benzene, but, to make sure, 2cc of this cut were treated with 10% fuming sulphuric acid and a residue of 0.85cc was obtained. The physical properties of this residue, d_4^{20} of 0.754 and n_D^{20} of 1.414, were similar to cyclopentane or methyl-cyclopentane.

Fraction 2 was confirmed to be largely benzene by converting it to nitrobenzene.

The 160-190°C fraction was also treated by the methods of the previous experiment and it was found to be mainly unchanged phenol.

D. Experiment III

The autoclave was heated for five hours at 500°C, and the decrease of pressure amounted to 14 atmospheres. The gas remaining in the autoclave after the reaction, consisted of 94.0% hydrogen and 6.0% (n=1.2) saturated hydrocarbons. From these results, the quantity of converted hydrogen into reaction products was calculated to be 1.8 mol percent of original hydrogen, and that, converted into gaseous hydrocarbons was 0.6 mol percent. The liquid product (86 gm) was fractionated into the following cuts:

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65-85°C Fraction	43.9 gm
85-179°C Fraction	1.5 gm
179-195°C Fraction	26.6 gm
Residue	Trace
Water	9.8

The 65-85°C fraction was redistilled and the specific gravity and refractive index of each fraction were measured as shown in Table III(B)1.

Fraction 1 (1.500) was treated with fuming sulphuric acid and 0.9cc of residue was obtained with d_4^{15} of 0.764 and n_D^{15} of 1.417. By comparison with previous results, it was concluded that fraction 2 was mainly benzene. Similarly, it was concluded that the 179-195°C fraction was phenol.

III. CONCLUSIONS

The results of these experiments are summarized in Table IV(B)1.

When phenol was heated two hours at 475°C with high pressure hydrogen, 20% was dissociated. Since no compounds such as diphenyl, diphenyl-ether were found in the reaction products, the reaction may be carried out according to the following equation:



This dehydration proceeded three times as fast at 500°C, and gaseous saturated hydrocarbons were produced although the quantity was small.

The yield of benzene was higher when the time of reaction was longer, and it is clear from the analysis of the reaction products that benzene was chiefly obtained by the above reaction.

The thermal conversion of phenol to benzene under the normal pressure has been explained as due to phenol being first changed to ether, and then dissociating to phenol and benzene. But in this case, under high pressure of hydrogen, the reaction mechanism was probably only a simple dehydration reaction.

In the experiment carried out at 100 atmospheres of hydrogen pressure, and 500°C, a small amount of compounds with properties corresponding to cyclohexane and methyl cyclopentene, was obtained. This result showed that cracking and hydrogenation of the benzene ring occurred under high pressure and temperature conditions. The production of methane in the reaction also proved evidence that the before-mentioned reaction took place.

Table I(B)1
PHYSICAL PROPERTIES OF 75°C-83°C FRACTION

Fraction	B.P.(°C)	Yield(gm)	Sp. Gravity(25°/4°C)	Refractive Index(n_D^{25})
1	76-79	2.0	0.8427	1.4713
2	79-81	4.5	0.8504	1.4892
3	Residue	0.5	-	-

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Table II(B)1
PHYSICAL PROPERTIES OF 50°C-160°C FRACTION

Fraction	B.P.(°C)	Yield(gm)	Specific Gravity	Refractive Index(n_D^{15})
1	58-75	2.0	0.8117 (15°/4°C)	1.4596
2	75-85	30.7	0.8556 (25°/4°C)	1.4860
3	85-180	0.4	-	-

Table III(B)1
PHYSICAL PROPERTIES OF 65°C-85°C FRACTION

Fraction	B.P.(°C)	Yield(gm)	Specific Gravity	Refractive Index
1	65-75	1.6	0.7984 (15°/4°C)	1.4450 (n_D^{15})
2	75-85	40.0	0.8640 (25°/4°C)	1.4902 (n_D^{25})

Table IV(B)1
THERMOCRACKING OF PHENOL

Exp. No.	Experiment Condition*			React. Prod. (mol/mol phenol)				
	Temp. (°C)	Time (hr)	Pressure Drop (atmospheres)	H ₂ Absorption (mol %)	CH ₄	H ₂ O	C ₆ H ₆	C ₆ H ₅ OH
1	475	2	-	-	-	0.15	0.1	0.8
2	500	3	10	1.2	0.5	0.4	0.4	0.4
3	500	5	14	1.8	0.6	0.6	0.5	0.3

*For all experiments, 100 gm samples and an initial pressure of 100 atmospheres were used.