ENCLOSURE (B) 12

# STUDIES ON TAR FOR PASTE

by

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## SUMMARY

Partially hydrogenated polycyclic compounds, such as tetralin, were tested and found to be suitable components for coal hydrogenation past oils.

## I. INTRODUCTION

In experimental work, coal is usually hydrogenated in an autoclave by heating coal powder with a catalyst under high pressure of hydrogen. However, in industrial operations, a coal paste is employed in order to promote the hydrogenation action and to facilitate handling. The present experiments, therefore, were undertaken to test the relative effectiveness of several compounds as paste oils in coal hydrogenation.

## II. DETAILED DESCRIPTION

The compounds used as paste oils in these experiments were tetralin, decalin, naphthalene, and cyclohexane.

These compounds, except naphthalene, were prepared from naphthalene and benzene by hydrogenation.

Oyama coal of the following properties was used:

| | |
|---|---|
| Water | 5.5 % |
| Ash | 7.0 % |
| Volatile Matter | 41.1 % |
| Fixed Carbon | 46.4 % |
| C | 73.2 % |
| H | 5.7 % |
| O | 12.0 % |
| N | 1.2 % |
| S | 0.7% |
| Water | 5.5 % |
| Ash | 7.0 % |
| Resin | 3.4 % |
| Coal Substance | 80.5 % |
| Vegetable Matter | 3.6 % |

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A 625 cc autoclave was used in these experiments, and the following reaction conditions are listed below. $ZnCl_2$ was used as a catalyst (3-5 % by wt. of coal).

Exp. (I) 50 grams of the coal were heated at 480°C for 2 hours under 60 atmospheres of nitrogen.

Exp. (II) A mixture of 50 grams of the coal and 50 grams of the solvent was treated at 480°C for 2 hours under 60 atmospheres of nitrogen.

Exp. (III) A mixture of 50 grams of the coal and 50 grams of the solvent was heated at 480°C for 3 hours under 92 atmospheres of hydrogen.

Exp. (IV) 50 grams of tetralin were heated at 480°C for 2 hours under 60 atmospheres of hydrogen.

After cooling the reaction vessel, the volume and composition of the gas, and the solubility of the reaction product in benzene was determined. The results of the experiments are shown in Table I(B)12.

The benzene soluble substance in the hydrogenated coal, when tetralin was used as a solvent, was distilled under 3.3mm of pressure to 300°C. The residual pitch had the following analysis:

| | |
|---|---|
| C | 90.4 % |
| H | 6.7 % |
| S | 0.1 % |
| N | 2.0 % |
| O (by diff.) | 0.8 % |
| Ash | 1.3 % |
| Volatile Matter | 59.9 % |
| Fixed Carbon | 38.2 % |

50 grams of the pitch were hydrogenated in an autoclave at 450°C for 3 hours under 92 atmospheres hydrogen with and without a catalyst. The reaction products were treated in the same manner as in the previous experiments, and the results are shown in Table II(B)12.

The pitch in the coal hydrogenation products was easily hydrogenated without catalyst.

## III. CONCLUSIONS

Under the experimental conditions, coal was appreciably soluble in tetralin, and its solubility decreased in order of decalin, cyclohexane and naphthalene. When coal was hydrogenated with these compounds, under high temperature and high pressure of hydrogen, the yield of hydrogenated liquid from the coal paralleled the solubility in these solvents. The presence of partially hydrogenated polycylic compounds, such as tetralin, in paste oil would have a beneficial effect on the hydrogenation of coal.

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Table I(B)12
AUTOCLAVE TESTS OF VARIOUS PASTE OIL COMPONENTS

| Exp. No. | Solvent | Pressure Increase (atm) | Gas Used | Produced Gas Composition | | | | Benzene Solubility. (Wt.% of original Oil) |
|---|---|---|---|---|---|---|---|---|
| | | | | $CO_2+CO$ | $H_2$ | $C_nH_{2n+2}$ | $N_2$ | |
| I | None | 7 | $N_2$ | 3.6 | 0.6 | 8.0 | 87.8 | |
| | Naphthalene | 8 | N | 3.2 | 1.9 | 0.3 | 94.6 | 22 |
| | Tetralin | 12 | N | 2.0 | 0.1 | 0.9 | 94.1 | 48 |
| II | Decalin | 17 | N | 2.0 | 1.3 | 34.6 | 61.8 | 31 |
| | Cyclohexane | 21 | N | 2.4 | 1.9 | 31.3 | 64.4 | 24 |
| | | | | | | | | Liquefied* wt. % |
| III | Naphthalene | -40 | $H_2$ | 5.7 | 61.2 | 32.1 | | 64.2 |
| | Tetralin | -29 | H | 2.1 | 74.5 | 20.7 | | 83.3 |
| | Decalin | -48 | H | 3.0 | 55.0 | 39.6 | | 73.5 |
| | Cyclohexane | -36 | H | 1.5 | 73.1 | 19.2 | | 67.2 |
| IV | Tetralin (alone) | -13 | H | | 83.3 | 16.7 | | |

*Liquefied Wt. % = $\frac{\text{Pure coal-(benzene insoluble + gas from pure coal)}}{\text{Pure Coal}}$

Table II(B)12
HYDROGENATION OF PITCH

| Catalyst | Pressure Drop. (atm) | Gas Composition | | | Benzene Insoluble (gm) | Liquefied (wt. %) |
|---|---|---|---|---|---|---|
| | | $CO_2+CO$ | $H_2$ | $C_nH_{2n+2}$ | | |
| None | 31 | 0.6 | 75.9 | 18.7 | 5.5 | 75.8 |
| Ni | 34 | 0.5 | 71.0 | 26.6 | 3.0 | 75.5 |
| $Fe_2O_3$ | 33 | 0.4 | 78.0 | 18.8 | 7.0 | 73.0 |