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# STUDIES ON SHALY COAL TAR

by

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SUMMARY

A study was made of the suitability of the distillation products of shaly coal tar for use as boiler fuels. The distillate boiling between 200°C and 350°C is suitable for this purpose. The yield of this product is about 52.9% (by weight) and the physical properties are as follows:

| | |
|---|---|
| Sp. gr. (25/4) | 0.9813 |
| Flash point | 34.3°C |
| Freezing point | 7°C |
| Viscocity at 30°C, sec. (Redwood No.1) | 64.3 |

In this work some interesting facts were discovered Unexpected boiling occurs violently at 346°C, distillation temperature, and the phenomenon is due to the alkali-soluble matter. Also when the distillate of the tar is mixed with oil, such as petroleum, shale oil, and soya bean oil, a deposit will be seen. Such a deposit is due to olefine hydrocarbons, mainly di-olefines. Acid materials tend to prevent this deposition.

## I. INTRODUCTION

Studies on the carbonization of shaly coal were underway at this station, and it was desired to utilize the tarry product formed during this process.

This work was undertaken in an attempt to find a product which would be suitable for use as a boiler fuel. A fuel having a freezing point below (+) 15°C and forming no deposits when mixed with other fuels was desired.

The project was started in January, 1945 and was not completed. The key personnel that worked on project were Chem. Eng. Lt. Cmdr. M. KURAMOTO and Chem. Eng. Lt. F. HOSINO.

## II. DETAILED DESCRIPTION

### A. Test Apparatus

The test apparatus for determining the decomposition of tar is shown in Fig. 1(B)21

### B. Test Procedure

About 315 grams of shaly coal tar samples were fractionated and the temperatures of the oil and the vapor were observed.

At higher temperatures, gases were evolved and the gas volume was measured. The determination of paraffin was carried out by Holde's Method.

For observation of deposits which occurred by mixing with other fuels, the boiler fuel from this tar was mixed with others in various ratios and kept standing in the open air for 13 days. Upon inclining the mixture, a deposit could be seen at the bottom of the vessel.

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C. Experimental Results

When the shaly coal was dry-distilled, crude tar was obtained with a 2 to 4% yield, based on charging stock. The differences of yield were due to variation in the amount of ash in shaly coal. The crude tar has the following properties:

| | |
|---|---|
| Sp. gr. (20/20) ..... | 1.136 |
| Water | 6.0 |
| Solid matter included | 1.35 % |
| 10% NaOH soluble | 32.5 % |
| Ash | 0.19 % |
| Flash point | 99.0°C |
| Freezing point | 11.0°C |
| Viscocity at 50°C (sec.) (Redwood No. 1) | 124 |

Decomposition temperature is determined by means of measuring the gas volume evolved during distillation. These data are shown in Table I(B)21 and Figure 2(B)21.

The decomposition temperature is about 240°C, and the amount of gas evolved increases with increasing temperature. It is interesting that an unexpected boiling occurs at 346°C, distillation temperature. Therefore, it is necessary to distill in vacuo in order to prevent decomposition, and to keep the distillation below 340°C, for the purpose of safety. Such unexpected boiling is due to the alkali-soluble matter. This is known because in the distillation of tarry acid, the same phenomenon is observed, but does not occur if the oil has had sufficient alkali washing.

An investigation was made of the resulting freezing point and deposition which occurred when mixed with other fuels such as petroleum, soya bean oil, and shale oil.

Crude shaly coal tar was distilled and 10°C fractionations over 200°C were obtained. For each fraction, we determined the above properties. The results are recorded in Table II(B)21.

Paraffin waxes which have the most effect on freezing point begin to appear in the 250° to 260°C fraction, and the amount increases with increasing temperature. Therefore, to remove the paraffin waxes commercially, distillation must be carried out in 2 steps; the first step is 200°C to 270°C and the second step 270° to 340°C. Acidic materials, 10% NaOH soluble, are, for the most part, included in the fraction below 270°C.

Several boiler fuels were prepared and their properties are given in Table III(B)21.

If the acidic material is removed, the freezing point will be raised. For example, in the case of alkali-washed oil, the freezing point is + 25°C and the freezing point of untreated oil is +7°C.

Results of mixing the 200°C - 340°C untreated distillation products with other oils are tabulated in Table IV (B)21.

Since no deposits were observed when the oil had been washed with 80% $H_2SO_4$, and since alkali washing did not materially effect the formation of deposit, it can be concluded that deposition is due to the presence

of olefines in the oil.

Thus, to obtain as much boiler fuel as possible, it is necessary to distill the tar, and the boiling range of 200°C to 340°C is suitable.

The prepared boiler fuel has the following properties:

| | |
|---|---|
| Yield | 52.9% |
| Sp. gr. (25/4) | 0.9813 |
| Red. No. | 1 |
| Vis. at 30°C, sec. | 64.3 |
| Flash point | 34.3°C |
| Freezing point | 7°C |
| Ash point | 0.0°C |
| 10% NaOH-Soluble | 32.0% |

D. Summary of Data

A tar-distiller must be concerned with distillation of tar for the preparation of boiler fuel, and the distillate between 200°C and 340°C should be used for this purpose. The yield is about 52.5%.

In regard to the distribution of paraffin waxes and acidic matter, paraffin waxes begin to appear in the 250°C to 260°C fraction and the amount increases with increasing temperature. However, acidic matter is for the most part included in the lower fractions.

At 346°C distillation temperature, an unexpected boiling occurs which is thought to be due to the alkali-soluble material.

A deposit, which is thought to be due to olefines, and mainly di-olefine hydrocarbons, occurs when the oil from tar is mixed with other fuels such as petroleum, shale oil, or soya bean oil. This deposit may be prevented by treating the distilled oil with 10% $H_2SO_4$.

## III. CONCLUSIONS

As a result of this experiment, the decomposition temperature of shaly coal tar was determined, the distribution of paraffin waxes and acidic materials was investigated, as well as the influence of olefine and acidic material on the deposition.

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Table I(B)21
DETERMINATION OF THE DECOMPOSITION OF TAR

| Time | $T_2$ | $T_1$ | Distillate (cc) | Gas (cc) |
|---|---|---|---|---|
| 0.00 | 20 | | | |
| 19 | 40 | | | |
| 20 | 60 | | | |
| 28 | 80 | | | |
| 53 | 100 | | | |
| 1.03 | 110 | 100 | I.D. | |
| 16 | 120 | 100 | 12 | |
| 24 | 140 | 103 | 15 | |
| 29 | 160 | 103 | 16 | |
| 33 | 180 | 103 | 17 | |
| 38 | 200 | 103 | — | |
| 46 | 220 | 103 | 19 | |
| 57 | 240 | 103 | — | |
| 2.04 | 260 | 164 | 20 | |
| 8 | 255 | 195 | 27 | |
| 9 | 260 | 203 | 30 | |
| 14 | 270 | 215 | 44 | |
| 19 | 290 | 230 | 65 | 2 |
| 26 | 310 | 243 | 88 | — |
| 32 | 330 | 350 | 108 | 9 |
| 35 | 335 | 254 | 127 | 26 |
| 36 | 340 | 257 | 131 | 39.0 |
| 39 | 350 | 370 | 141 | 95.5 |
| 40 | 352 | 276 | 145 | 110 |
| 41 | 358 | 280 | 151 | 134 |
| 43 | 363 | 285 | 160 | 172 |

Remarks: $T_2$ = Oil temperature (°C).
$T_1$ = Distillation temperature (°C) atomospheric pressure.

Table II(B)21
DISTRIBUTION OF PARAFFIN WAXES AND ACID MATERIALS

| Boiling Range °C | Yield (%) | 10% NaOH Soluble(%) | Paraffin Wax (%) |
|---|---|---|---|
| I.D.-200 | 3.71 | 32.0 | |
| 200-210 | 3.17 | 39 | |
| 210-220 | 2.88 | 38 | |
| 220-230 | 4.55 | 37.5 | |
| 230-240 | 3.81 | 34.0 | |
| 240-250 | 3.76 | 35.7 | |
| 250-260 | 3.62 | 31.0 | 0.75 |
| 260-270 | 4.94 | 26.5 | 1.32 |
| 270-280 | 1.50 | | — |
| 280-290 | 0.69 | | 4.55 |
| 290-300 | 2.44 | | 7.64 |
| 300-310 | 2.13 | 24.0 | 9.59 |
| 310-320 | 2.41 | | 13.78 |
| 320-330 | 8.27 | | 17.21 |
| 330-340 | 12.57 | | 20.15 |

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Table III(B)21
PROPERTIES OF PREPARED OILS

| Oil | Preparation(°C) | | Properties | | |
|---|---|---|---|---|---|
| | First step | Second step | Sp. gr.(25/4) | Freezing pt. (°C) | Viscosity(sec) Redwood No. I |
| A | 200-340 untreated | | 0.9707 | +7 | 64.3 |
| B | 200-270 Alkali treated | 270-340 untreated | 0.9667 | +25 | 64.7 |
| C | 200-270 Alkali treated | 270-340 Alkali-treated and dewaxed | 0.9510 | +2 | 43.3 |
| D | 200-270 untreated | | 0.9645 | below -16 | 43.2 |
| E | 200-270 untreated | 270-340 dewaxed | 0.9655 | -2 | |

Table IV(B)21
EFFECT OF MIXING 200-340°C OIL WITH VARIOUS OTHER OILS

| Treatment | Deposition on Mixing with | | |
|---|---|---|---|
| | Petroleum Oil | Soya bean oil | Shale Oil |
| None | Deposit | Deposit | Deposit |
| 80% $H_2SO_4$ | No Deposit | No Deposit | No Deposit |
| 10% $H_2SO_4$ | No Deposit | No Deposit | Trace |
| 10% NaOH | Deposit | Deposit | Deposit |

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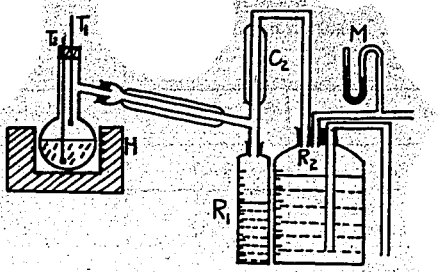


Figure 1(B)21

TEST APPARATUS FOR DETERMINING THE DECOMPOSITION TEMPERATURE

$T_1$ = Thermometer for distillation temp.
$T_2$ = Thermometer for oil temp.
$R_1$ = Receiver for distillate
$R_2$ = Gas holder
$C_1, C_2$ Condenser
H Heater

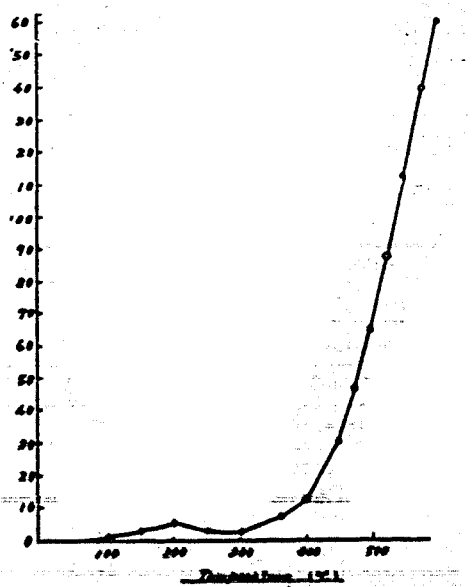


Figure 2(B)21
GAS VOLUME EVOLVED AT DIFFERENT TEMPERATURES