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CANADA CENTRE FOR MINERAL AND ENERGY TECHNOLOGY
(Former Mines Branch)

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October 1975.

ENERGY RESEARCH PROGRAM

ENERGY RESEARCH LABORATORIES
REPORT ERP/ERL 75-113 (TR)

A Comparison of Pitch Content Measurements Obtained with a Podbielniak Equilibrium Flash Still and a Modified Hempel Distillation Apparatus

by

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INTRODUCTION

Experimental programs directed toward the hydrocracking of bitumen from the Athabasca Oil Sands and other heavy oils and tars are presently in progress in both the Catalysis Research Section and the Process Engineering Section. One of the most important measurements in these experiments is the molecular weight reduction or, more specifically, the extent of conversion of the $+975^{o}F$ ($+524^{o}C$) pitch to lower boiling distillates. Relatively large samples of liquid product are obtained from the pilot plant experiments performed in the Process Engineering Section[1]. The fraction of pitch in these samples is usually determined using the Podbielniak Equilibrium Flash Still. This analysis requires a sample volume of approximately 1 liter. Smaller quantities of liquid samples are normally obtained in the bench scale studies performed in the Catalysis Research Section. The fraction of pitch in these samples is determined using a Modified Hempel Distillation Apparatus which only requires a 100 ml sample. The experiments described in this report were performed in order to compare the results obtained by the two different methods.

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EXPERIMENTAL

The Podbielniak Equilibrium Falsh Still, Model 500, is a continuously fed vacuum distillation apparatus. Details of its construction and operation have been given elsewhere[2, 3]. The Modified Hempel method is a batch distillation. Smith and co-workers[4] have described it in a comprehensive manner.

Two sets of samples were analyzed. One set was obtained by mixing various proportions of Athabasca bitumen and a heavy gas oil. The Athabasca bitumen was obtained from the Great Canadian Oil Sands Company at Fort McMurray, Alberta. Its properties are shown in Table 1. The heavy gas oil was the 650-975°F (324-524°C) portion of liquid product obtained by processing Athabasca bitumen in the thermal hydrocracking pilot plant. Its properties are shown in Table 2. The proportions of each component in the mixtures are shown in Table 3. The second set of samples consisted of heavy end liquid products also obtained from pilot plant thermal hydrocracking experiments. These samples contained considerably less hydrocarbon material boiling in the 650-975°F (324-524°C) range than did samples in the first set. The thermal hydrocracking conditions used to prepare the second set of samples are given in Table 3.

RESULTS AND DISCUSSION

The +975°F (+524°C) pitch content in the first set of samples as determined by the two distillation procedures, is given in Figure 1 and in Table 3. The two methods produced essentially the same result for the 100% Athabasca bitumen sample; 50.9 wt % from the Podbielniak Still and 51.6 wt % from the Modified Hempel Apparatus. These analyses are consistent with data reported in the literature (5, 6). The results from the two procedures diverged as the pitch content of the samples decreased. In Figure 1, the

TABLE 1

Properties of the Bitumen Feed Stock as Received from Great Canadian Oil Sands Ltd.

Specific gravity 60/60°F	1.000
Ash (wt %) 700°C	0.70
Nickel (ppm)	68
Vanadium (ppm)	189
Pentane insolubles (wt %)	15.83
Benzene insolubles (wt %)	0.90
Carbon Disulphide insolubles (wt %)	0.88
Sulphur (wt %)	4.72
Nitrogen (wt %)	0.38
Oxygen (wt %)	1.0
Viscosity, Kinematic (cSt) at 210°F	85
Viscosity, Kinematic (cSt) at 130°F	1140
Viscosity, Kinematic (cSt) at 100°F	4818

TABLE 2

General Properties of the Heavy Gas Oil

Physical Properties and Chemical Analyses	Thermally Hydrocracked Gas-Oil
Boiling Range (°F)	650-975
Specific Gravity 60/60°F	0.992
Conradson Carbon (wt %)	0.97
Sulphur (wt %)	3.59
Nitrogen (wt %)	0.38
Ash (wt %)	trace
Vanadium (ppm)	<1
Viscosity, Kinematic (cSt) at 100°F	108.8

TABLE 3

Properties of Samples Analyzed

Sample Indentification				+975°F (+524°C) Pitch Analyses	
Sample Number	wt % Bitumen	wt % Heavy Gas Oil	Processing Temp* °C	Modified Hempel	Podbielniak Flash Still
SF78	100	-	NOT APPLICABLE	51.6	50.9
75-7	50	50		32.6	25.7
75-8	33.33	66.67		24.4	16.7
75-9	20	80		18.6	10.0
75-10	10	90		12.6	4.6
81-1-1	NOT APPLICABLE		470	28.0	20.3
81-3-1			480	20.2	12.7
81-4-1			485	10.5	3.1

* Other Processing Conditions were: 3000 psig (20.8 MPa) operating pressure, 2.0 hr^{-1} (0.556ks^{-1}) liquid space velocity, 85% H_2 recycle gas concentration, 1.5 ft^3/hr (11.8 l/ks) at operating pressure gas recycle rate.

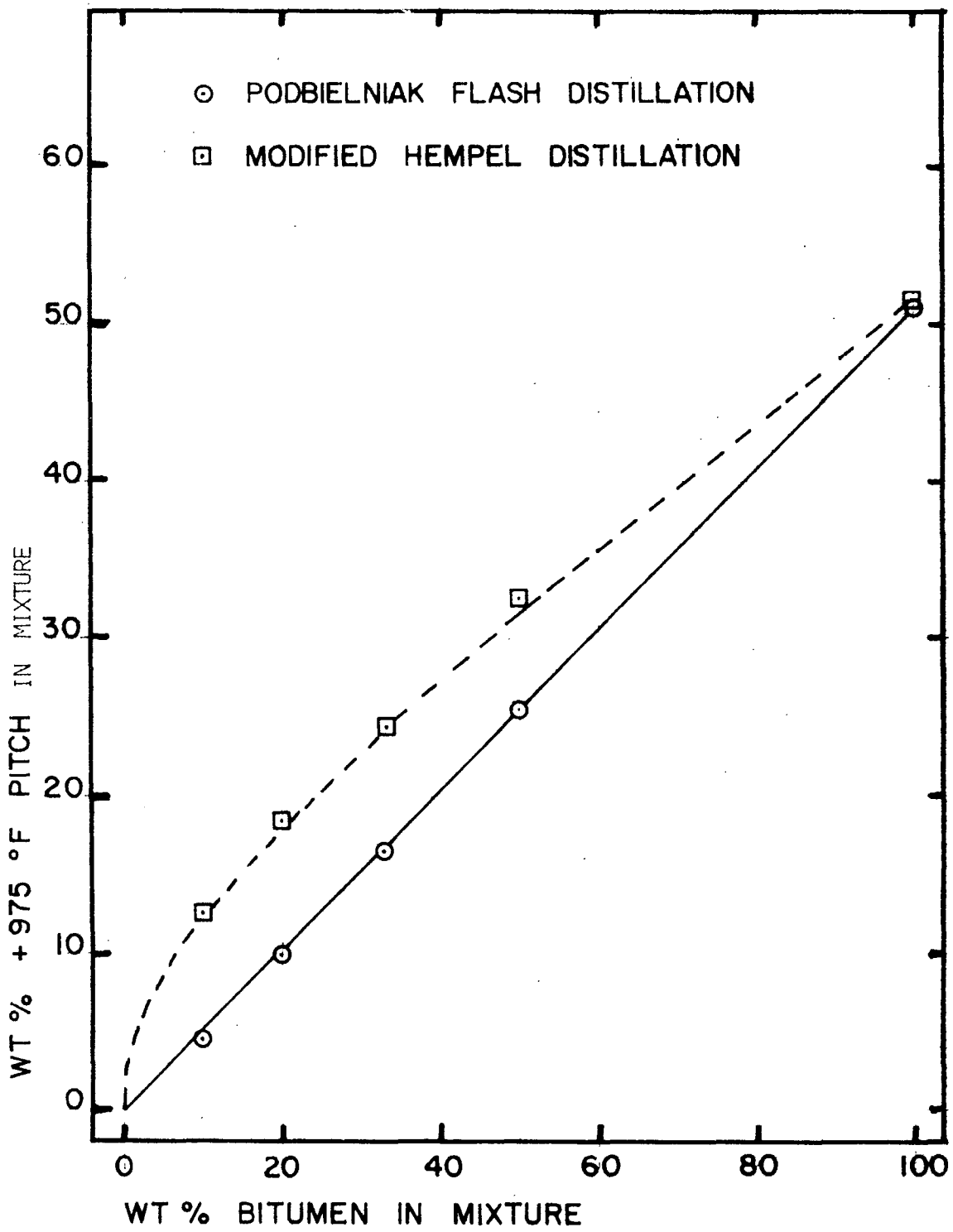

FIGURE 1

Wt% + 975°F Pitch versus wt% Bitumen in Bitumen - Heavy Gas Oil Mixture

pitch results from the Podbielniak Still fall on a straight line passing through the origin. This shows that the Podbielniak pitch results are consistent with the amount of bitumen in the samples. In contrast, the pitch results from the Modified Hempel apparatus are not consistent with the amount of bitumen in the samples.

The pitch analyses obtained by the two methods are compared in Figure 2. The data show that there is a linear relationship between the results of the two procedures. The same relationship is valid for both sets of samples. All of the non-pitch compounds in the mixtures of bitumen and heavy gas oil boiled above 650°F (324°C). Whereas a large proportion of the non-pitch compounds in the heavy end samples of liquid product from thermal hydrocracking experiments contained hydrocarbons boiling below 650°F (324°C). This suggests that the proportion of 650-975°F (324-524°C) material in the samples does not affect the pitch analyses obtained by the Modified Hempel procedure.

A less extensive investigation performed earlier indicated that the Podbielniak and Modified Hempel distillation results were not the same. Indications were that 0.855 x wt % pitch obtained by the Modified Hempel procedure was equivalent to the wt % pitch obtained by the Podbielniak Still. Therefore, all previous distillation results reported by the Catalysis Research Section were adjusted in the above manner. The present investigation shows that this adjustment was not correct, and that the pitch contents reported previously were still too high. It also shows that the required adjustment is a function of pitch content. Equation 1 is the functional relationship between the two quantities and is valid for samples having pitch contents between 5 and 25 weight percent.

$$x = y - c \qquad (1)$$

where

x = wt % pitch in sample determined by the Podbielniak EFS method

y = wt % pitch in sample measured by the Modified Hempel method

$c = 8$

The line in Figure 2 is plotted from this equation. The data points from Table 3 fall reasonably close to this line. It is readily apparent from Figure 1 that Equation 1 would not be valid for all samples. However, the vast majority of samples being analyzed contain 3 to 25 wt % pitch. Therefore, Equation 1 may be considered as a useful working relationship.

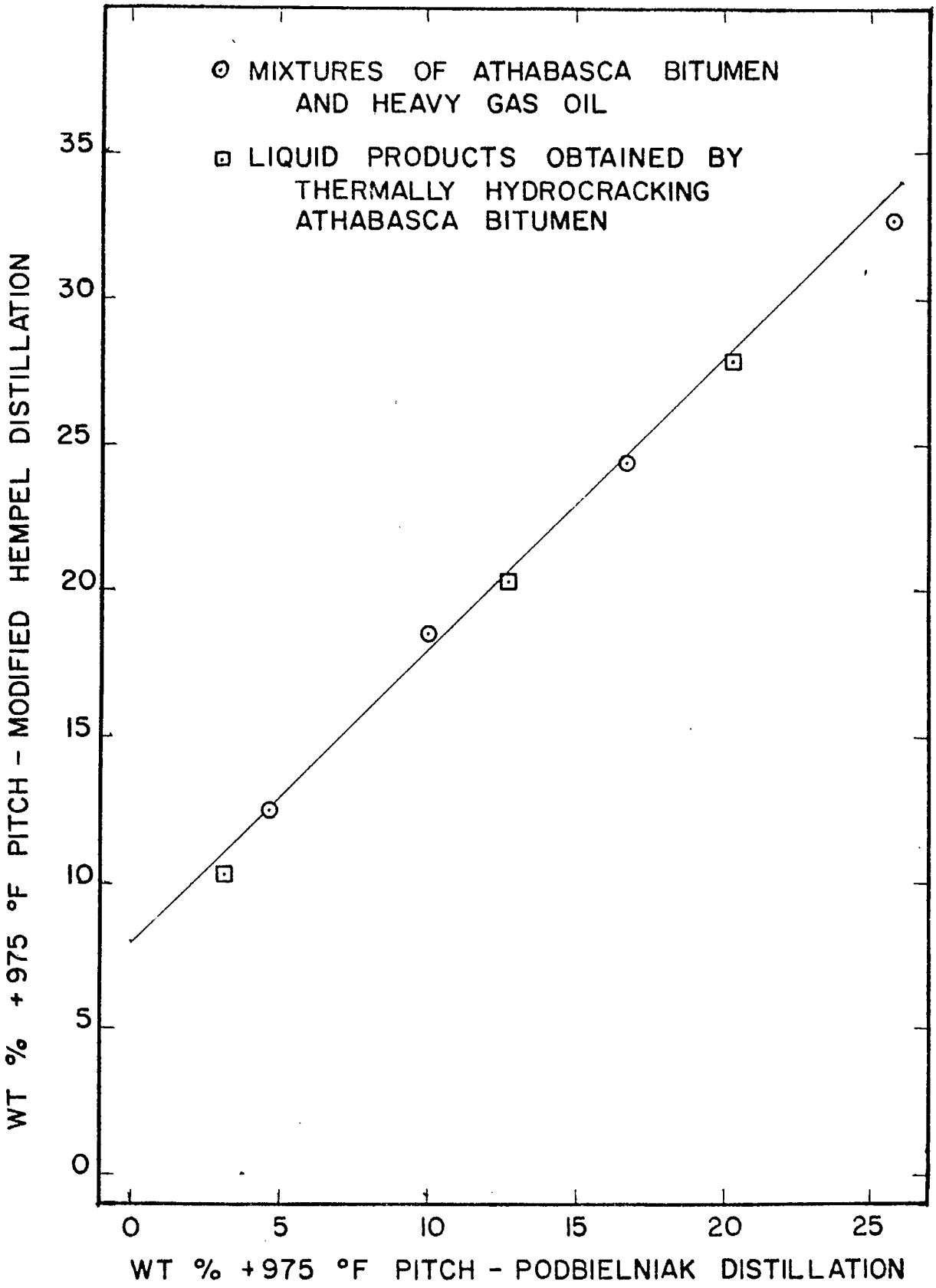

FIGURE 2

WE% + 975°F Pitch measured by the Modified Hempel Distillation Apparatus versus wt% + 975° Pitch Measured by the Podbielniak Equilibrium Flash Still

The significance of the experimental findings may be summarized as follows:

1. The pitch analyses obtained using the Podbielniak Equilibrium Flash Still have been found to be consistent with the known amount of bitumen in prepared samples.
2. The measurements of pitch content obtained with the Modified Hempel Distillation Apparatus have been found to be significantly higher than the pitch content determined by the Podbielniak Still.
3. A linear relationship between pitch content measured using the Podbielniak Still and pitch content using the Modified Hempel Apparatus has been established. The data indicate that this relationship will be valid for pitch contents varying from 5 wt % to 25 wt %.
4. The extent of pitch conversion which actually occurred in earlier experiments will have been higher than the values stated in previous reports from the Catalysis Research Section.

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