

APPLICATION OF HIGH VACUUM MICRO-DISTILLATION TO THE STUDY OF
COAL-TAR AND PETROLEUM PITCHES

L. P. Charette and G. Bishofberger*

Aluminium Laboratories Limited, Arvida, Quebec (Canada)

INTRODUCTION

The binder pitches used in the manufacture of carbon electrodes are of coal-tar or petroleum origin and exhibit pronounced differences in their properties depending on their source and mode of production. Various means have been devised to detect these differences, but distillation has very seldom been used. Obviously there are many reasons for this lack of interest in distillation, but the main one is probably the thermal lability of this type of material or at least of some of its constituents. However, the difficulty associated with the thermal lability can be overcome by making use of high vacuum technique.

There are a number of molecular stills commercially available, but, in general they require the use of fairly large samples. In the investigation described herein this was a major handicap since the available samples were mostly experimental and of limited supply. Furthermore, we were not interested in collecting fractions and studying each fraction as the amount of work involved would have been prohibitive, especially in view of the fact that it was intended to test a fairly large number of samples; past experience in our own laboratory had clearly indicated that work based on only a few samples cannot be really informative as the conclusions drawn can be greatly influenced by the type of pitch used and the treatment the pitch has undergone. Our main interest was to find out whether distillation could yield significantly different data which might be useful in pitch evaluation. The micro-molecular still used by Sims⁽¹⁾ for the analytical distillation of organic mixtures appeared to offer the desired features; the technique was reasonably rapid and requires only milligram quantities of material. With such a still the amount of distillate at various temperatures is calculated from the measured contraction of a calibrated quartz helix.

EXPERIMENTAL

Still. - The apparatus (Figure 1) consists essentially of a pan suspended from a quartz helix in an evacuated Pyrex tube. The sample is heated by an internal heating coil and the contraction of the quartz helix due to the loss of weight of the sample in the course of distillation is measured by a sensitive-reading cathetometer.

The sample pan is made of aluminium. A disk of 5/8 in. diameter is stamped out of a sheet of aluminium foil by using a steel punch, and formed into a cylindrical pan of 3/8 in. diameter and 1/8 in. high wall in a specially designed mould. The aluminium pan has an area of 0.75 cm² and weighs approximately 10 mg.

The stirrup, which holds the pan, is cut from a sheet of stainless steel of approximately 0.0065 in. thickness. It is in the shape of a cross with arms 1 1/2 mm wide; the length of the 3 short arms is 6 mm, the length of the long arm, 33 mm. The ends of the arms are bent upwards in such a way that the pan can be placed between them. The end of the long arm is shaped into a hook to be inserted into the loop of the Pyrex filament which in turn is hung on the quartz helix (Figure 1). The weight of the stirrup is reduced to approximately 50 mg by immersion in hydrochloric acid.

The heating coil, 6 in. long and 1/2 in. in diameter, has a resistance of 14 ohms. It is made of 24 gauge Chromel "A" wire and is wound on three strip-mica spacers. The voltage is controlled by a variable transformer (Variac), with a range of 0-135 volts and a maximum output current of 7.5 amperes. The maximum temperature of 350° C inside the heating coil is obtained by operating at a Variac setting of 60 (60 volts).

* Now with Aluminium Industrie A. G. Chippis, Switzerland.

Since the pan containing the sample is continuously moving upwards during a distillation, due to the loss of weight, it was important to know the temperature distribution inside the heating coil. The temperature, after the still had been evacuated, was raised to 350° C at a rate of approximately 6.6° C per minute by increasing the Variac by one scale division every minute; the temperature was measured by means of the chromel-alumel thermocouple on the central axis of the heating coil. The thermocouple was moved in steps of 1/2 in. and at each position the heating cycle was repeated and temperatures were recorded. The position of the thermocouple was measured by means of a scale printed on the wall of the still proper; the zero of the scale was level with the top of the heating coil. Figure 2 shows the axial temperature distribution of the heating coil.

The heating rate of approximately 6.6° C/minute was initially selected because of practical considerations. A higher heating rate was not desirable since gas evolution during distillation would be too fast. A slower heating rate (Variac setting increased by one scale division every second minute, which meant double distillation time) was tried, but did not change the results significantly; the shape of the elimination curve stayed the same except that the peak of the curve moved slightly towards a lower temperature.

By raising the Variac by one scale division every minute, the temperature, however, did not increase at a satisfactorily uniform rate; the heating rate was slightly higher at the beginning than at the end of distillation. A modified scale was prepared for the Variac and it was then possible to obtain a heating rate of 6.6° C/minute throughout the distillation.

Vacuum System. - The system was evacuated by a Duo-seal, two-stage vacuum pump. (Canadian Laboratory Supplies Limited, Catalogue No. A-72-703B). High vacuum was obtained by a Supervac OD-25 Oil Diffusion Pump, (Central Scientific Company, Catalogue No. 93330, No. 1), and was measured by a McLeod gauge. Apiezon grease "N" was used for all glass joints and stopcocks.

Measuring Device. - The relative position of the pan - and thus the weight loss of the sample during a distillation - was measured by a Wild cathetometer (H. Wild, Surveying Instruments Supply Company, Ltd., Heerbrugg, Switzerland). The cathetometer consists of a horizontal telescope with a magnification of 12x, mounted so as to slide upon an upright pillar with an attached glass staff. The telescope is adjusted in height by rack and pinion action until its crosshairs coincide with the lowest end of the quartz helix. The position of the telescope upon the vertical, graduated glass staff can then be read by means of a microscope. Direct reading to 0.1 mm and safe estimation to 0.01 mm can be made with this instrument.

Calibration of Quartz Helix. - Analytical balance weights, covering a range up to 100 mg, were placed in the sample pan and the extension of the quartz helix caused by each weight increase measured with the cathetometer. For each one milligram increment in load, the helix was lengthened by 1.1092 mm.

Contraction of the quartz helix in the course of a distillation was due to two causes: (a) reduction in load as a result of distillation and (b) heating of the quartz helix. The thermal contraction of the helix was measured over the entire temperature range from room temperature to 350° C; it was found to be roughly 0.01 mm per 6.6° C within the normal distance travelled by the pan during a distillation. Positive corrections were accordingly made to all cathetometer readings.

Sample Preparation. - Preliminary distillations had shown that at a temperature between 80 and 150° C, bubbles due to gas evolution started to form on the surface of the pitch. The bubbles gradually increased in size and finally collapsed, imparting a jerking motion to the pan so that it was impossible to take readings on the cathetometer. It was finally found that with a mixture of 30% pitch and 70% calcined petroleum coke no bubbling occurred and the readings on the cathetometer could be made without difficulty. A blank distillation run with coke alone showed that no trace of volatile was present in the coke.

Coke, calcined at 1400° C and ground to -35 +48 mesh, was mixed in a mortar with finely ground pitch (-20 mesh) in the ratio of 2:1. From this mixture, 166.5 mg (55.5 mg pitch) were weighed into the aluminium pan. This particular sample size was chosen because (a) the cathetometer readings could be multiplied directly by the factor 2 in order to obtain the percentage distilled, and (b) the pan remained within a zone of reasonably uniform temperature throughout the complete distillation cycle, as shown in Figure 2.

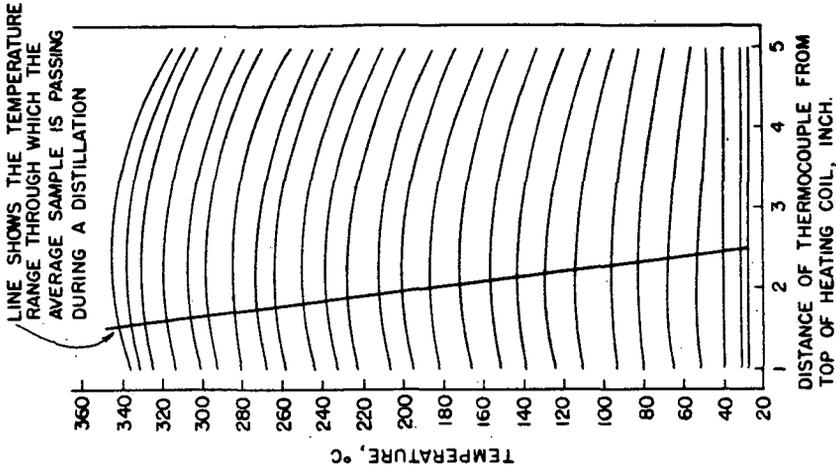


FIGURE 2

AXIAL TEMPERATURE DISTRIBUTION OF HEATING COIL.

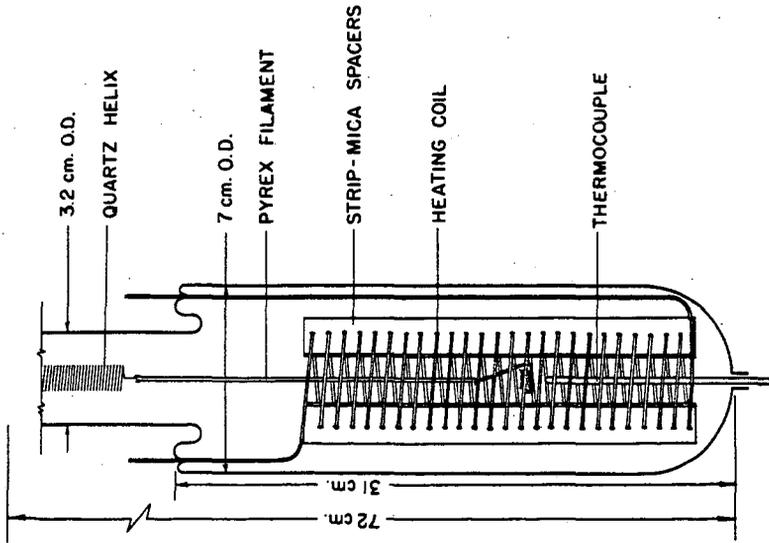


FIGURE 1

MICRO POT-TYPE STILL

Distillation Procedure. - After the pressure of the system has been reduced to 10^{-5} mm Hg as read on the McLeod gauge, the sample was gradually heated up to 350° C. In the course of the distillation, the contraction of the helix was recorded at constant intervals of one minute. To prevent condensation on the still wall facing the cathetometer and thus interference with the telescope readings, a jet of air was played on the appropriate area of the wall.

RESULTS

A series of 20 binders - 17 coal-tar pitches and 3 petroleum pitches - was tested. They are identified in Table 1 which also lists their respective melting point, coking value, atomic carbon-hydrogen ratio, and compressive strength of test electrodes prepared from a mixture of petroleum coke and binder pitch; this last property is considered as the best individual criterion of binder quality.

Distillation runs yielded more than 1000 readings, which it is impractical to reproduce. The data were plotted in two fashions, as elimination curves and as distillation curves. Elimination curves represent the amount of distillate in each fraction expressed as weight percentage of the initial sample weight, while distillation curves relate temperatures to cumulative distillate percentages.

For present purposes, a selection has been made of three pitches - two coal-tar and one petroleum pitches - that illustrate the general behaviour pattern and also the more or less extreme ranges encountered. Figure 3, shows elimination curves, Figure 4, cumulative distillation curves for the same three pitches.

TABLE 1

DESCRIPTION OF PITCH SAMPLES

Pitch Identification ^(a)	Melting Point ^(b) ° C	Coking Value ^(c) %	Carbon-Hydrogen Ratio (Atomic)	Compressive Strength of Test Electrodes (kg/cm ²)
<u>Coal-Tar Pitches</u>				
A-1	137	64.8	1.86	444
A-2	145	69.5	1.88	440
A-3	101	57.9	1.79	354
A-4	106	57.8	1.75	352
A-5	67	51.1	1.77	340
A-6	97	55.6	1.76	336
A-7	68	45.0	1.64	289
A-8	66	41.5	1.61	273
B-1	89	54.4	1.67	381
B-2	94	58.5	1.84	348
B-3	89	56.6	1.83	341
B-4	95	56.9	1.76	339
B-5	90	51.7	1.76	320
B-6	89	51.4	1.71	305
B-7	89	53.5	1.59	295
B-8	95	49.5	1.62	252
C-1	65	32.9	1.49	181
<u>Petroleum Pitches</u>				
D-1	111	53.3	0.98	210
D-2	111	43.1	0.93	169
E-1	70	42.9	1.12	135

(a) A, B, C, D, E indicate different suppliers.

(b) Cube-in-air method was used for melting points greater than 80° C; below 80° C, cube-in-water.

(c) Method described in literature reference (2).

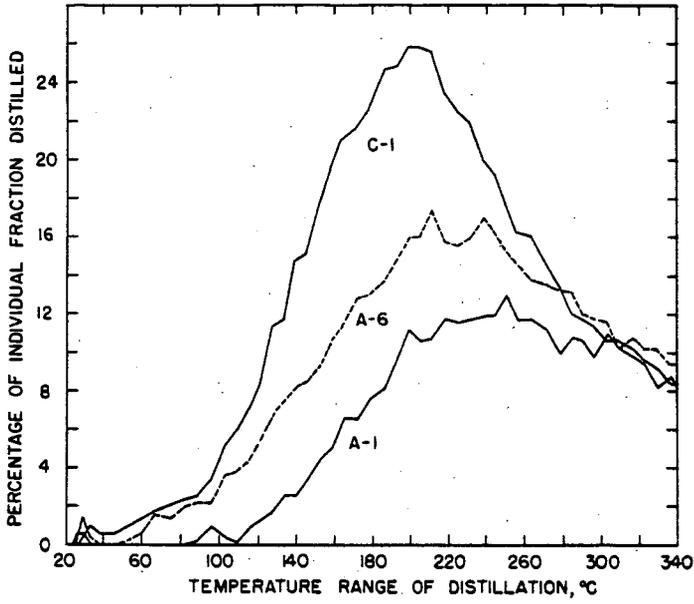


FIGURE 3

ELIMINATION CURVES OF PITCH SAMPLES

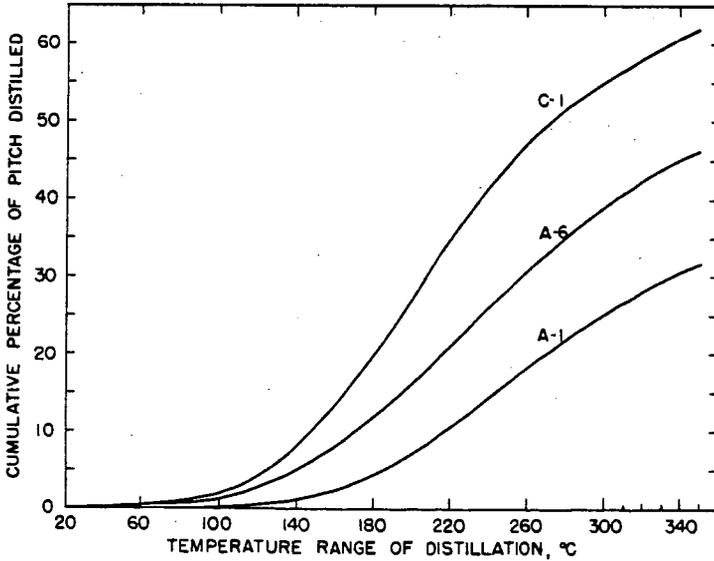


FIGURE 4

CUMULATIVE DISTILLATION CURVES OF PITCH SAMPLES

DISCUSSION

From examination of the various curves, the three variables which appeared to be of some significance for pitch characterization were estimated to be (a) the slope of the relatively straight portion of the cumulative distillation curve, (b) the temperature at which the greatest percentage was distilled (elimination maximum) and (c) the cumulative percentage corresponding to the elimination maximum.

In general these three variables could have been obtained from the distillation curves, but in some cases the precision was inadequate. This difficulty was overcome by establishing the mathematical equation of each cumulative distillation curve and subsequently deriving the values shown in Table 2. As can be observed in Figure 4, the shape of the cumulative distillation curves is that of an elongated S; the "Gompertz" equation⁽³⁾ was found to be satisfactory in defining such curves:

$$y = a \cdot b^{c^x} \quad \text{or}$$

$$\log y = \log a + c^x \log b$$

Inspection of Table 2 shows that low values of maximum slope (x_1) and amount distilled at the elimination maximum (x_2) tend to coincide with high values of compressive strength; this indicates some measure of individual relationships. Such a tendency does not exist for the elimination maximum (x_3). Inspection alone, however, is inadequate to give a full appraisal of relationships and a better picture is supplied by statistical study.

The statistical procedure applied was the Multiple Correlation Technique⁽⁴⁾ designed to assess the relationship between two or more variates. Complete statistical data are not reported herein; only those useful for the discussion of results are summarized in Table 3.

Statistically speaking the correlation coefficients given in Table 3 for maximum slope ($R = 0.903$) and for % distilled ($R = 0.766$) are highly significant but, from a practical viewpoint, the standard deviations about regression of compressive strength on either one of the two independent variables ($\sigma = 36.7$ and 54.7 kg/cm² respectively) are rather high. In other words, although the maximum slope alone accounts for 81.4% (R^2) of the variations in compressive strength, and % distilled alone, for 58.7%, the proportion of variations in compressive strength not accounted for is undeniably high. It was thought then that, taken together, variations in slope and % distilled, or even variations in all three independent variables might account for a much higher proportion of the variations in compressive strength. However, tests 3, 4 and 5 of Table 3 clearly indicate that this was not the case. In fact the correlation between compressive strength and slope alone (test 1) is as good as the correlation between compressive strength and any combinations of two or three independent variables.

From the above discussion, it can be concluded that high vacuum micro-distillation of pitch, as carried out during this investigation, represents another analytical tool which permits a certain differentiation between various pitches, but this differentiation is not considered satisfactory for prediction of pitch quality. However, it is believed that, because of its good reproducibility, it could be used advantageously as another means of controlling pitch uniformity.

ACKNOWLEDGEMENTS

The authors acknowledge the help of the National Research Council (Ottawa, Canada) in constructing the still, and also express their appreciation to Aluminium Laboratories Limited for permission to publish.

REFERENCES

- (1) Sims, R. P. A., Vacuum II, 245-256 (1952).
- (2) Charette, L. P., and Girolami, L., Fuel, XXXVII, 382-392 (1958).
- (3) Davis, Dave S., Empirical equations and nomography. First Edition, New York and London, McGraw-Hill Inc., 1943, p. 57.
- (4) Dwyer, Paul S., Recent development in correlation technique. J. A. M. Statistical Association, 37, 441-460 (1942).

TABLE 2
MAXIMUM SLOPE, PERCENTAGE DISTILLED AT ELIMINATION MAXIMUM AND
ELIMINATION MAXIMUM OF PITCH SAMPLES
 (in order of decreasing compressive strength of test electrodes)

Pitch Identification	Compressive Strength kg/cm ²	Maximum Slope (x ₁) %/° C	Amount Distilled (x ₂) %	Elimination Maximum (x ₃) ° C
<u>Coal-Tar Pitches</u>				
A-1	444	.1848	15.2	243
A-2	440	.1824	15.4	259
E-1	381	.1998	19.4	191
A-3	354	.1993	19.2	207
A-4	352	.2170	20.4	235
B-2	348	.2192	20.8	220
B-3	341	.2348	20.6	217
A-5	340	.2626	21.4	192
B-4	339	.2294	24.8	236
A-6	336	.2421	21.2	218
B-5	320	.2035	21.5	216
B-6	305	.2270	23.2	225
B-7	295	.2486	22.4	217
A-7	289	.2956	22.8	182
A-8	273	.3135	26.0	199
B-8	252	.2269	20.0	200
C-1	181	.3706	25.8	194
<u>Petroleum Pitches</u>				
D-1	210	.3116	22.3	286
D-2	169	.3470	24.8	289
E-1	135	.3698	23.9	251

TABLE 3
CORRELATION BETWEEN COMPRESSIVE STRENGTH AND DISTILLATION DATA

Test No.	Variables ^(a)	Correlation Data ^(b)		Standard Deviation ^(c) (kg/cm ²)
		R	R ²	
1	x ₁	0.903	0.814	36.7
2	x ₂	0.766	0.587	54.7
3	x ₁ , x ₂	0.910	0.828	36.4
4	x ₁ , x ₃	0.905	0.819	37.3
5	x ₁ , x ₂ , x ₃	0.916	0.838	36.3

(a) x₁ = maximum slope; x₂ = % distilled at elimination maximum;
 x₃ = elimination maximum.

(b) R₂ = correlation coefficient
 R x 100 = % of total variation in compressive strength accounted for by
 the variations in the specified independent variables or combinations
 of them.

(c) Standard deviation about regression of compressive strength on the
 independent variables or combinations of them.