

276. *Separation of Normal Long-chain Hydrocarbons by Fractional Distillation in High Vacuum.*

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UNTIL recently all investigations of this subject have been carried out with natural waxes, Kraft (*Ber.*, 1908, **40**, 4779) using lignite, and Francis (*J.*, 1922, **121**, 1529) Scotch paraffin wax. The problem of separation by distillation, in these cases, is complicated by the fact that the constitution of the original substance is entirely unknown. Carothers and his co-workers (*J. Amer. Chem. Soc.*, 1930, **52**, 5279) have, however, prepared from decamethylene

bromide a mixture of hydrocarbons containing multiples of ten carbon atoms and separated these in a Washburn molecular still (*Bur. Stand. J. Res.*, 1929, **2**, 476). In this case, although the constituents can be predicted, the proportions in which they occur are indefinite.

In order to determine the optimum conditions of fractionation, it was decided to examine definite mixtures of pure synthetic long-chain hydrocarbons. Müller (*Proc. Roy. Soc., A*, 1928, **120**, 439) has described an apparatus designed in this laboratory for the distillation and fractionation of very small quantities of such material in a vacuum. At his suggestion, an extension of this work was undertaken.

Kraft and Francis (*loc. cit.*) effected identification by the usual analytical methods (molecular weight, refractive index, etc.). Later, however, Piper, Brown, and Dymont (*J.*, 1925, **127**, 2194) examined seven of Francis's distillation products by the X-ray method which he had employed in the investigation of the sodium salts of the fatty acids (*Proc. Physical Soc.*, 1923, **35**, 267) and which Müller (*J.*, 1923, **123**, 2043) used for the investigation of the fatty acids themselves. As the X-ray method has obvious advantages, it was adopted in the examination of the various fractions obtained.

EXPERIMENTAL.

The distillation apparatus used is shown diagrammatically in the figure. The substance to be distilled is placed in a platinum crucible *A*, blackened on the outer surface, which fits into a copper block *B*. This is indirectly heated by a platinum spiral *C*. *D* is a hollow copper tube which, during the experiment, is filled with a cooling mixture of solid CO₂ and methylated spirits. On the end of this tube, in thermal contact, is a thin glass cover-slip *E*. This receives the distillate which is later identified by the X-ray photographic method of analysis. *F* is a mercury-vapour trap. The electrode *G* is connected to a small induction coil and this allows a rough estimation of the vacuum to be made at the spark-gap *H*.

The temp. produced in the crucible by the various currents has not yet been completely determined. To obtain a rough estimate, however, various pure synthetic hydrocarbons were melted in the crucible under the conditions of distillation, at a current of 1 amp. These experiments indicated that, with this current, the max. temp.—about 70°—was reached in approx. $\frac{1}{2}$ hr.

The current necessary for heating the spiral depends upon the dimensions of the apparatus and the type of fractionation desired.

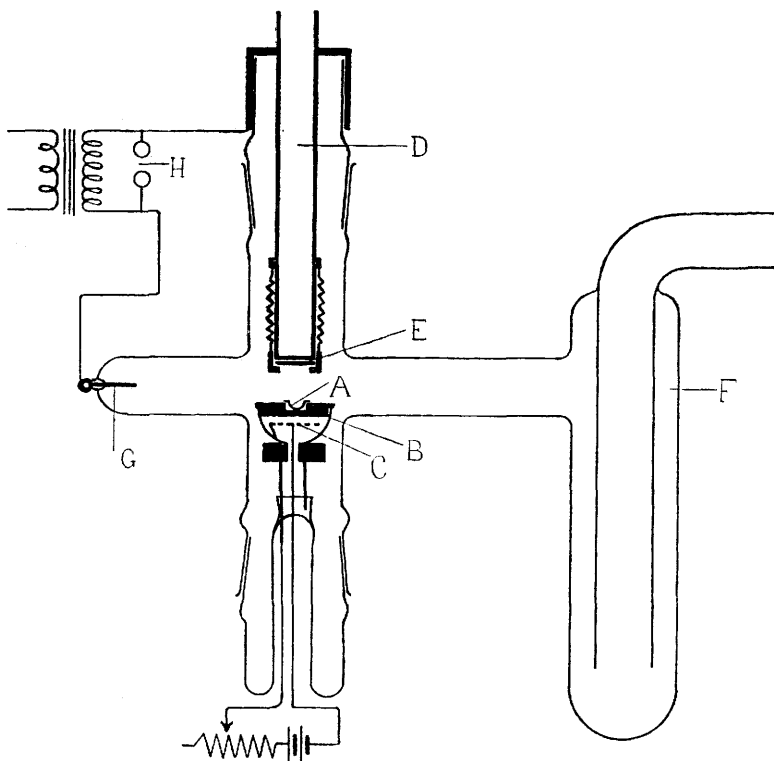
The rate of heating is very important and it was found that, where no separation was at first obtained, if the heating current was reduced and the time of distillation greatly increased, a perfect separation resulted (see below).

The substances to be examined were weighed into the platinum crucible and mixed by melting and stirring. After the apparatus had been evacuated to a pressure of approx. 10^{-4} mm., the sample was heated by means of a definite current and various fractions of distillate were collected. It is obvious

that the removal of each fraction necessitated restoration to atmospheric pressure and consequent cooling of the copper block.

The substances employed in the experiments described were eicosane ($C_{20}H_{42}$) and triacontane ($C_{30}H_{62}$). The former was prepared by reduction of the corresponding ketone (Müller, *Proc. Roy. Soc., A*, 1928, **120**, 437), and the latter by electrolysis of palmitic acid (Müller and Saville, *J.*, 1925, **127**, 599). These were mixed in various proportions, ranging from 50% $C_{20}H_{42}$ + 50% $C_{30}H_{62}$ to 1.3% $C_{20}H_{42}$ + 98.7% $C_{30}H_{62}$.

In the X-ray analysis of the distillates obtained, at least one fraction was



found in each case which showed only lines identical within experimental error (approx. 2%) with those corresponding to $C_{20}H_{42}$. The middle fractions in some cases showed both sets of lines, the later fractions only those corresponding to $C_{30}H_{62}$.

Preliminary experiments with the larger percentages (50, 30, 15, and 10%) of $C_{20}H_{42}$ were successful and showed clearly that the separation of mixtures containing lower proportions of the same hydrocarbon might be attempted under suitable conditions of rate of heating. The results obtained in the latter case, along with the optimum conditions, are given in Table I.

TABLE I.

Series.	Time of heating, hrs.	Current, amp.	Fraction.	X-Ray photograph showed
I. { 5% C ₂₀ H ₄₂ 95% C ₃₀ H ₆₂	{ 2 3	0.75	1	C ₂₀ H ₄₂
		0.75	2	C ₂₀ H ₄₂
		0.75	3	C ₃₀ H ₆₂
II. { 3% C ₂₀ H ₄₂ 97% C ₃₀ H ₆₂	{ 1½ 3	0.75	1	C ₂₀ H ₄₂
		0.85	2	C ₃₀ H ₆₂
		0.9	3	C ₃₀ H ₆₂
III. { 1.5% C ₂₀ H ₄₂ 98.5% C ₃₀ H ₆₂	{ 3 3	0.75	1	C ₂₀ H ₄₂ and C ₃₀ H ₆₂
		0.75	2	C ₂₀ H ₄₂ and C ₃₀ H ₆₂
IV. { 1.3% C ₂₀ H ₄₂ 98.7% C ₃₀ H ₆₂	{ 1½ 2	0.70	1	C ₂₀ H ₄₂
		0.70	2	C ₃₀ H ₆₂
		0.65	2	C ₂₀ H ₄₂
V. { 1.3% C ₂₀ H ₄₂ 98.7% C ₃₀ H ₆₂	{ 3½ 1	0.7	1	C ₂₀ H ₄₂
		0.85	3	C ₃₀ H ₆₂
		0.75	1	C ₂₀ H ₄₂
VI. { 3% C ₂₄ H ₅₀ 97% C ₃₀ H ₆₂	{ 1½ 1½ 1½	0.75	1	C ₂₄ H ₅₀
		0.75	2	C ₃₀ H ₆₂
		0.75	3	C ₃₀ H ₆₂

A further experiment was carried out with a mixture containing 3% tetra-*cosane* (C₂₄H₅₀), obtained by the reduction of the corresponding ketone, and 97% triacontane (C₃₀H₆₂). Here again a satisfactory separation was effected.

The X-ray photographs were taken with the actual layer as deposited on the cover-glass during distillation. In no case did the wt. of the layer exceed 1 mg., and this was spread over a surface of approx. ½" square. At the lower percentages, considerably thinner layers were used, as the amount of C₂₀H₄₂ had to be extremely small, the total capacity of the cup being about 75 mg.

As the percentage of the lower hydrocarbon decreases, it appears necessary to use a smaller current in order to effect a separation. Thus in Series I, 0.75 amp. gives two fractions C₂₀H₄₂, whereas in Series II only one fraction is obtained. In Series III at the same temp., no clear separation takes place, while lowering of the current in Series IV and V gives the desired results.

To obtain an estimate of the sensitivity given by the X-ray analytical methods adopted, the two hydrocarbons C₂₀H₄₂ and C₃₀H₆₂ were mixed in various proportions in solution, and the solution was evaporated on a cover-glass. The hydrocarbon film, without being subjected to any distillation process, was then photographed in the usual manner. A mixture of 5% C₂₀H₄₂ and 95% C₃₀H₆₂ or *vice versa* still showed both sets of lines. From this, one may conclude that distilled samples (even when as little as 1.3% is originally present in the mixture) which give only one set of lines are pure, at least to the extent indicated in the above experiment.

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