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CONSTANT-TEMPERATURE STILL HEAD FOR LIGHT-OIL FRACTIONATION

BY

FREDERICK M. WASHBURN, Assistant Chemist

Bureau of Standards

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I. GENERAL CONSIDERATIONS

Because of the greatly increased production of coke-oven light oil and the growing importance of the benzol industry, it was felt that a more accurate method of analysis for light oils was needed, as there is frequently a great discrepancy between the results of analysis of the same light oil, using different methods, and between the results obtained by different analysts, using the same method. This paper represents the results of a brief search for an improved method for the determination of benzene, toluene, and solvent naphtha in coke-oven or coal-tar light oil.

After the light oil has passed through the usual treatment for the determination of the percentage of wash oil present and the determination of the percentage of loss on washing with concentrated sulphuric acid, it is practically a mixture of benzene, toluene, the three isomeric xylenes, and higher aromatic hydrocarbons, together with the small amounts of paraffins usually present. The xylenes and the higher hydrocarbons boiling between 135 and 160° C are classed as solvent naphtha, so that the problem resolves itself into a separation of a mixture of benzene, toluene, and solvent naphtha. Fractional distillation furnishes the easiest means of accomplishing this.

There are three main types of methods generally in use for the fractional distillation of light oil. In the first of these, the light oil is distilled through a fractionating column and separated

into two fractions, one a mixture of benzene and toluene and the other a mixture of toluene and xylene. A portion of each of the two fractions obtained is subjected to distillation in a side-neck flask, and the percentages of benzene and toluene, and of toluene and xylene are read off from the curves or tables giving the relation between the composition of the fraction distilled, and the temperature of distillation. The method of Hugh W. James [1] is an example of this type. This method is open to objection on account of the serious errors introduced by the estimation of the percentage composition from the boiling-point curves or tables, since small amounts of impurities materially influence the boiling points of the fractions.

In the second type of method, distillation is made through an efficient fractionating column, and the receiver is changed at 95° C and at 125° C. The fraction under 95° C is considered as benzene, the fraction 95 to 125° C as toluene, and the residue as solvent naphtha. The method of Gustav Egloff [2] is an example of this type.

This method is more logical than the first, since it aims at a more complete separation of the mixture, but it gives fractions which are not pure. The first fraction consists of a mixture of benzene and toluene, the second of benzene, toluene, and xylene, and the residue of toluene and xylene. The results obtained depend upon the assumption that there is the same amount of toluene in the benzene fraction as there is benzene in the toluene fraction; and similarly, as much xylene in the toluene fraction as there is toluene in the residue, in which case the errors introduced by assuming the fractions to be pure would neutralize each other. The objection to this method is that this relation does not usually exist, since the amount of toluene distilling below 95° C, the amount of benzene distilling above 95° C, and the amount of xylene distilling below 125° C vary with the rate of distillation, efficiency of the column, composition of the oil, etc.

In the third type of method the light oil is separated into the largest possible fractions, which distill, respectively, below 81.0° C (for benzene), and from 109.0 to 111.5° C (for toluene). The intermediate fractions (81.0 to 109.0° C and 111.5 to 137.0° C) are then subjected to distillation in a side-neck flask. The percentage composition of the intermediates is then read off from previously constructed curves, similar to those in Figs. 3 and 4. The amounts

[1] Jour. Soc. Chem. Ind., 35, p. 236.

[2] Met. and Chem., Eng., 16, p. 259.

of benzene, toluene, and xylene obtained from these intermediates are added to the benzene, toluene, and solvent naphtha fractions, respectively, to give the total percentages. The method of Dyke Wilson and Ivan Roberts[3] is an example of this type. This method is the most logical of the three, since the percentage composition of the intermediates is actually determined, giving less probability of error than if the percentages were taken as some arbitrary amount. Furthermore, the error introduced by estimating the percentage composition by boiling-point curves is comparatively small, since it is applied to small volumes.

The fractionating apparatus used by Wilson and Roberts consists of a 40-inch Hempel column, filled for 36 inches of its length with glass beads; above this is a vertical reflux condenser, the purpose of which is to condense out the higher boiling constituents, and allow only the lower boiling constitutents to pass. The objection to this form of apparatus lies in the difficulty of control of the temperature of the reflux condenser, or dephlegmator. This temperature is regulated by the flow of liquid through the jacket of the condenser. Near the end of a fraction, the variation of $^1/_5$° C in the temperature will mean the difference between completely condensing the vapors and allowing the lower boiling constituent to pass. For this reason, it is practically impossible to use the dephlegmator efficiently, as the temperature is extremely difficult to control with any degree of accuracy.

II. CONSTANT-TEMPERATURE STILL-HEAD APPARATUS

1. DESCRIPTION

The constant-temperature still head is merely an improvement on the dephlegmator used in the Wilson and Roberts still. With its use it is possible to control absolutely the vapor temperature, thus making it possible to condense out practically the last traces of constituents having a higher boiling point than the fraction desired. It is not a new idea, but was first worked out by Frederick A. Brown.[4]

The fractionating apparatus used in the experiments described below consisted of two parts—a Hempel column and the constant-temperature still head. This latter consisted of a spiral of iron pipe, immersed in a bath of oil. The temperature of the oil bath was controlled by means of a thermostat, the bath being heated electrically and stirred by a motor-driven agitator.

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[3] Gas Record, p. 210; March, 1916.

[4] Trans. Chem. Soc., 37, p. 49; 1880.

The pipe spiral was made from a 12-foot length of ⅜-inch wrought-iron pipe, bent cold around a mandrel of 5 inches diameter, giving a coil of about 6 inches in diameter, and ¾ inch between the turns. A piece of copper tubing ¼ inch inside diameter was soldered to the coil as shown, to act as the outlet to the condenser.

The Hempel column was made of glass, 1⅛ inches inside diameter, and so formed that a thermometer could be inserted in the top. A metal column would be better, because there is

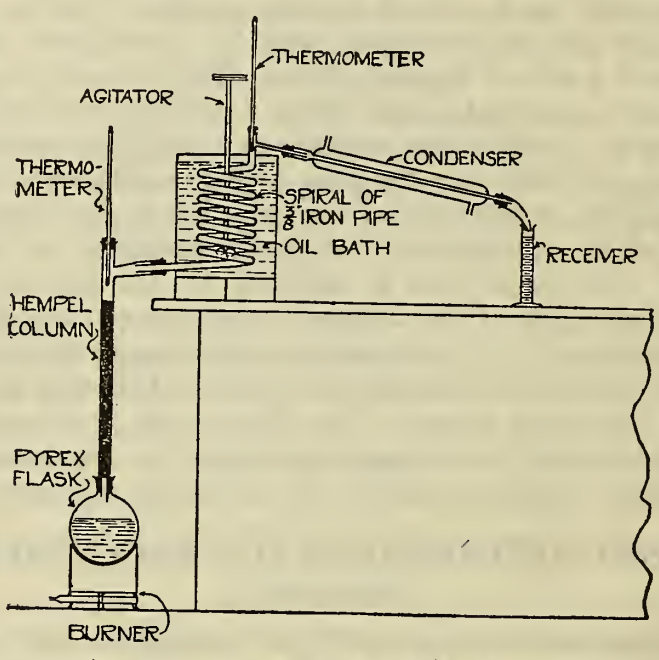

FIG. 1.—*Constant-temperature still-head apparatus*

danger from fire in case of breakage of the glass column. A 1500 cc Pyrex glass flask was used, but here again metal would be more suitable, for the same reason. The flask was heated by means of a Rose burner, with a hemispherical top covered with an asbestos-covered gauze. Three high-precision thermometers (70 to 200° C) were used—one at the top of the Hempel column, one at the top of the spiral, and one immersed in the oil bath.

2. OPERATING DIRECTIONS

The bath was brought up to the required temperature by means of a coil of resistance wire immersed in the bath, and was maintained at that temperature by means of four 50-watt tubular car-

bon lamps. A mercury thermoregulator of the usual type, used with a relay, controlled the temperature of the bath to 1/10° C.

A 1000 cc sample, measured at 15.5° C, was used. The temperature of the bath was brought rapidly up to 75° C by means of the heating coil and then slowly up to the temperature necessary to allow the vapors to pass through the coil when the liquid in the flask was boiling briskly. The temperature of the oil bath was then controlled by regulation of the thermoregulator so that three to four drops per second fell from the end of the condenser. This temperature was about 1/10° C below the vapor temperature at the top of the still head, as may be seen from the curve given in Fig. 2. Toward the end of the benzene fraction it was necessary to raise the temperature of the bath to allow the vapors to pass through. This was done gradually, keeping the vapor temperature at the top of the still head under 81.0° C. The rate of distillation gradually slowed down to about one drop per 10 seconds, when the temperature of 81.0° C was reached. The receiver was then changed, and the temperature of the bath gradually raised, keeping the rate of distillation under one drop per second until a temperature of 110.0° C was reached. The receiver was then changed, and the temperature of the oil bath was held by the thermoregulator at such a temperature that the rate of distillation was about two drops per second, and the vapor temperature was under 111.5° C. Near the end of the toluene fraction it was necessary to raise the temperature of the bath, as was done in the benzene fraction, until the vapor temperature of 111.5° C was reached. The receiver was then changed, and the temperature of the oil bath gradually raised, keeping a rate of distillation of under one drop per second, until the vapor temperature of 137.0° C was reached. The distillation was then stopped, and the residue allowed to cool. The residue was then drained carefully into a graduate and measured.

The intermediate fractions were distilled in a standard boiling-point apparatus,[5] except that a 50 cc Pyrex flask was used in place of the larger flask, and the rate of distillation kept at one drop per second. A 60 to 140° C thermometer, graduated in one-fifth degrees, was used. The temperature at which exactly one-half of the liquid passed over was noted, and the percentage of benzene and toluene and of toluene and xylene read off from previously constructed curves. (See Figs. 3 and 4.) The amounts of ben-

[5] Jour. Ind. and Eng. Chem., 10, No. 12, p. 1006; 1918.

zene and toluene obtained from the intermediate fractions were added to the amounts obtained in the benzene and toluene fractions to give the percentage of benzene and toluene, and the amount of xylene obtained from the toluene-xylene intermediate fraction added to the residue to give the percentage of solvent naphtha. The distillation loss was determined by subtracting

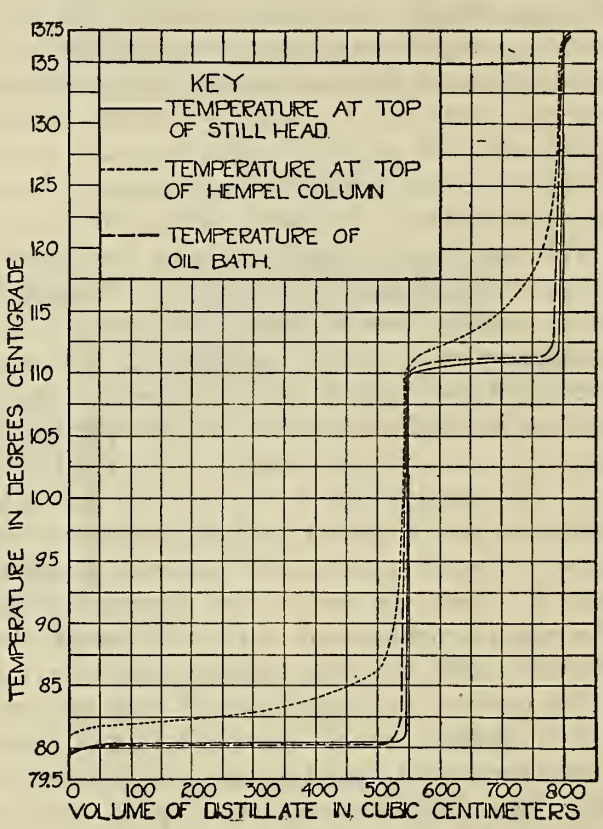

Fig. 2.—*Typical distillation curves obtained*

the total amount of distillate plus the residue from the volume taken for distillation. All volume measurements were made at a temperature of 15.5° C.

3. RESULTS OBTAINED

Table 1 gives the results of fractionating mixtures made up of known amounts of pure benzene, toluene, and xylene, and shows the high degree of accuracy obtainable. It also shows that the apparatus works equally well with varied percentages of benzene, toluene, and xylene, even though one of the components may be present in a comparatively small amount.

TABLE 1.—Results of Distillation of Mixtures of Known Composition

Distillation No.	Benzene—		Toluene—		Xylene—		Distillation loss
	Present	Found	Present	Found	Present	Found	
	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
I	80.00	80.05	10.00	9.99	10.00	9.93	0.03
II	70.00	70.12	20.00	19.81	10.00	9.84	.23
III	67.50	67.52	17.50	17.22	15.00	14.80	.46
IV	57.50	57.59	30.00	29.87	12.50	12.47	.05
V	55.00	55.07	25.00	24.72	20.00	19.85	.36
VI	40.00	40.18	45.00	45.02	15.00	14.69	.11
VII	30.00	29.92	55.00	55.66	15.00	14.40	.02
VIII	20.00	20.21	67.50	67.65	12.50	12.04	.10
IX	10.00	10.47	75.00	75.16	15.00	14.09	.28

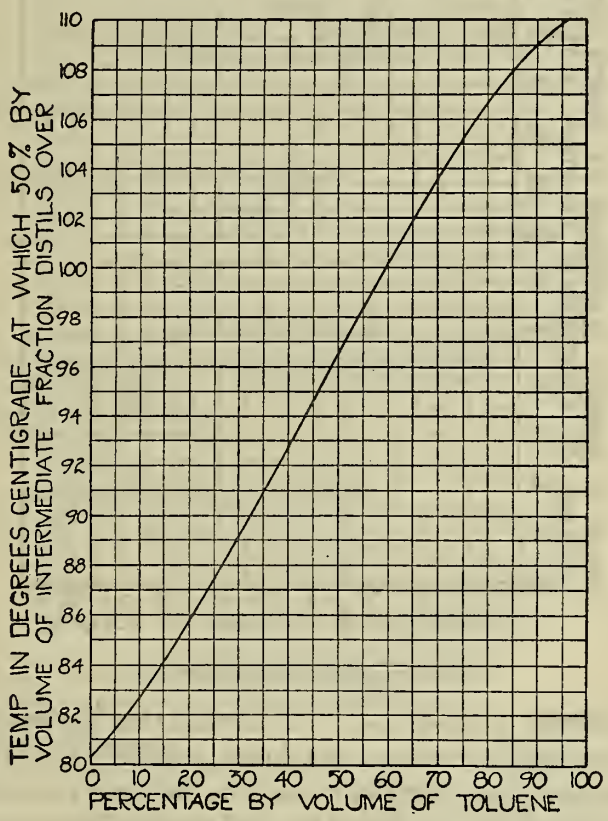

FIG. 3.—*Benzene-toluene intermediate*

Fig. 2 shows a set of typical distillation curves obtained with the apparatus. The line showing the temperatures at the top of the Hempel column gives an idea of how the distillation would proceed if only a Hempel column of this length were used. The line

showing the temperatures at the top of the constant-temperature still head shows how the still head condenses out the higher boiling constituents, allowing only the lower boiling ones to pass, thus holding the temperature well within the range allowed for "pure" fractions. As may be seen from the curve, when the temperature at the top of the still head rises to 81.0° C, the upper limit for the benzene fraction, the temperature at the top of the

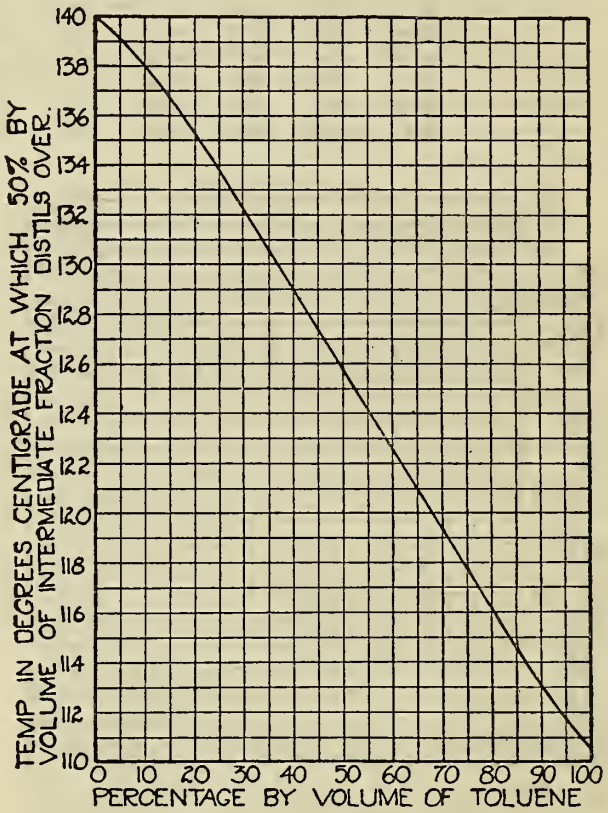

FIG. 4.—*Toluene-xylene intermediate*

Hempel column is about 105.0° C, showing that the vapor at that point consists almost entirely of toluene, with only a small amount of benzene, so that practically the only benzene remaining is in the form of vapor in the coil of the still head. Theoretically, it is possible to allow all of the benzene to pass through the coil and into the receiver, without allowing any of the toluene to pass, but practically, this would be very difficult and tedious, if not impossible, so that it is much easier to "sweep out" these last small amounts of benzene with toluene, thus giving a small intermediate

fraction. The same considerations apply to the latter part of the toluene fraction and to the toluene-xylene intermediate.

The large volumes of pure fractions, and likewise the degree of their purity is shown by length and straightness of the curve within the temperature ranges of 0 to 81.0° C, and 110.0 to 111.5° C, and the sharpness of separation by the very small rounding of the curves at the points where the receivers are changed (81.0° C, 110.0° C, and 111.5° C).

The comparatively high degree of purity of the fractions obtained with this apparatus is shown by Table 2, which also shows the method of calculation used.

TABLE 2.—Results of a Typical Distillation with the Constant-Temperature Still Head

[Mixture distilled contained 57.50 per cent of benzene, 30.00 per cent toluene, and 12.50 per cent of xylene. All temperatures are corrected]

Benzene fraction (under 81.0° C)=565.8 cc

Specific gravity at $\frac{15.5° C}{15.5}$= 0.884

Distillation of fraction in standard boiling point apparatus:	°C
1st drop	80.0
5 cc	80.1
50 cc	80.3
95 cc	81.3
Dry	82.5
Range	2.5

Benzene-toluene intermediate (81.0 to 110.0° C)=12.1 cc (1/2 distilled over at 85° C)

From curve=83 per cent benzene=10.1 cc (to be added to benzene fraction)

=17 per cent toluene = 2.0 (to be added to toluene fraction)

Toluene fraction (110.0 to 111.5° C)=289.2 cc

Specific gravity at $\frac{15.5° C}{15.5}$= 0.870

Distillation of fraction in standard boiling point apparatus:	° C
1st drop	110.0
5 cc	110.2
50 cc	110.5
95 cc	112.8
Dry	113.2
Range	3.2

Toluene-xylene intermediate (111.5 to 137.0° C)=15 cc (1/2 distilled over at 125° C)

From curve=52 per cent toluene=7.8 cc (to be added to toluene fraction)

=48 per cent xylene =7.2 cc (to be added to xylene fraction)

Residue (above 137.0° C)=117.5 cc

These results give the following:

Fraction	Volume found	Percentage found	Percentage actually present	Error
	cc			Per cent
Benzene	575.9	57.59	57.50	+0.09
Toluene	298.9	29.89	30.00	−.11
Xylene	124.7	12.47	12.50	−.03
Loss	.5	.05	.....	.....

III. SUMMARY

The three types of methods generally in use for the fractionation of light oil and the determination of benzene, toluene, and solvent naphtha are discussed. An apparatus which is an improvement on the dephlegmator of the Wilson and Roberts still is described, and the details of its operation are given. The apparatus is easily and inexpensively constructed and requires no greater attention or time than others used. Exceptionally large volumes of "pure" fractions are obtained which have a very small boiling point range, showing that they contain only negligible amounts of impurities. Almost all of each of the components of the mixture distilled is obtained in practically the pure state since the volumes of each of the intermediate fractions are only about 1.5 per cent of the volume taken for distillation. The composition of each of the intermediate fractions is actually determined, and the error introduced by this determination is small, since it is applied to only small volumes. The apparatus works well on mixtures containing widely varying percentages of benzene, toulene, and solvent naphtha.

WASHINGTON, June 10, 1919.