A CONTINUOUS HIGH-VACUUM STILL AND BOILING-POINT APPARATUS, AND THE SYSTEMATIC DISTILLATION OF A DEWAXED LUBRICANT FRACTION OF PETROLEUM [1]

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ABSTRACT

A sample of lubricant stock having about the properties of light automobile lubricating oil was obtained from a refinery supplied with crude oil from the Oklahoma City field. Two hundred and forty gallons were distilled through a semicommercial vacuum still. A continuous high-vacuum laboratory still and an apparatus for determining boiling points was constructed and the material was distilled systematically three times with their aid. After the third distillation, there remained 762 kg of material which distilled between 135° and 270° C at 1 mm Hg. The material tended to concentrate in four boiling ranges. The results of the distillation of the lubricant fraction and of the naphtha fraction from a Ponca City petroleum are compared at the same stages.

CONTENTS

I. INTRODUCTION

When Research Project 6 of the American Petroleum Institute was initiated, it was intended that all its investigations would be made on a single lot of crude oil, but in the fall of 1933, when work was begun on lubricating oil,[3] the percentage of heavy oil available was small (67 kg) from the 600-gallon lot on which had been done the work on the naphtha fraction. It was evident that while the isolation and identification of types of hydrocarbons might be possible, the isolation of constituents would be difficult from such small quantities as

would remain after careful fractionation. Consequently, in September 1936, the Advisory Committee for Research Project 6 decided to obtain, for the purpose of isolating the constituent hydrocarbons, a quantity of oil 10 or 15 times as large as the lubricant fraction available from the oil from the Ponca City field.[4]

II. SELECTION OF LUBRICATING-OIL STOCK

For the investigation, it was decided that the material should be:

1. Of definite origin, preferably from the South Ponca field, and so be comparable to the original stock of oil.

2. Unaltered by refining treatments except for dewaxing. The wax constituents were considered of insufficient interest to warrant investigation at the present time.

3. Of interest to manufacturers of commercial products. The large quantities of lubricants of 10- and 20-W SAE viscosities used by the automotive industry make of particular importance the fraction of crude oil ranging in viscosity from 150 to 200 Saybolt seconds at 100° F (about 0.32 to 0.54 stoke KV).

4. Of as simple constitution as possible. It is to be expected that lower-boiling fractions contain compounds of lower molecular weight and consequently fewer isomers than the higher-boiling ones. To avoid complicating the problem unnecessarily, the low-boiling lubricant fraction was favored.

5. An oil about which as much as possible is already known. Research has centered on the lower-boiling fractions of the heavy oil, viz, the work of Mair and others of this Project. Less information is available on synthetic hydrocarbons of high boiling points than on those of lower boiling points.

After consideration of lubricating oils from various sources, a stock produced by the Continental Oil Co. was tentatively chosen. An assay distillation was made in the laboratory of the stocks of that company designated as 150 Pale Raw and 400 Pale Raw, and the results are shown in figure 1. These distillations were made under high vacuum (10⁻⁴ mm Hg) in the glass still shown in figure 2. Temperatures were read on a thermometer inserted in the well at the top of the column. The graph shows that both stocks yield distillates having viscosities between 0.32 and 0.54 stoke (150 to 200 Saybolt seconds) though the 400 Pale Raw increases to a considerably higher value. The curves of boiling point and refractive index also indicated the ranges in these properties which were to be expected. In figure 3 is reproduced the chart furnished by the Continental Oil Co. showing the history of the refining operations to which the products had been subjected. It is obvious that if the two Pale Raw stocks are combined in approximately equal proportions (7.75 to 7.3%) the resulting mixture represents all of the crude oil above the gas-oil fraction except the wax portion which was removed by pressing and by the Barisol process (refrigeration and centrifuging with benzene and ethylene chloride), the vacuum flux, and the vacuum residue. The stock was described as a well-segregated Oklahoma City crude oil and therefore reasonably easily reproduced in the future. Consideration of these characteristics led to the final choice of this oil.

[4] Frederick D. Rossini, Proc. Am. Petroleum Inst. (Nov. 1937); Oil Gas J. **36**, No. 26, 193 (1937); Refiner Natural Gasoline Mfr. **16, 545** (1937).
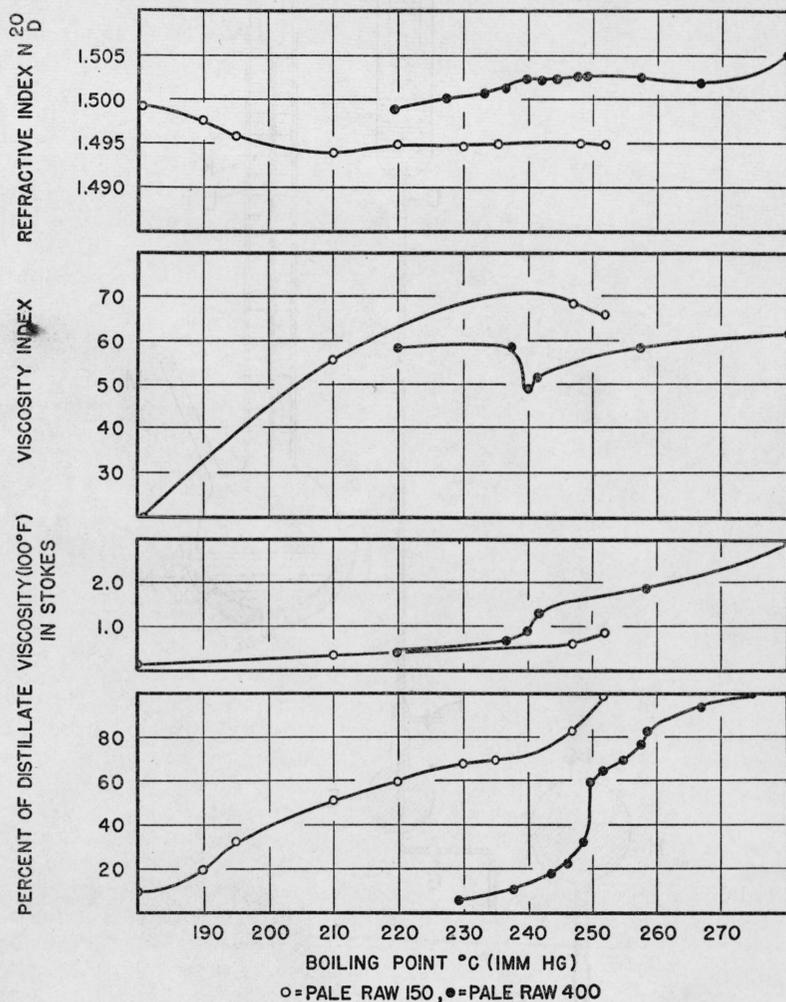
FIGURE 1.—*Assay distillation of samples of 150 Pale Raw and 450 Pale Raw oil from the Oklahoma City field.*
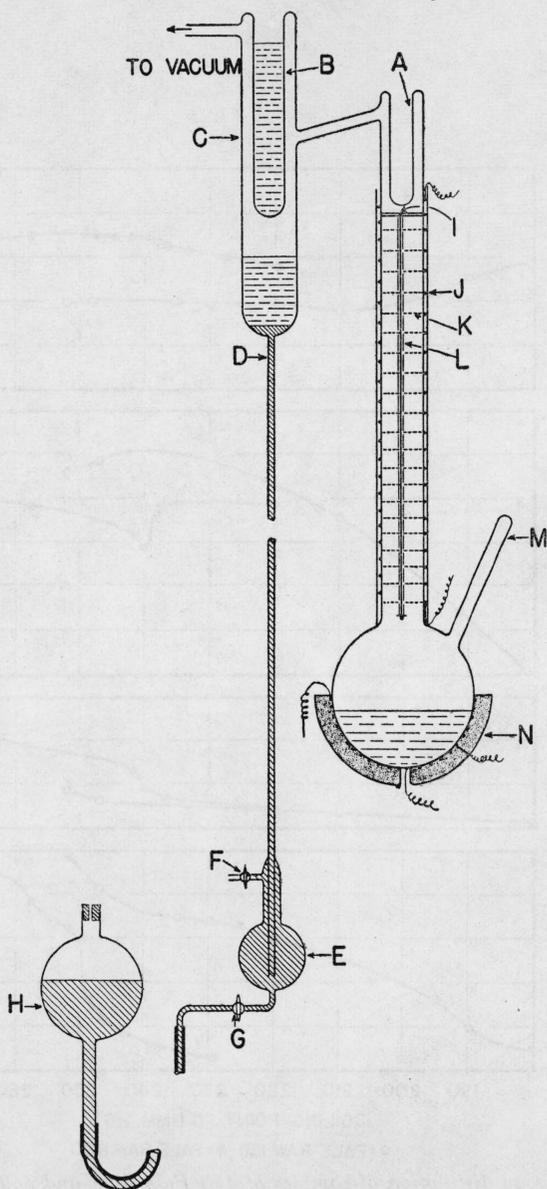
FIGURE 2.—*Small glass still for high-vacuum distillation with arrangement for removing fractions through mercury seal without interrupting the distillations.*

A, cooler for producing reflux when necessary; B, condenser for distillate; C, receiver for distillate; D, mercury column barometric height; E, mercury seal through which distillate is removed by lowering mercury level; F, stopcock through which oil is discharged after collecting above the lowered mercury level; G, stopcock for keeping mercury in E while distillate is condensing; H, leveling bulb for drawing mercury out of E when distillate is removed; I, center rod of steel suspended from glass cross bar; J, heating coil sheathed on outside with mica; K, disks made from perforated aluminum sheet; L, spacers made of sections of steel tube; M, tube for filling; N, electric heater.
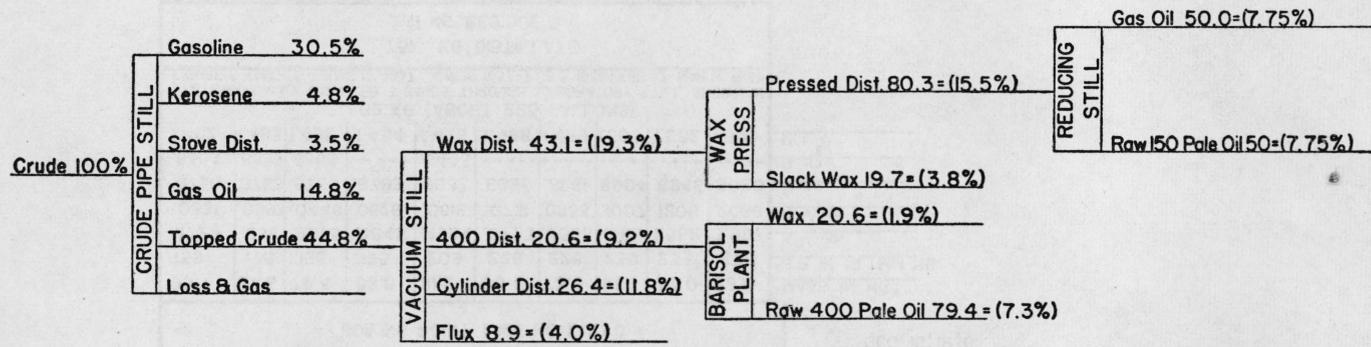
YIELD RAW LUBES FROM OKLAHOMA CITY CRUDE

(FIGURES IN PARENTHESES ARE BASED ON CRUDE)

FIGURE 3.—*Diagram showing treatment of crude oil at Continental Oil Refinery to produce material designated as 150 and 450 Pale Raw Oil.*

(Courtesy of L. L. Davis, supervisor of Process Division, Continental Oil Co.)

RECEIVED FROM REFINERY NOV. 1936 (OKLAHOMA CITY CRUDE REFINED BY CONTINENTAL OIL CO. AT PONCA CITY) SHIPPED TO SUN OIL CO, FOR DISTILLATION IN SEMI-COMMERCIAL STILL.　　　　APPROXIMATE MASS 1095 KG*

RECEIVED FROM REFINERY, DEC. 1936 SHIPPED TO A.P.I. PROJECT 6, NAT. B. OF S.

555 KG* OF "150 PALE RAW"	
DENSITY $\frac{20}{4}$	.8931
SAYBOLT UNIVERSAL VIS. 100	156
KINEMATIC VISCOSITY 100	.3339
KINEMATIC VISCOSITY 210	.0487
REFRACTIVE INDEX $^{20}_D$	1.486
VISCOSITY INDEX	58
BOILING POINT °C 1 MM HG	201

540 KG* OF "450 PALE RAW"	
DENSITY $\frac{20}{4}$	.9048
SAYBOLT UNIVERSAL VIS. 100	487
KINEMATIC VISCOSITY 100	1.130
KINEMATIC VISCOSITY 210	.0984
REFRACTIVE INDEX $^{20}_D$	1.503
VISCOSITY INDEX	51
BOILING POINT °C 1 MM HG	231

VACUUM CYLINDER DISTILLATE 183 KG.† — 42† KG. VAC. RES.

405 KG (120 GALLONS) OF 150 PALE RAW AND 410 KG OF 450 PALE RAW MIXED AND DISTILLED THROUGH SEMI-COMMERCIAL VACUUM STILL

UNDISTILLED | UNDISTILLED
150 PALE RAW | 450 PALE RAW

815 KG* (240 GALLONS)
SAYBOLT UNIVERSAL VISCOSITY 100 269
BOILING POINT 1 MM HG 212 °C

151 KG† 126 KG†
SHIPPED TO PROJECT 6
DEC. 16, 1936

93.7	67.6	79.4	88.5	81.2	88.8	73.9	66.1	77.0	86.0	MASS IN KG†
159	178	185	195	209	228	228	239	238	278	B.P. IN °C 1 MM HG.
.1729	.2311	.2875	.3845	.4994	.6773	.8508	1.163	1.582	3.897	K.V. 100
.0331	.0393	.0448	.0528	.0612	.0731	.0833	.1007	.1208	.2086	K.V. 210
.8750	.8763	.8769	.8799	.8832	.8866	.8881	.8904	.8946	.9020	D 100
.8354	.8359	.8363	-----	.8443	-----	-----	-----	-----	-----	D 210
1.492	1.492	1.492	1.494	1.496	1.498	1.499	1.500	1.502	1.509	R.I. $^{25}_D$

802 KG. (ABOUT 225 GALLONS)
SYSTEMATICALLY DISTILLED 3 TIMES THROUGH LABORATORY STILL SHOWN IN FIGURE 5 (MAR. 5 - JUNE 17, 1937 ; AUG 18 1937 - FEB 3 1938 ; FEB 10 - MAR. 14 1938

751 KG† DISTILLATE
11 KG RESIDUE

227 FRACTIONS OF ABOUT 1 GALLON EACH

* CALCULATED FROM VOLUME
† WEIGHED

FIGURE 4.—*Chart giving history and properties of the Oklahoma City lubricating oil being investigated by Project 6 of American Petroleum Institute.*
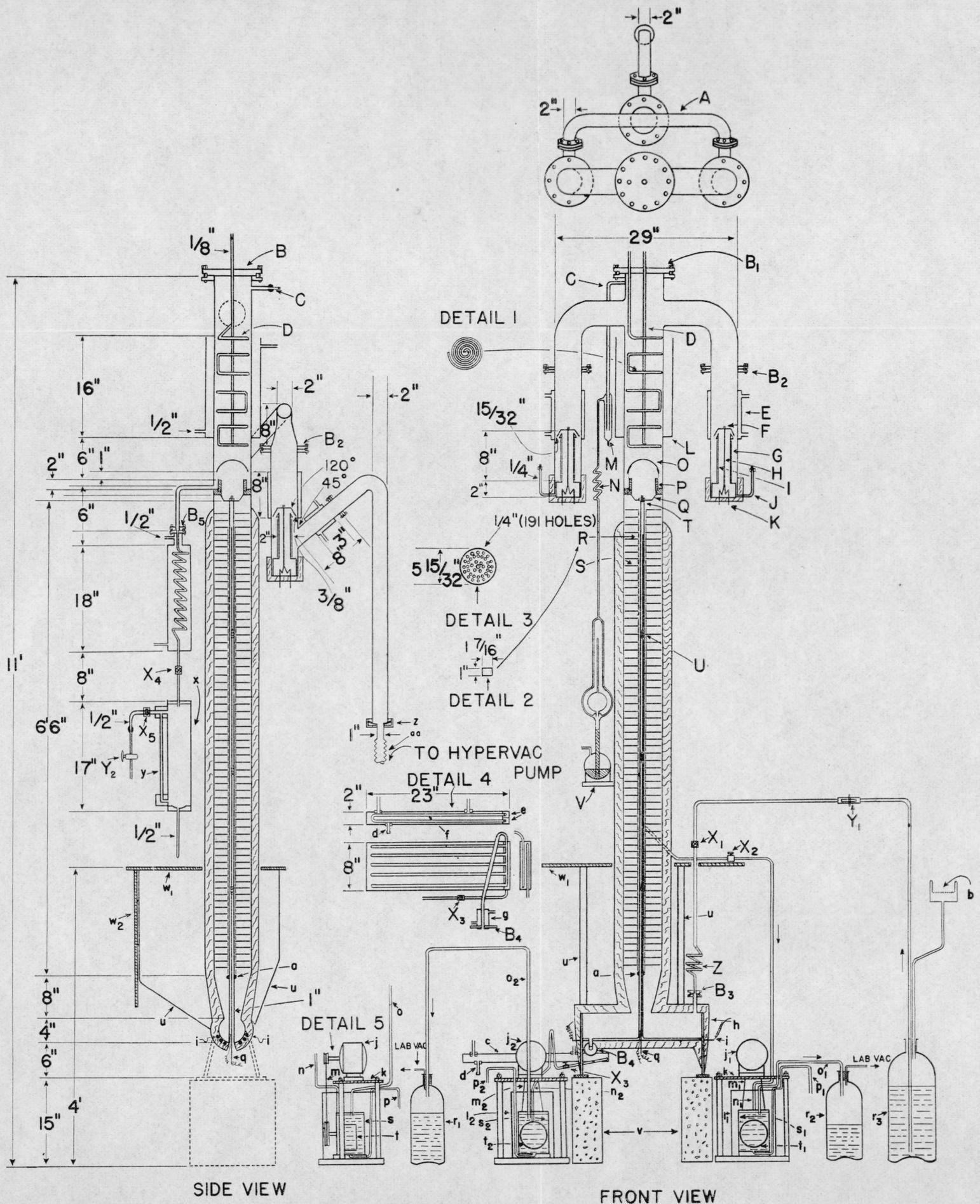
FIGURE 5.—High-vacuum still for distilling noncorrosive materials by the continuous passage method at rates of several gallons a day.

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III. PRELIMINARY TREATMENT OF THE OIL

Through the courtesy of the Sun Oil Co., the oil was distilled through a semicommercial vacuum still into fractions which could be handled conveniently in the laboratory. In November 1936, the Sun Oil Co. received from the Continental Oil Co., Ponca City, Okla., 165 gallons of Pale Raw having a viscosity of 156 Saybolt seconds (0.32 stoke) and 157 gallons having a viscosity of 487 seconds (1.03 stokes). 120 gallons of each were blended [resulting in a mixture having a viscosity of 269 Saybolt seconds (0.57 stoke)] and cut by a succession of passes through the vaporizer of the still into nine 10-percent fractions of distillate and a 10-percent residue of unvaporized material and "tower-holdup." For each passage the temperature of the vaporizer was regulated to obtain the desired volume of distillate. The oil was passed through the vaporizer at a rate of about 1 to 2 gallons a minute, and the pressure in the vaporizer was maintained at about 5 to 8 mm Hg, with a maximum temperature of 343° C (650° F). Each of these fractions was run into a new 30-gallon drum which had been purged with nitrogen. The fractions, together with 24 gallons of the undistilled lighter and 35 gallons of the heavier stock were sent to the laboratory in December 1936. Later approximately 51 gallons (183 kg) of "vacuum cylinder distillate" and 11 gallons (42 kg) of "vacuum flux" were received at the laboratory from the Continental Oil Co. Figure 4 shows the history of the oil from the refinery through the third distillation in the laboratory and the properties of the material up to the laboratory distillations.

IV. DESIGN OF LABORATORY STILL

Since distillation is the foundation of the production of most petroleum products, a careful study was planned of the distillation of the material before the removal of any constituents. For further fractionation of the oil in the laboratory, it was necessary to design a still which could (a) be erected in a limited laboratory space, (b) accommodate the 800 kg of oil which was to be distilled, (c) be used later on small quantities, (d) function at vacua obtainable by diffusion pumps, (e) have a small "hold-up" and pressure drop between vaporizer and condenser, and (f) be as efficient as compatible with the other requirements.

Figure 5 shows the still in detail as developed, except for minor changes which would be expected to improve the design. The still may be used either for continuous distillation of large quantities or for batch operation where only small quantities are available. The still in this laboratory has been used almost continuously 24 hours a day and 5 days a week for a year without major repairs. When operating properly, the McLeod gage which was attached at the head of the column showed pressures of the order of 10^{-4} mm Hg. All 10 fractions from the preliminary distillation, including the residue, were distilled through it. About 11 kg of undistilled material and washings from the still remained after the third distillation. This material resembled thin tar in color and viscosity.

The column, shells of the diffusion pumps, and the vaporizer were made of welded pipe fittings.[5] The vacuum was maintained by the three diffusion pumps, two of which were arranged in parallel and supported by the third, as shown on *A* of figure 5. The diffusion pumps were backed by a large mechanical pump as shown (Hypervac 20, marketed by Central Scientific Co.). These diffusion pumps were of the usual umbrella type of construction and were operated with oil instead of mercury. Oils suitable for the purpose are obtainable commercially.[6] The oil was boiled by ½ kw Calrods, *K*, wound into coils and welded into the bottom of the shell as shown. The heat was controlled by a variable resistance in series. The umbrellas of the two fast, fine pumps were made from aluminum muffin pans by expanding and shaping them slightly, and the umbrella of the coarse pump was made from a dipper. As shown in the figure, the clearance between the edge of the umbrellas and the walls of the shells was greater for the two fine pumps than for the coarse pump. These are the only shaped parts which would otherwise require spinning. The copper rod, *H*, was brazed to the Calrod and served the double purpose of conducting heat up the path of the hot vapors and of supporting the umbrellas which were held in place by nut *F*. The chimneys, *I*, were of brass and fabricated by spinning the joints together. The lower section of the chimneys fitted loosely into the shells of the pumps and were serrated on the lower edge so that the condensed oil could return to the heated zone. *G* was a glass tube surrounding the chimney for thermal insulation. Oil was introduced into the pumps through the ¼-inch iron tubes, *J*, which were closed by soldered iron plugs. The condensers, *E*, were of brass and brazed to the iron shells of the pumps. Each pump requires about 200 ml of oil. The oil was found to lose its effectiveness after about 3 weeks' use but could be reclaimed by distillation in the glass still. A spiral, *N*, was necessary in the tube, *C*, attaching the McLeod gage to the head of the still to allow for the expansion of the column as it was heated. *M* is the vapor trap for the gage. The upper part of *C* was ½-inch copper tube and the glass trap was joined to it with wax. The diffusion pumps were supported by a large mechanical vacuum pump (Cenco Hypervac 20) which was connected to the still by a section of flexible metal tube, *aa*, and a pipe union, *z*, the faces of which were coated with "glyptal resin" before tightening.

All the flanged joints, B_1, B_2, B_3, B_4, and B_5, were made tight with lead gaskets cut from ⅛-inch lead sheet. Water jackets, *g*, were built in contact with flanges B_4 and B_5 (fig. 1) because they became hot enough, when the very high fractions were being distilled, to cause the lead gaskets to flow.

To remove the distillate and residue, if the still was to be run continuously, it was necessary to design a pumping system since there was insufficient height available in the laboratory for a vacuum leg. The pumps used did not need to produce as high vacuum as that within the still, because of the weight of the short column of oil above them. Two Cenco laboratory pumps were adapted to the purpose, as shown

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[5] At the time of construction, the welding operations cost about $430; the water jackets of the pumps, jets of the pumps, the perforated aluminum disks, and the iron rings for spacing the disks cost about $180; and the Calrods used for heating the pumps and still cost about $50.

[6] It was possible to make a satisfactory oil for the pumps from Cenco pump oil. This was done by three successive treatments of bubbling air through the hot oil for a period of 30 minutes and distilling in the small glass still, and finally passing the fraction boiling at about 220° C. at 1 mm Hg through silica gel.

at the bottom of the figure. The oil was drawn into the ports, n_1, and n_2, ordinarily used for pumping gases and discharged into the boxes of the pumps, s_1 and s_2, where it formed its own seal around the working parts, t_1 and t_2. Oil was kept at the normal level in the pumps by drawing it out into containers, r_1 and r_2, through tubes o_1 and o_2 which projected down into the boxes to the proper depth. The pumps were placed below the driving motors, j_1 and j_2, and were set in tanks, l_1 and l_2, to catch overflows and leaks of oil from the pump boxes. Water coolers were placed in both the distillate and residue lines to lower the vapor pressure of the more volatile material so that it could be pumped. The cooler for the distillate was a copper coil as shown. For the residue, however, the multiple passage unit shown at c and in detail 4 was adopted because the material to be cooled was hotter and more viscous than the distillate. The headers, e, were made from single blocks of brass and the tubes, f, were brazed in place. d was a drain for emptying the jacket. The coolers, c and g, were brazed together because occasionally they became hot enough to soften solder. Both pumps had drain tubes from the bottom, p_1 and p_2, so that they could be emptied completely. By using the receiver, x, in the distillate line, the fractions could be separated without contamination (see section V). This receiver was also used to accumulate enough distillate to prime the pump. The gage glass, y, was calibrated to show the volume in the receiver.

The vaporizer was heated by three 1-kw Calrods wound around it, but the method shown in figure 5 of heating with six ½-kw Calrods, i, placed parallel would be an improvement. The heat was controlled by the number of Calrods used and by varying the voltage with a 3-kw transformer.

Arrangement was made to compensate heat losses in the column by heat from the units, q, in the central tube, u, of the column, but this was found necessary only for very high-boiling material. As shown by the figure, u was closed at the top and welded through the vaporizer at the bottom. All the heating units and motors were controlled from the transite panel, W_2, which was supported by a strap iron frame, u. The preheater, Z, was used only when the oil was being passed into the still at the rate of 3 or 4 gallons an hour.

All the valves in the vacuum system were Kerotest diaphragm valves with ¼-inch bores (X_1, X_2, X_3, X_4, and X_5). No trouble was experienced at any time with leaks through the stems of these valves, but when they were open to the atmosphere the precaution was taken to place a stopcock in series (Y_2). A stopcock alone was not satisfactory because the grease was sometimes dissolved by the oil. Regulation of the oil flow into the still by these valves was not satisfactory. It was found more satisfactory to open valve X_1 wide and depend on stopcock Y_1 to regulate the flow from the supply reservoir, r_3.

Sight glasses, not shown in the figure, through which the streams of oil could be observed were placed in the inlet line and the outlet line of the residue. The material admitted to the still was filtered through the fine copper gauze, b, to remove sediment which tended to clog valves.

The water jacket, L, at the top of the still was not sufficient alone to prevent oil vapor from passing over into the diffusion pumps. The flat spirals of ¼-inch copper tube, D, shown in the drawing and in

detail 1 were found effective without much pressure-drop through them. The cooling water had to be kept down to 20° to 25° C in the still and the diffusion pumps. The perforated aluminum plates, S and detail 3, were used for evaporating surface because they were not corroded by sulfur in the oil and because they produce only a small drop in pressure. There were 65 of these plates and they fitted snugly into the column but dropped into place without force. These were spaced in the column by the iron rings, R, the dimensions of which are shown in detail 2. The rings were made to fit loosely over the central tube, U, and the whole column of rings and aluminum disks rested on the ring welded on the central tube at a.

The collecting ring at P was made in two parts, the collar being tapered at the bottom to fit into the flat ring. The flat ring was split and made to fit tightly into the column of the still by forcing a wedge into the split. Q was a support made of a strip of brass bolted to the central tube at T.

V. OPERATION OF VACUUM STILL [7]

To start a distillation, the pump, s_2 was filled with undistilled oil and started, valve X_2 was closed and the still evacuated by the diffusion and Hypervac pumps. About 15 minutes was required to reach a pressure of the order of 10^{-4} mm Hg. Oil was then admitted slowly to the still until it began to collect in the residue bottle, r_1. Valves X_1 and X_3 were then closed. The siphon tube near X_3 insured that the vaporizer contained oil to the height of the bend. The heat was then applied until distillate began to collect in the receiver. A small stream of oil was admitted to the still through X_1 and Y_1 and the distillation continued until about a liter had accumulated in the receiver. X_4 was closed, X_5 and stopcock Y_2 opened, and X_2 opened to allow the oil to run into pump t_1. Valve X_5 and the stopcock were then closed, and the receiver was exhausted by the pump. Valve X_3 was opened, and the rate of return to the top of the column regulated as desired by partially closing X_4. The ratio of return to the distillate was determined by comparing the rates of accumulation in the receiver with valve X_4 open and with it adjusted to running conditions. If the distillate was to be taken off in batches, X_2 was closed, the content of the Cenco pump was drawn out through p_1 and the process of emptying the receiver into the pump as described above was repeated when another fraction of distillate had accumulated. If the fractions were to be drawn off continuously, valve X_2 was left open with the pump running and the oil was kept at the normal level in the pump by drawing into bottle r_2, as described above for the residue.

For the first distillation the oil was fed into the still from the drum containing fraction 1, the distillate collected in gallon glass bottles, and the residue run into a second drum. The oil was passed through at a rate of about 3 gallons an hour and about half was taken off as distillate. The second fraction was then fed in and the residue collected in the same drum with the residue from the first fraction. The combined residues were then fed through, followed by the third fraction. This procedure was continued until all the cuts had passed through the still and about half a barrel of residue remained. Towards

the end of the distillation no water was run through cooler, e, because the residue was very viscous. Samples of about 25 ml were reserved from each fraction of distillate for the determination of the boiling point and refractive index. For this distillation X_4 was kept open so that practically no oil was returned to the top of the column.

The second distillation was run at the rate of a liter an hour with X_4 set so that about three-quarters of the distillate was returned to

1.504   1.501   1.498   1.495   1.492   1.489

GRAPH OF FIRST DISTILLATION UNDER HIGH VACUUM OF A HEAVY FRACTION OF OIL
FROM PONCA CITY, OKLAHOMA
BOILING RANGE IN °C (1 MM HG)

150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300

70 60 50 40 30 20 10
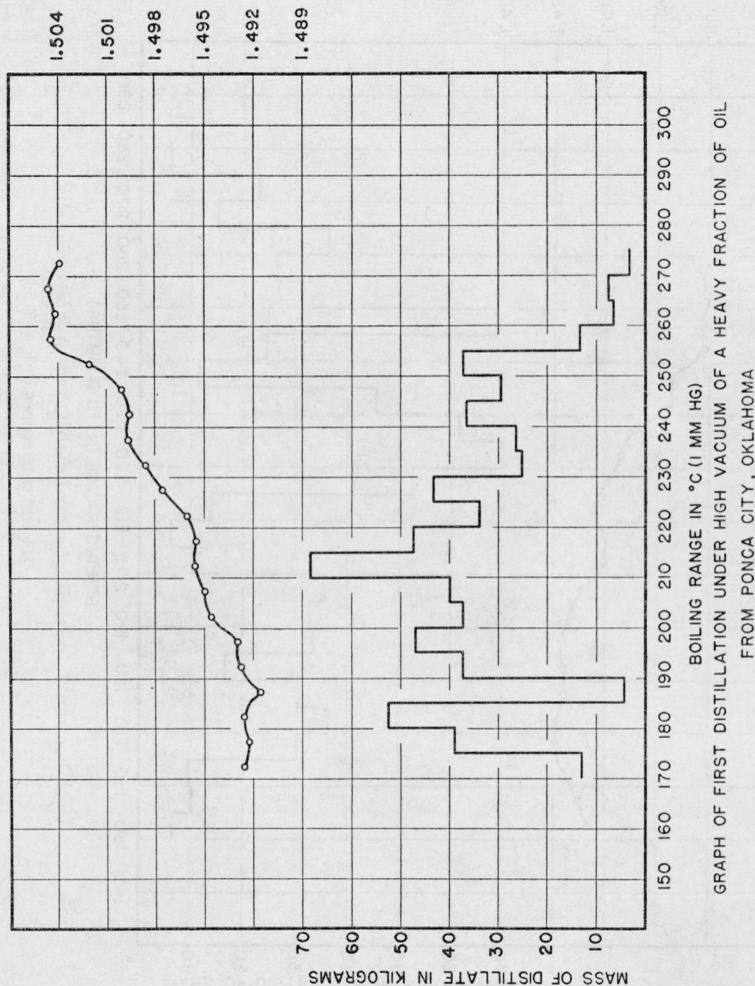
MASS OF DISTILLATE IN KILOGRAMS

FIGURE 6.—*Graph of first distillation in laboratory still.*
[Cut in approximately 1-gallon fractions, but plotted in 5° intervals.]

the column. The fractions from the first distillation were fed into the reservoir, r_3, in rotation interspersed with residues, as with the first distillation. Figures 6 and 7 show graphs of the first two distillations. The boiling points were determined on the small samples after the distillations were completed, because a suitable apparatus was not available at the time of the distillation.

The third distillation was run in the same way, except that all the fractions of distillate and residue were fed into the supply reservoir
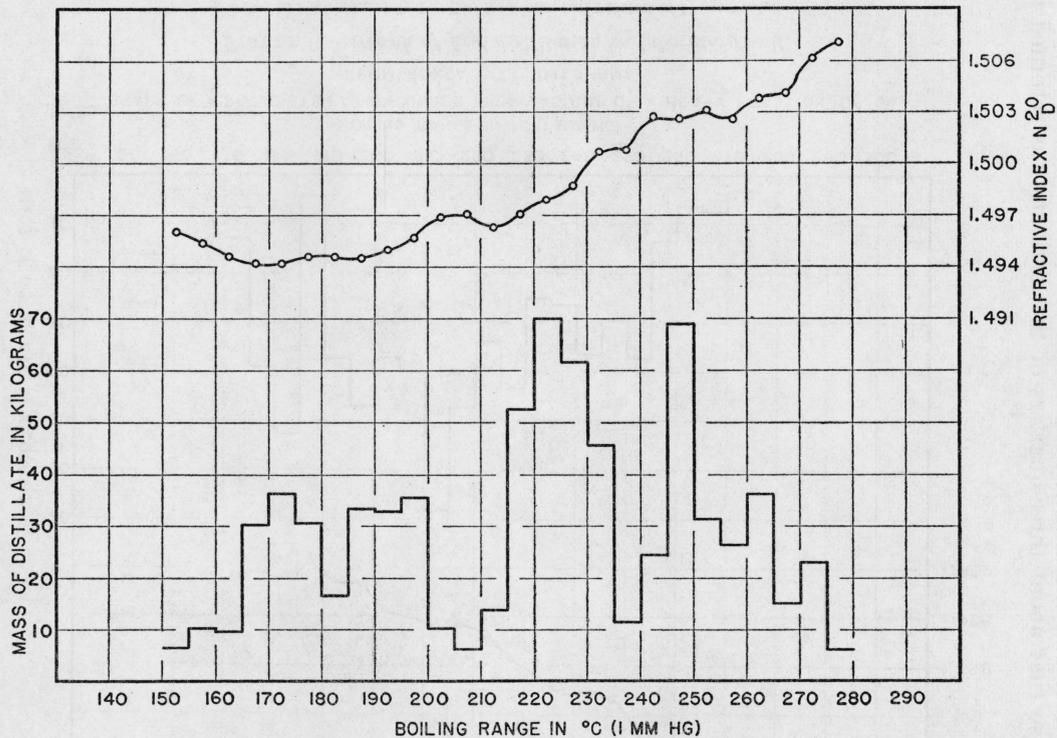
FIGURE 7.—*Graph of second distillation in laboratory still.*

[Plotted as in figure 6.]

as nearly as possible in order of boiling points.   It was found that the
fractions from the distillations were not always successively higher-
boiling, probably because high-boiling residues had been mixed with
low-boiling fractions or because of the operation of the still.   Figure
8 shows the graph of the third distillation.

VI. APPARATUS FOR DETERMINING BOILING POINTS AT LOW PRESSURES

Since the pressure in the still was not constant, it was impossible to
determine the boiling points of the cuts by their condensation points
at the top of the column.   The apparatus described by Schicktanz [8] for
determining boiling points at low pressures was not sufficiently rapid
to keep pace with the distillation.   Therefore, it was necessary to
build an apparatus for the purpose.

Figure 9 shows the construction of one unit from a battery of six
which was finally used.   The oil was stirred and sprayed over a
thermometer by a pump which consisted of a metal plunger, J, worked
up and down inside the evacuated apparatus by the solenoid, H.   As
the plunger dropped, boiling oil was pumped through Q and reservoir
P and was thrown over the bulb of the thermometer, I, from the jets,
L.   When the plungers rose, the oil drained back to the boiler again
through O.   Tube G was necessary to equalize the pressure above and
below the plungers when gas was admitted rapidly into the apparatus.

The plungers were made in two sections, the upper of iron and the
lower of aluminum for lightness, and to allow for expansion on heating
were not fitted tightly into the tubes.   Some difficulty was experienced
with warping until the metal became annealed.   The springs, F,
above and below the plunger absorbed the recoil when the apparatus
contained no oil.

The solenoid was wound with 2 pounds of No. 28 copper wire and
operated directly on 110 volts d-c, drawing about ½ ampere.   The
solenoid was connected through plug S with a neon sign flashing unit.
With the proper condenser across the contacts of the flasher to prevent
arcing, all six solenoids could be operated simultaneously.   Individual
light flashers were tried but were not sufficiently rugged.

The heater, N, was made by winding about 25 ohms of No. 20
Chromel wire around the framework of the box and covering with wet
asbestos paper.   The heater was controlled by a rheostat and a snap
switch, U.   The box was suspended by wires from the supporting
frame, and electrical connections were made through the plug, T, so
that it was easily removed.

The pressures were read with a compound McLeod gage calibrated
to multiply the pressure by 10, 200, and by 10^4.   An attempt was
made to use the decomposition pressures of silver carbonate at several
temperatures for regulating the pressure, but they were not constant.
Instead, the pressure was changed by introducing small quantities of
gas through the three-way stopcock, R, and reading the pressures
directly on the gage.

The thermometers were calibrated in 0.5° intervals with a range
from 150° to 300° C and were easily removed through the cap, A, for
checking the calibration.

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[8] Sylvester T. Schicktanz, J. Research NBS 14, 685 (1935) RP796.
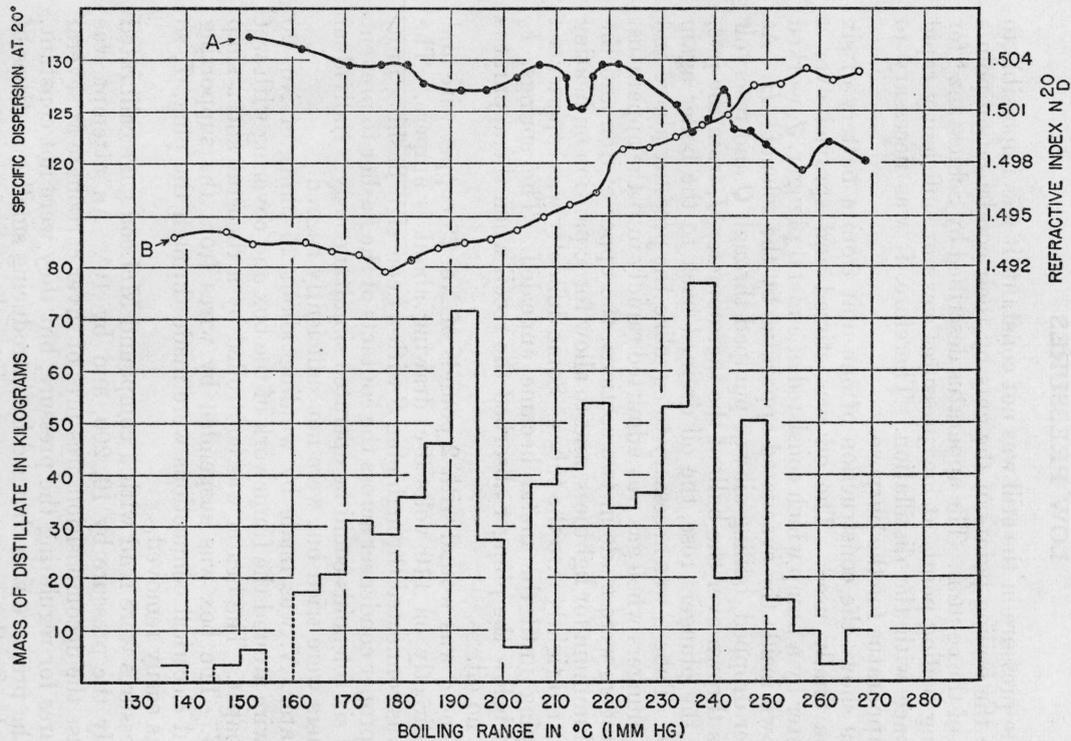
GRAPH OF THIRD DISTILLATION UNDER HIGH VACUUM OF A HEAVY FRACTION OF OIL
FROM PONCA CITY, OKLAHOMA

FIGURE 8.—*Graph of third distillation in laboratory still.*

[Plotted as in figure 6.]

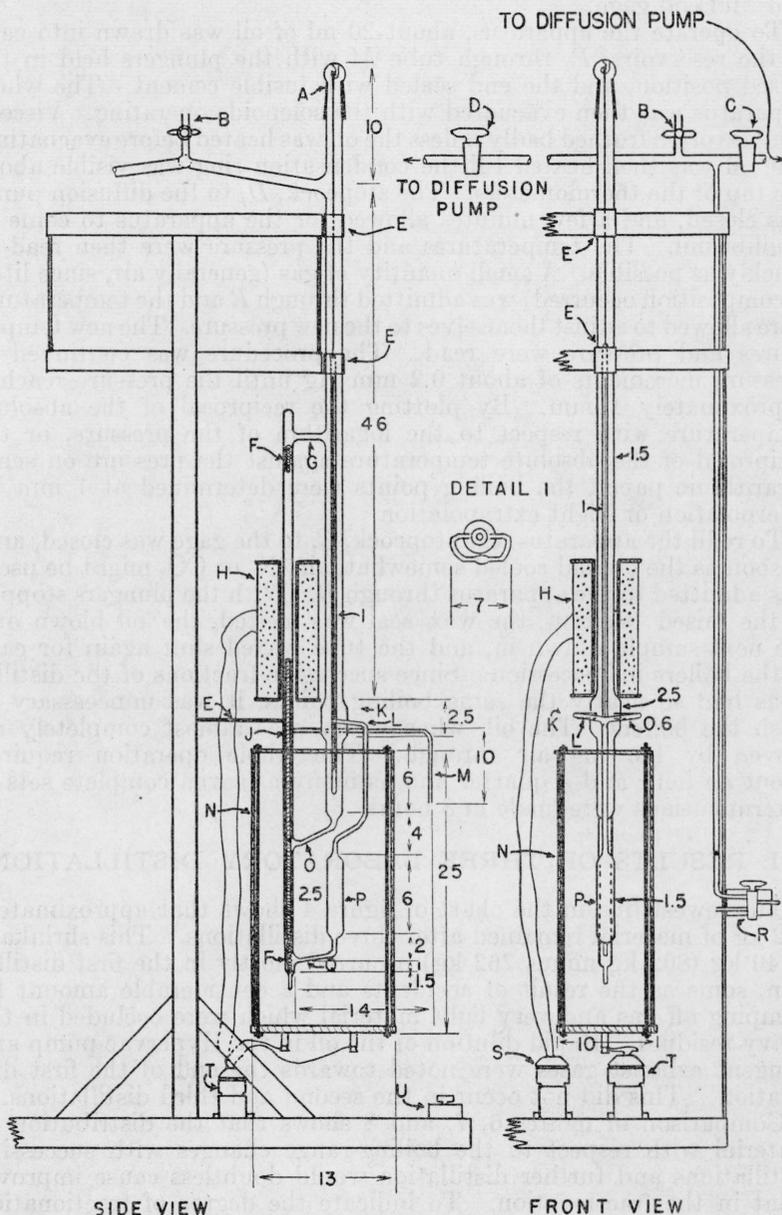*A*, Curve of specific dispersion; *B*, curve of refractive index.

FIGURE 9.—*Unit of multiple apparatus for determining rapidly boiling points at low pressures.*

Six of these units were mounted compactly on an iron frame (fastened by clamps at E) and connected to a common diffusion pump and McLeod gage.

To operate the apparatus, about 20 ml of oil was drawn into each of the reservoirs, P, through tube M with the plungers held in the raised position, and the end sealed with fusible cement. The whole apparatus was then evacuated with the solenoids operating. Viscous samples often frothed badly unless the oil was heated before evacuating. The oil was then heated till the condensation ring was visible about the top of the thermometers. The stopcock, D, to the diffusion pump was closed, and a few minutes allowed for the apparatus to come to equilibrium. The temperatures and the pressure were then read as quickly as possible. A small quantity of gas (generally air, since little decomposition occurred) was admitted through R and the temperatures were allowed to adjust themselves to the new pressure. The new temperatures and pressure were read. The procedure was continued in pressure increments of about 0.2 mm Hg until the pressure reached approximately 1 mm. By plotting the reciprocal of the absolute temperature with respect to the logarithm of the pressure, or the reciprocal of the absolute temperature against the pressure on semilogarithmic paper, the boiling points were determined at 1 mm by interpolation or slight extrapolation.

To refill the apparatus, the stopcock, C, to the gage was closed, and, as soon as the oil had cooled somewhat, air (N_2 or CO_2 might be used) was admitted to the apparatus through B. With the plungers stopped in the raised position, the wax seal was melted, the oil blown out, the next sample drawn in, and the tube waxed shut again for each of the boilers in succession. Since successive fractions of the distillations had so nearly the same boiling points, it was unnecessary to wash the boilers. The oil, when warm, was almost completely removed by blowing air through. The whole operation required about an hour and a quarter and as many as seven complete sets of determinations were made in 8 hours.

VII. RESULTS OF THREE LABORATORY DISTILLATIONS

The lowest line in the chart of figure 4 shows that approximately 762 kg of material remained after three distillations. This shrinkage of 40 kg (802 kg minus 762 kg) occurred mostly in the first distillation, some as the result of accidents and a considerable amount by pumping off gas and very light material which were occluded in the heavy residues. Rapid dilution of the oil in the Hypervac pump and pungent exhaust gases were noted towards the end of the first distillation. This did not occur in the second and third distillations.

Comparison of figures 6, 7, and 8 shows that the distribution of material with respect to the boiling-range changes with successive distillations and further distillation would doubtless cause improvement in the fractionation. To indicate the degree of fractionation which was obtained, samples of fractions from the third distillation boiling at 198°, 241°, and 253° C, respectively, were distilled in the small glass still. The boiling points of the distillate ranged over 20° to 30°, but 30 to 40 percent of each sample boiled within a range of 5°. The boiling points of the samples themselves were within 5° of the temperatures of the constant-boiling portions and were con-

siderably more easily determined than the latter values. The boiling points of the fractions were, therefore, used in plotting the distillation curves of the figures. The tendency to concentrate in four temperature ranges is marked in both the second and third distillations; namely, between 183° and 200°, between 210° and 225°, between 230° and 240° (240° and 250° on second distillation), and between 245° and 250° (260° to 265° on second distillation).

TABLE 1.—*Effect of change in pressure on the boiling points of fractions from the third distillation*

Fraction	Boiling point			
	0.1 mm Hg	1.0 mm Hg	10 mm Hg	40 mm Hg
	°C	°C	°C	°C
3	149	159	199	243
5	158	166	203	248
19	164	175	214	263
38	177	183	224	269
68	179	196	234	276
90	190	201	239	287
96	192	206	253	295
105	196	208	249	298
126	217	222	261	301
142	201	232	273	312
183	237	253	288	322
Average Δt	13	40		43

The effect on the boiling points of varying the pressure is shown in table 1 for some of the fractions from the third distillation. Boiling points above 295° C were obtained by extrapolation but are considered fairly reliable, because the relation between the reciprocal of the absolute temperatures and the logarithms of the pressures is nearly linear at the higher pressures. At pressures less than about 1 mm Hg, the rate of decrease in the boiling point with decreasing pressure apparently becomes less. The behavior may be caused by the relatively greater effect of superheating resulting from the hydrostatic head of oil in the apparatus.

The curves of refractive index of all three distillations bear a general resemblance but the scales are large and the details cannot be interpreted too closely. The curve of specific dispersion [9] which is shown for the third distillation is also plotted on a large scale. Some of the variations are greater than the precision of the measurements (±2), however, and minima in the specific dispersion curve appear to coincide roughly with the large volumes of distillate.

Figure 10 compares the preliminary distillation of the naphtha fraction of the oil on which the earlier work of this project had been done with the third distillation of the new lot of lubricating oil. It is to be observed that considerably more material is available in about the same range of temperature for the work on the lubricating oil than was available for work on the naphtha fraction.[10] Large concentrations in volume in small ranges of temperature occur in both
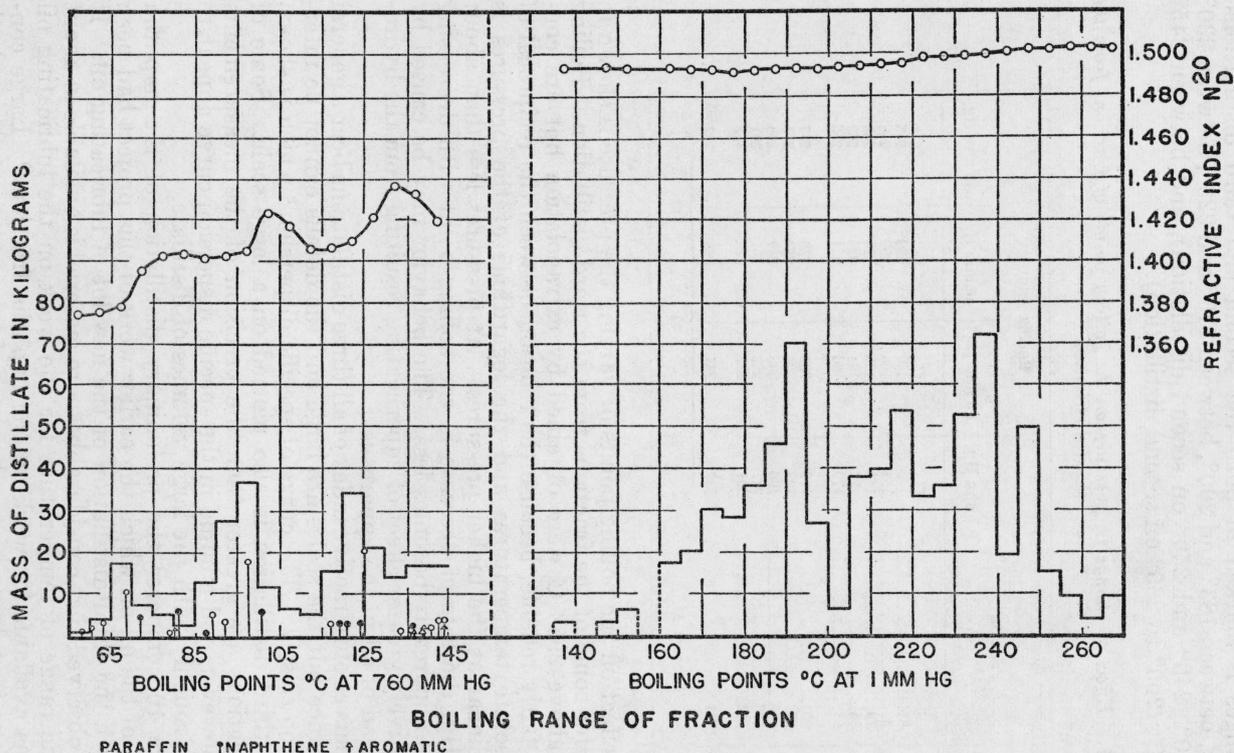
FIGURE 10.—*Graph comparing the results of three distillations of the naphtha fraction from the Ponca City crude petroleum used for the original investigation with those of the three distillations of the lubricating fraction of the Oklahoma City crude petroleum to be used for this investigation.*

fractions, but the refractive index shows much less variation in the distillate of the lubricant than of the naphtha fraction. The smaller variation probably indicates, as was found in the work on another midcontinent petroleum, that a large percentage of molecules were not "pure types" but contained both alkyl groups and naphthene rings [11] or alkyl groups, naphthene rings, and aromatic rings,[12] rather than being purely paraffinic, naphthenic, or aromatic.

It should be noted that the two graphs are not strictly comparable since the wax (the readily crystallized material) was removed from the lubricant material before distillation. The analogous material (readily crystallized) in the naphtha fraction proved to be the normal hydrocarbons, and these also constituted the major portion of the large concentrations in volume. The wax which was removed probably contained a large percentage of normal hydrocarbons, since the melting points of most of the hydrocarbons with molecular weights likely to be found in this material [13 to 21] are reported in the literature as above room temperature. However, it has been shown that the wax contains other types of hydrocarbons as well. It may be expected also that considerable normal compounds and compounds with high melting points were retained in solution in the liquid constituents. It seems probable, therefore, that "dewaxing" would remove normal hydrocarbons and compounds with long chains in the largest proportion but also remove other high-melting compounds which were present in considerable concentrations. It is also probable that none of these types of compounds was removed completely. This is especially likely since many of the molecules which boil in this range are not pure types.

In the naphtha fraction the large volumes occurred near the boiling points of the normal hydrocarbons. Though no values for the boiling points of hydrocarbons of high molecular weight are available in the literature, it is not likely that the concentrations in volume of distillate in the lubricating oil are caused by successive normal hydrocarbons. It is suspected that the six-membered ring is the unit of difference in molecular weight of the families of hydrocarbons in the lubricating oil which boil close together.

WASHINGTON, July 19, 1938.

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