Production of creosote oil by medium temperature carbonization of two Montana coals
by Yasushi Ichikawa

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering
Montana State University

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Coal tar of the grade A specification for creosote-coal tar solutions was produced from Roundup and Red Lodge coal tar by centrifugation.

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ABSTRACT

Production of the A.W.P.A. (American Wood Preservers' Association) specification grade of creosote oil was the purpose of this thesis. Montana State College Engineering Experiment Station has been producing char from coal from Montana and neighboring states. Coal tar is the main byproduct of char. Oil products examined from this plant were produced at moderate carbonization temperature (650-800 C). Yields of product oil were 12 gallons per ton of Red Lodge coal and 10 gallons per ton of Roundup coal.

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I INTRODUCTION

For the past several years the Engineering Experiment Station of Montana State College has been working on the production of char for phosphorous manufacture from coal from Montana and its neighboring states (4,5). It has a semi-commercial plant which can treat about six or seven tons of coal a day. This thesis was aimed at obtaining an A.W.P.A. (American Wood Preservers' Association) specification grade of creosote oil from the liquid product of the char plant (1).

The coal which was used in the char plant may be classified as a sub-bituminous, and is produced in the western states of Montana, Wyoming, Utah and Washington. The characteristics of this coal are that it does not make coke by carbonization. Coal for this investigation came from Roundup and Red Lodge, Montana.

Its approximate analyses are as follows:

	Roundup	Red Lodge
Water	10.1 %	6.0 %
Volatile Matter	31.0 %	38.3 %
Fixed Carbon	52.8 %	46.7 %
Ash	6.0 %	7.0 %

Tars were usually a dark liquid which were brown or red-brown when viewed in thin layers.

The operating temperature of the char plant was about 1500 F. This temperature is classified as mid-temperature.

The yield and properties of liquid products vary with the temperature of carbonization. The yield of tar from low or mid-temperature carbonization is higher than that of high temperature carbonization, usually 8-12 % from the former, 3-6 % from the latter (2). The coal used here produced 10 gallons of oils per ton of coal for Roundup coal, 12 gallons for Red Lodge coal.

Main differences of properties between the tar of high and low temperature carbonization are that the former contains much more aromatics than the latter (6).

The tar from low temperature carbonization has a lower specific gravity. It varies from 1.05 to 1.10. Low specific gravity was one of the main problems in producing a specification grade of creosote oil from these tars. Creosote made from a low temperature carbonization method usually does not meet the A.W.P.A. specification.

Farmers are customers for creosote oil from the char plant and have been using it for post treating and stock disinfecting. Railroads are potential customers for creosote oil, if the creosote can be produced to meet A.W.P.A. specification.

Three coal tars were tested:

(1) Coal tar from Roundup, Montana coal

(2) Coal tar from Red Lodge, Montana coal - I

(3) Coal tar from Red Lodge, Montana coal - II

The difference between (2) and (3) was that the former was produced at 1500 F and the latter was produced at about 1200-1400 F. Roundup coal

came from the Roundup Mining Company, Roundup, Montana. Red Lodge coal came from the Smith Mine, Montana Coal and Iron Company, Red Lodge, Montana.

II DISTILLATION OF COAL TAR

The A.W.P.A. specification of the distillation test for creosote oil is as follows:

> The distillate on a water-free base shall be within the following limits at 760 mm Hg.:
>
> Up to 210 C not more than 5 %
> Up to 235 C not more than 25 % nor less than 5 %
> Up to 270 C not less than 20 %
> Up to 355 C not more than 85 % nor less than 60 %.

Because of the altitude, the atmospheric pressure in Bozeman is around 640 mm Hg. Adjustment of distillation test temperature was done by means of A.W.P.A. Manual's correction table (1).

A. Vacuum Distillation

The correction table in the A.W.P.A. Manual deals only with pressures between 596 to 795 mm Hg. For lower pressure, no boiling point data for coal tar or creosote was found. Vacuum distillation was done at several pressures to get distillation data.

Coal tar is the complex mixture of many organic compounds and its composition and properties depend principally on the temperature of carbonization and on the coal which is charred. The coal tar tested was produced at a temperature of 1500 F from Roundup coal and from Red Lodge coal-I, and 1300 F for coal from Red Lodge-II. Simple distillation under several pressures, 5, 8, 25, 640 mm

Hg gave a plot of temperature versus percent distilled for each pressure. We may assume that the composition of creosote distilled is the same independent of the pressure at which it was distilled. Figure 5 is a plot of the reciprocal of the temperature of boiling of a given fraction of creosote versus the natural logarithm of the pressure. Figure 4 is a graphical illustration of the method of preparation of Figure 5 from Figures 1, 2, and 3. The left figure is a general sketch of a plot of temperature versus percent distilled. A, B, C, and D show the same percent distilled at various pressures. These pressures are plotted in logarithm scale against reciprocal of corresponding temperatures in Kelvin, right figure.

The plot gave straight lines, AB, CD, and EF. These lines, AB, CD, and EF in Figure 5 correspond to the fraction boiling up to 210, 235, and 270 C, respectively, at 760 mm Hg. Extension of these straight lines converged at a point. For high boiling point fractions, those boiling above 280 C at 760 mm Hg, it was very difficult to collect and weight the distillate accurately because it was semi-solid at the condenser temperature. At temperature about 120 C, the fractions were liquid but they were too viscous to collect easily.

The dotted lines, GH, IJ, represent the fraction boiling up to 315 C and 355 C, respectively. These dotted lines were made by connecting the point of convergence with 315 C and 355 C at

760 mm Hg.

B. Cracking.

One big problem in distillation was the instability of the coal tar at high temperature. The coal tar started to crack about 300 C. We do not know the mechanism of this cracking, but coal tar from Roundup, Red Lodge-I and Red Lodge-II coal started cracking and produced vigorously a yellow gas at 318, 325, 313 C at 640 mm Hg, respectively. After an appreciable amount of gas came out, the temperature, which was measured at the top of the distillation flask, went down and no more distillate came out. The cracking temperature was not the same at the several pressures of 5, 8, 25, and 640 mm Hg. As the pressure increased, the temperature of cracking increased. See Figures 1, 2, and 3.

According to the theory of cracking, cracking is proportional to both contact time and temperature. The reason why the cracking temperature decreased with reducing pressure might be that the distillation time was considerably longer at reduced pressure than at atmospheric pressure.

III ADDITIVES

Since coal tar was unstable at high temperature, the fraction which was distilled between 315 and 355 C, as required by the specification for creosote could not be obtained. Additives which boiled higher than 355 C were sought. Carter heavy cycle oil is one of the

products of Carter Oil Company, Billings, Montana. It is a greenish-brown liquid product of catalytic cracking. It contains a large amount of wax. Distillation showed that 51 % of this oil boiled higher than 355 C. The properties of this Carter heavy cycle oil were:

Distillation Test:	
Up to 355 C	48.4 %
Above 355 C	51.6 %
Specific gravity of the fraction over 355 C 25/15	1.047

A mixture comprising 80 % of distillate tar and 20 % of Carter heavy cycle oil was tested. Distilled tar was the portion which was separated by distillation from light oil and which boiled above 205 C. When combined, the mixture possessed the specific gravity, boiling point range, benzene insoluble material, and coke residue properties listed in the A.W.P.A. specification for creosote. See Table I.

IV CENTRIFUGAL SEPARATION

The crude coal tars had solids or semi-solids in them. To separate these materials, centrifugal separation was carried out. The coal tars were very viscous at room temperature. To begin with, centrifugal separation at room temperature was tried, but it did not give a good separation. Then hot centrifugal separation was tried. First, coal tar was heated up to nearly boiling. This hot coal tar was far less viscous. It was poured quickly into the equipment and centrifuged. After 10 minutes, while it was still hot, it was taken off from the centrifuge and quickly separated. This was easy to do. Coal tars from

Roundup coal, Red Lodge coal-I and Red Lodge coal-II were tested.

A. Coal Tar From Roundup Coal.

Nine percent of a solid and semi-solid residue were separated from crude coal tar on centrifugation. The remaining liquid was distilled and separated into two portions, one which boiled below 202 C and a tar portion boiling above 202 C. Total yield of liquid boiling above 202 C was 69 %. This tar portion met the specification for the creosote-coal tar solutions, grade A. See Table II.

B. Coal Tar From Red Lodge Coal-I.

Eleven percent of solids and semi-solids was separated from crude tar from Red Lodge coal-I by the hot centrifugation. After cutting off the light oil portion at 205 C by distillation, total yield of tar portion was 70.8 %. This tar portion met the specification for creosote-coal tar solutions, grade A. See Table III.

C. Coal Tar From Red Lodge Coal-II.

The same procedure was followed and 13 % solids and semi-solids was removed by centrifugation. After cutting off the light oil portion at 200 C by distillation, total yield of tar portion was 76.5 %. This tar portion could not meet the specification of creosote-coal tar solutions. Specific gravity was 1.043 and the specification calls for more than 1.06.

To increase the specific gravity, the amount of solid or semi-solid removed should decrease. This increases the benzene insoluble materials and coke residue. These two properties were inconsistent

with specific gravity. This coal tar was produced at a little lower temperature than the other two coal tars, about 1200 F to 1400 F. The other two were produced at about 1500 F.

V LIGHT OIL

Boiling point properties and refractive index of light oil from Roundup coal were determined. Twenty-three percent of Roundup coal tar distilled below 210 C. According to the specification, the amount should be less than 5%. The light oil which boiled below 205 C in a long neck flask was separated and collected. After separation from water, it was redistilled in a glass ring packed fractionation column with mineral oil having a boiling point of 280-300 C as a chaser. The column had 25 to 30 theoretical plates. Temperature vs. percent distilled was plotted in Figure 6. More than 80 % boiled above 160 C at 640 mm Hg. From the refractive index analysis it was considered to be mainly aromatic compounds.

Refractive index is one of the methods of making an approximation of whether it is aromatic, naphthenic, or paraffinic. Refractive index of aromatics is usually in the range of 1.50 to 1.54, that of paraffins is under 1.40, and that of naphthenes is between aromatics and paraffins. Using benzene, cyclohexane, and n-octane as representative of aromatics, naphthenes, and paraffins, respectively, the refractive index of a mixture of these two and three pure compounds was measured. The refractive index of these mixtures showed a lower refractive index than would be obtained by assuming that the refractive index of the

mixture is proportional to the composition of the pure compounds. See Figure 7. From this it might be concluded that the portion boiling above 1.50 consists mainly of aromatics. These light oil portions undoubtedly included alkylated benzenes, pyridine- and cresol derivatives, and unsaturated benzene derivatives. The value of refractive index of 1.52 was a fairly high value for an aromatic mixture. Only unsaturated benzenes or naphthalene compounds have such high values. See below.

Some organic compounds which have a high refractive index are as follows (3):

Compounds	B.P. C	R.I.
1,2,3,5-tetra methyl benzene	198	1.5134
2- phenyl-2-butene	188-9	1.5299
3-phenyl-2-pentene	197-8	1.5266
1-phenyl-3-methyl-1-butene	201-2	1.532
Phenyl cyclobutane	190	1.5277
Indene	182	1.571

It might be reasonable to conclude that this portion of the light oil was a mixture of isomeric groups, having close boiling points and similar refractive indexes.

Alternatively, this fraction might have very high refractive index compounds such as indene, R.I. - 1.571. Even though the proportion of these compounds is very small, they could increase the refractive index of the mixture considerably.

Since the boiling point curve shows a very gradual increase and no plateaus above 160 C using the 30-plate fractionating column, it

was not possible to isolate any pure compounds from the mixture.

VI CONCLUSION

Coal tars from Roundup coal and Red Lodge coal were tested. Since the coal tar was unstable at high temperature, the fraction required by the A.W.P.A. specification for creosote which boiled between 315 and 355 C, and above, could not be obtained.

The mixture of distilled tar from crude Roundup coal tar and that portion of Carter heavy cycle oil boiling above 355 C, possessed the properties listed in the A.W.P.A. specification.

Coal tars of grade A specification for creosote-coal tar solutions was obtained from coal tar from Roundup coal and from coal tar from Red Lodge coal-I, by removing the solids and semi-solids by centrifugation.

Red Lodge coal-II was carbonized at about 1200-1400 F. Tar from this coal had a specific gravity of 1.043; specification calls for greater than 1.06.

ACKNOWLEDGEMENT

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The author acknowledges the help and guidance of Dr. Lloyd Berg of the Chemical Engineering Department.

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APPENDIX

TABLE I -- Properties of Tar and Creosote from Roundup Coal Compared with the A.W.P.A. Specification for Creosote.

	Crude Tar	Distillate with 355 C Heavy Cycle Oil Added	Specification
Specific Gravity Total	1.102	1.030	not less than 1.03
Fraction 235 to 315 C	1.025	1.025	not less than 1.025
Fraction 315 to 355 C	-----	1.086	not less than 1.085
Material Insoluble in Benzene	-----	None	not more than 0.5 %
Distillation Test Up to 210 C	22.0 %	4.0 %	not more than 5 %
Up to 235 C	31.4 %	18.2 %	not more than 25 %; not less than 5 %.
Up to 270 C	41.0 %	55.5 %	not less than 20 %.
Up to 355 C	68.3 %*	78.2 %	not more than 85 %; not less than 60 %.
Coke Residue	-----	None	not more than 2 %
Yield of Distillate from Crude Tar		46.7 %	

* Cracked at 318 C/640 mm Hg.

TABLE II -- Properties of Tar from Roundup Coal Compared with the A.W.P.A. Specification for Coal Tar-Creosote Solutions.

	Crude Tar	Centrifuged Tar with Light Oil Removed	Specification
Specific Gravity Total	1.102	1.081	not more than 1.11; not less than 1.06.
Fraction 235 to 315 C	1.025	1.025	not less than 1.025
Fraction 315 to 355 C	-----	1.091	not less than 1.085
Material Insoluble in Benzene	-----	2.0 %	not less than 2.0 %
Distillation Test Up to 210 C	22.0 %	4.7 %	not more than 5 %
Up to 235 C	31.4 %	19.0 %	not more than 25 %; not less than 5 %.
Up to 315 C	62.0 %	42.5 %	not less than 36 %.
Up to 355 C	68.3 % *	63.5 % **	not less than 60 %.
Coke Residue	-----	1.3 %	not more than 5.0 %.
Yield with Light Oil Removed from Crude Tar		69.0 %	

* Cracked at 318 C/640 mm Hg.
** Cracked at 333 C/640 mm Hg.

TABLE III -- Properties of Tar from Red Lodge Coal-I Compared with the A.W.P.A. Specification for Coal Tar-Creosote Solutions.

	Crude Tar	Centrifuged Tar with Light Oil Removed	Specification
Specific Gravity Total	1.089	1.060	not more than 1.11; not less than 1.06.
Fraction 235 to 315 C	1.029	1.029	not less than 1.025
Fraction 315 to 355 C	-----	1.086	not less than 1.085
Material Insoluble in Benzene	-----	2.0 %	not more than 2.0 %
Distillation Test Up to 210 C	20.0 %	2.4 %	not more than 5 %
Up to 235 C	33.1 %	21.0 %	not more than 25 %; not less than 5 %.
Up to 315 C	58.8 %	54.5 %	not less than 36 %.
Up to 355 C	69.5 % *	73.2 % *	not less than 60 %.
Coke Residue	-----	5.0 %	not more than 5 %.
Yield of Centrifuged Tar with Light Oil Removed from Crude Tar		70.8 %	

* Cracked at 325 C/640 mm Hg.
** Cracked at 328 C/640 mm Hg.

TABLE IV -- Properties of Tar from Red Lodge Coal-II Compared with the A.W.P.A. Specification for Coal Tar-Creosote Solutions, Grade A.

	Crude Tar	Centrifuged Tar with Light Oil Removed	Specification
Specific Gravity Total	1.050	1.043	not more than 1.11; not less than 1.06.
Fraction 235 to 315 C	1.028	1.027	not less than 1.025
Fraction 315 to 355 C	-----	1.086	not less than 1.085
Material Insoluble in Benzene	-----	2.0 %	not more than 2.0 %
Distillation Test Up to 210 C	13.5 %	4.5 %	not more than 5 %
Up to 235 C	26.1 %	22.1 %	not more than 25 %; not less than 5 %.
Up to 315 C	66.6 %	68.1 %	not less than 36 %.
Up to 355 C	68.0 % *	77.2 % **	not less than 60 %.
Coke Residue	-----	4.8 %	not less than 5 %
Yield of Centrifuged Tar with Light Oil Removed from Crude Tar	-----	76.5 %	

* Cracked at 313 C/640 mm Hg.
** Cracked at 318 C/640 mm Hg.

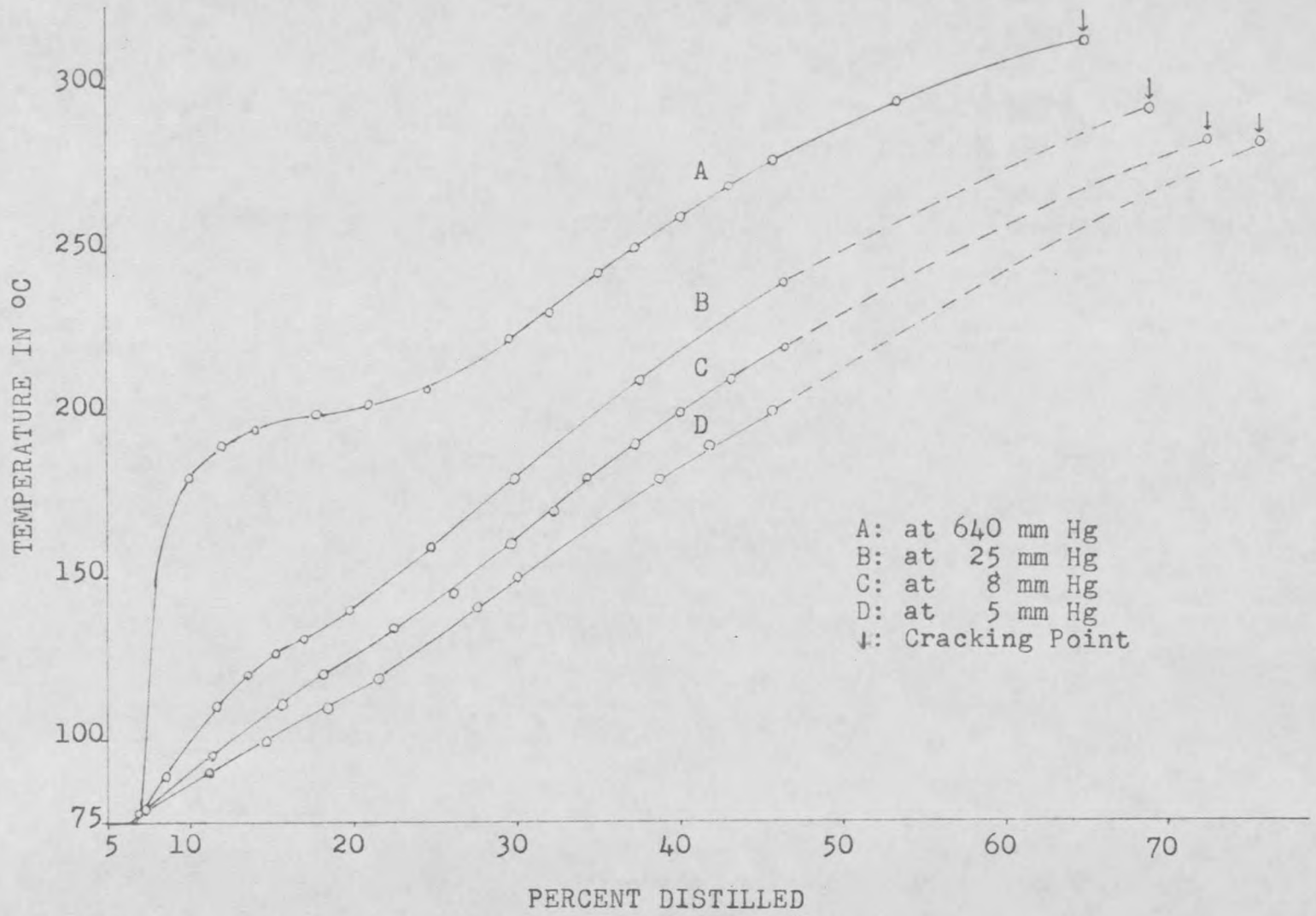


FIG.-1 DISTILLATION CURVE OF COAL TAR FROM ROUNDUP COAL AT VARIOUS PRESSURE

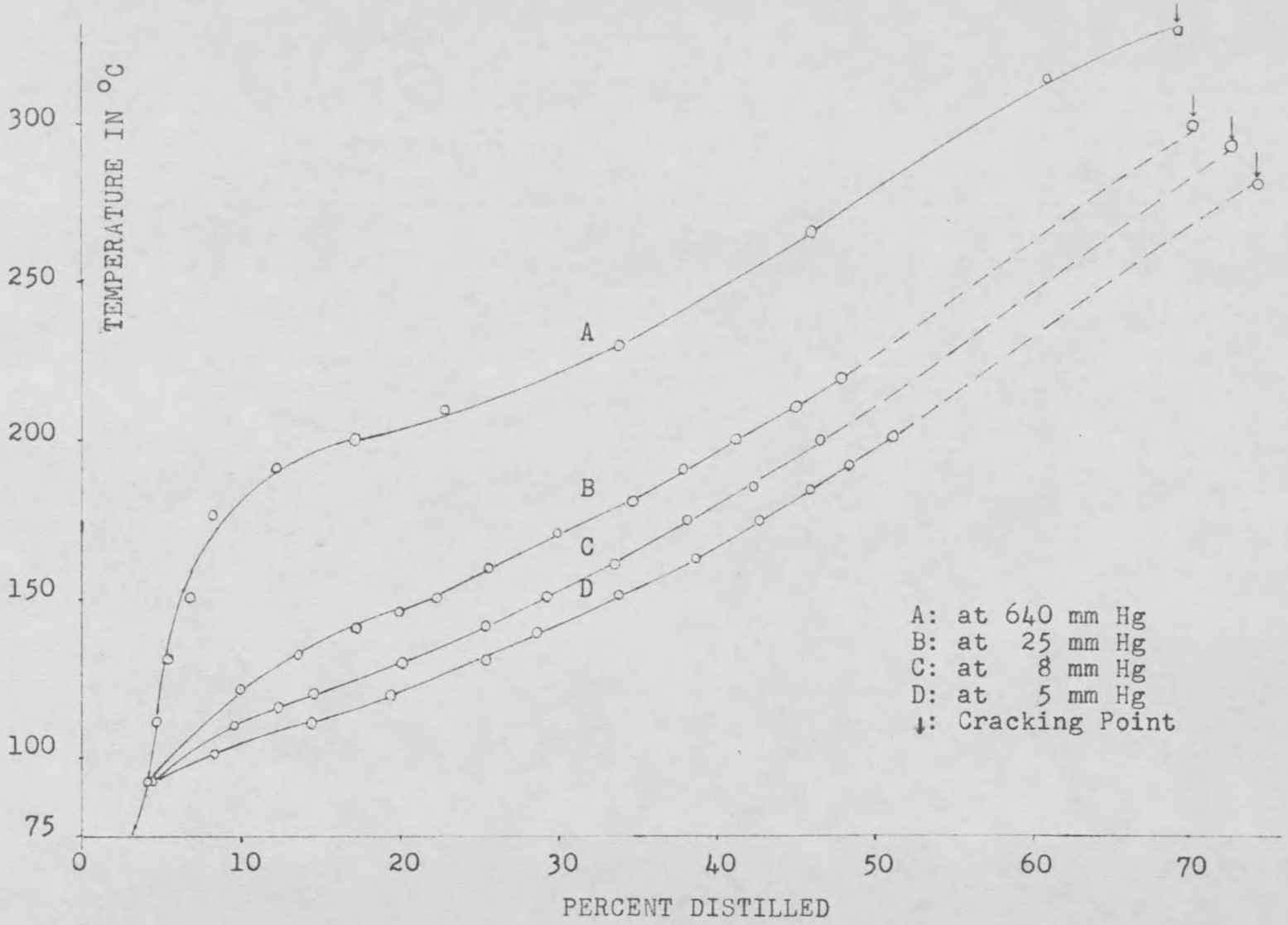


FIG.-2 DISTILLATION CURVE OF COAL TAR FROM RED LODGE COAL-I AT VARIOUS PRESSURE

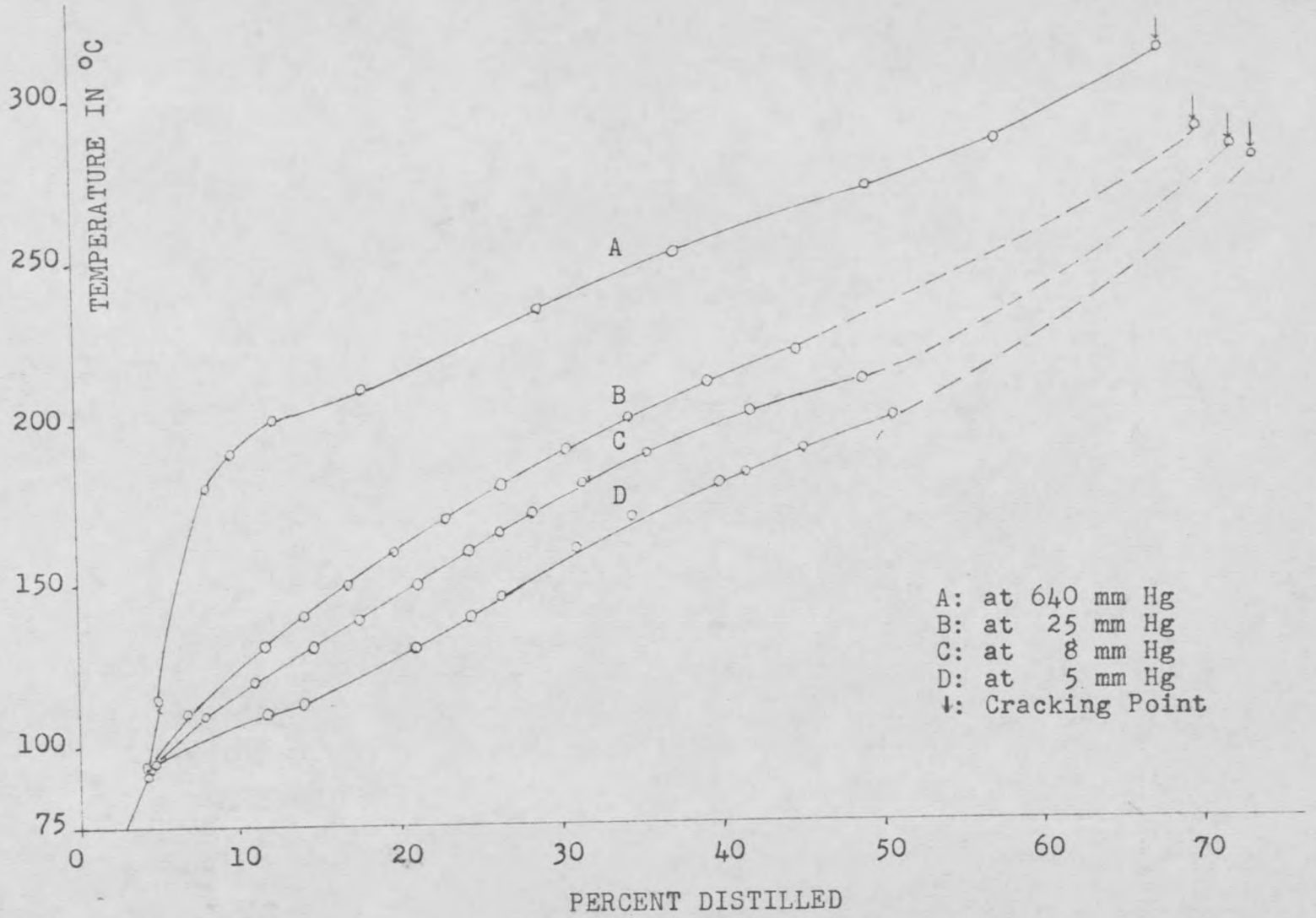
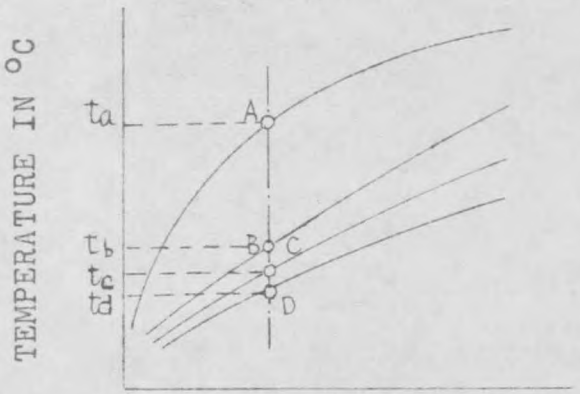
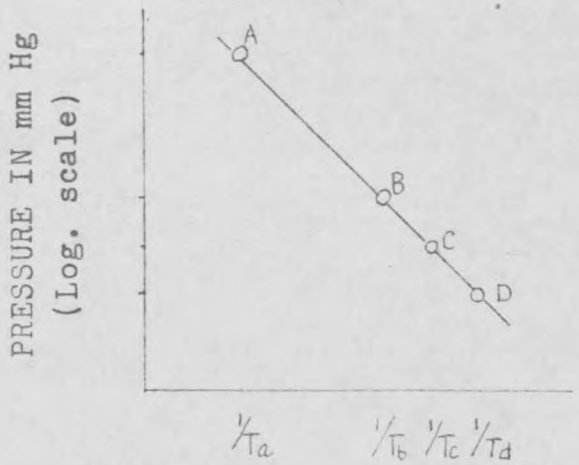


FIG.-3 DISTILLATION CURVE OF COAL TAR FROM RED LODGE COAL-II AT VARIOUS PRESSURE





A: at 640 mm Hg
B: at 25 mm Hg
C: at 8 mm Hg
D: at 5 mm Hg

FIG.-4 PREPARATION OF FIG.-5 FROM FIG.-1, 2, AND 3

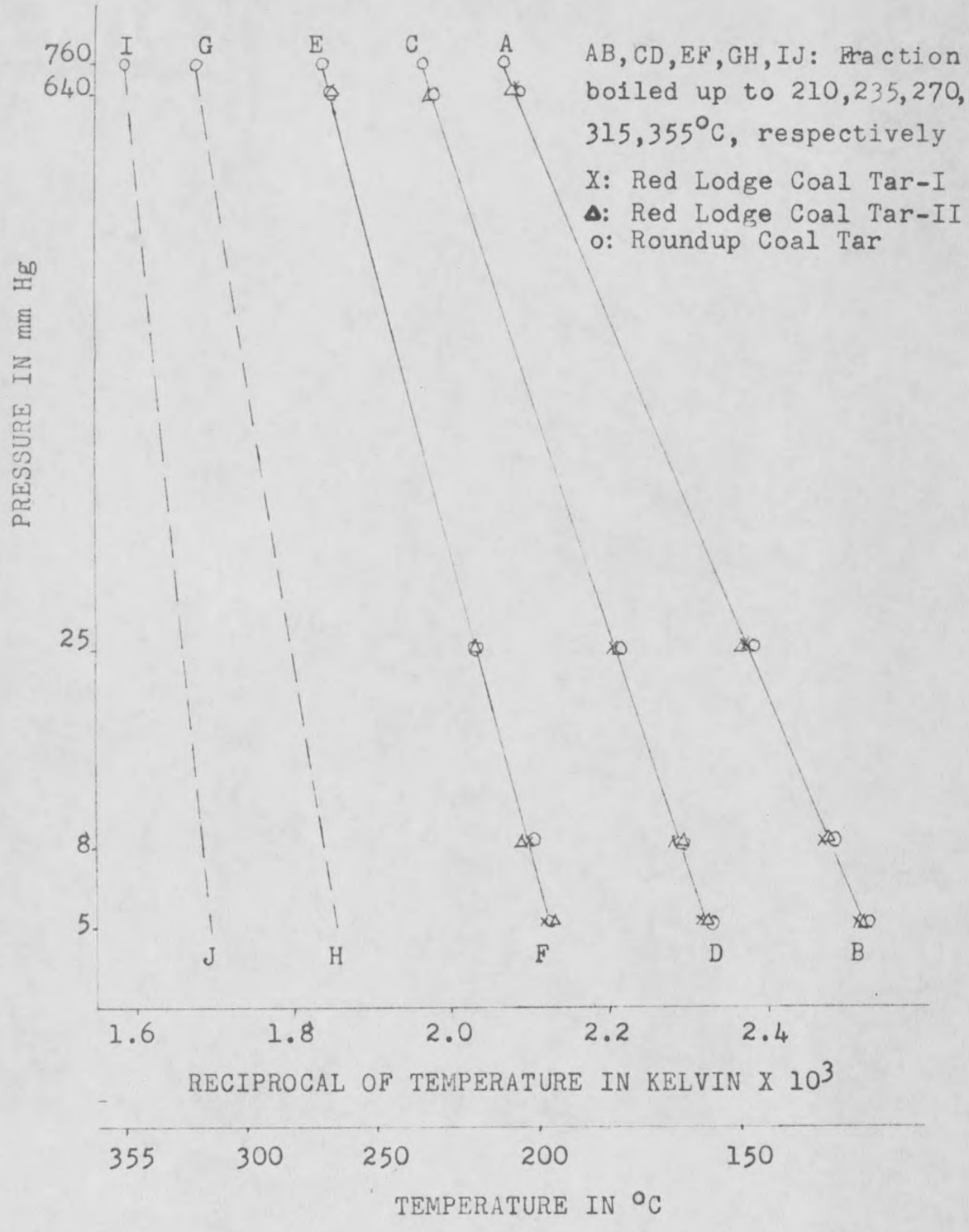


FIG.-5 VAPOUR PRESSURE OF COAL TAR AT VARIOUS TEMPERATURE

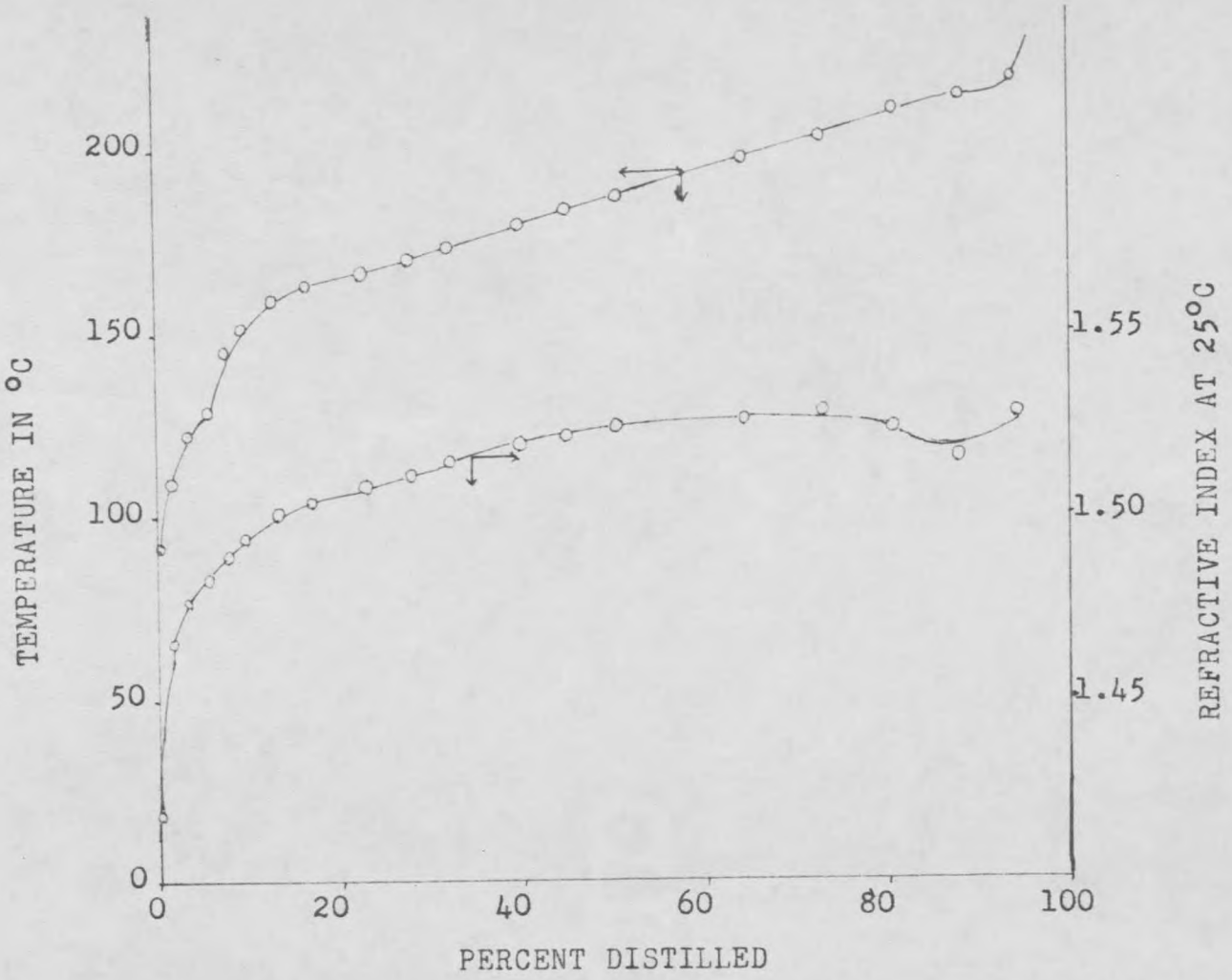
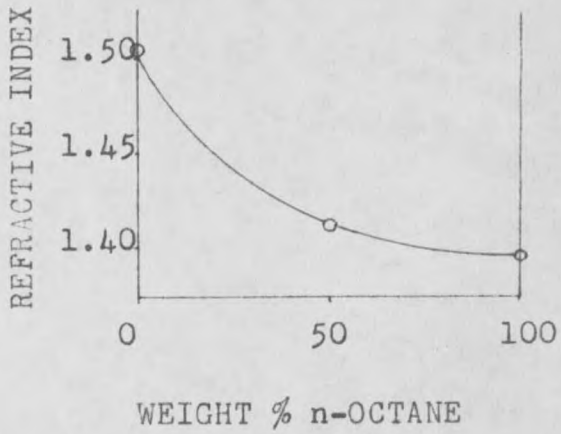


FIG.-6 BOILING POINT AND REFRACTIVE INDEX OF LIGHT OIL FROM ROUNDUP COAL TAR

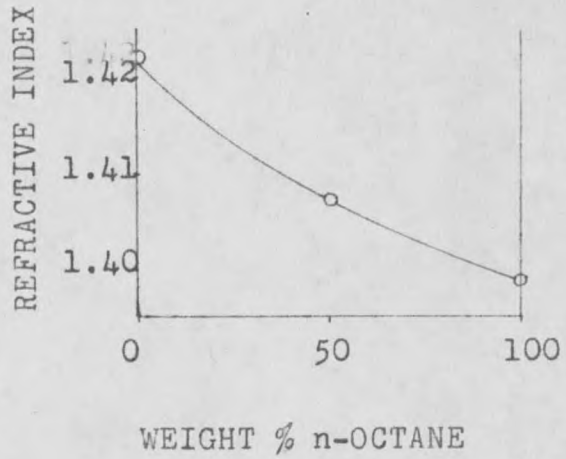
A. Refractive index of the mixture of benzene and n-octane

	R.I.
Benzene	1.5011
n-octane	1.3974



B. Refractive index of the mixture of cyclohexane and n-octane

	R.I.
Cyclohexane	1.4221
n-octane	1.3974



C. Refractive index of the mixture of benzene-cyclohexane solution and n-octane

Solution contained

Benzene	50 %
Cyclohexane	50 %

Refractive index 1.4581

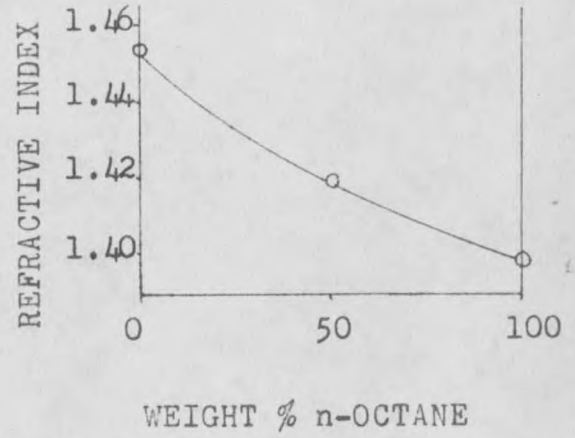


FIG.-7 REFRACTIVE INDEX OF THE MIXTURE OF BENZENE, CYCLOHEXANE AND n-OCTANE