

SEPARATION OF MULTI-COMPONENT
HYDROCARBONS BY LIQUID EXTRACTION

By

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SUMMARY

These tests illustrate how a multi-component hydrocarbon can be cut up into its molecular types such as aromatics, naphthenes, and paraffins by the use of liquid extraction. Such a separation was made in two successive extractions using methyl carbitol plus varying amounts of water as the solvent. The results are summarized below.

	<u>Feed</u>	<u>Aromatic Cut</u>	<u>Aromatic plus Naphthenic Cut</u>	<u>Paraffinic Cut</u>
Yield, Wt %	100	5.1	45.4	49.5
PCNA Analyses, Wt %				
Aromatics	12	86(a)	46	4
Naphthenes	68	10	53	28
Paraffins	20	4	1	68
Octane No., Clear				
Motor	67.8	-	76.0	58.9
Research	71.2	-	84.9	59.4

(a) 75 vol per cent toluene by ultra-violet analysis.

A continuous spray-type extractor was used in these tests and operation simulated that of a commercial 18-stage extractor with feed to the middle, solvent to the top and extract reflux to the bottom. A method for estimating equilibrium data for multi-component systems is also presented along with a calculation method for calculating separations by liquid extraction.

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
I Introduction	1
II Materials	
A Hydrocarbon feed to extractor	5
B Solvent	5
III Procedures	
A Operational	7
B Analytical.	9
IV Equipment	11
V Calculations	15
VI Discussion of Results	26
VII Conclusions.	31
VIII Suggested Further Work	32
IX Bibliography	33
X Appendix	35
Definitions and Abbreviations	37

Figures

1 Methyl Carbitol Extraction Unit (Flow Sheet)	14
2 Equilibrium Data for the System Methyl Carbitol plus 20 wt per cent Water - Aromatics - Naphthenes plus Paraffins at 85°F.	21
3 Flows and Compositions for Aromatic Separation	22
4 Equilibrium Data for the System Methyl Carbitol plus 5 wt per cent Water - Aromatics plus Naphthenes - Paraffins at 85°F	24
5 Naphthene Paraffin Separation	25
6 Extraction of Hydrocarbon with Methyl Carbitol	30

Tables

I Inspection tests of hydrocarbon feed stream to ex- tractor	5
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II	Physical properties of methyl carbitol	6
III	Solubility of hydrocarbons in methyl carbitol at 85F .	16
IV	Average hydrocarbon solubilities in methyl carbitol. .	17
V	Calculation of equilibrium data for system aromatics, naphthenes plus paraffins and methyl carbitol plus 20 wt % water.	19
VI	Estimated equilibrium data for methyl carbitol plus 5 wt per cent water-hydrocarbon system	23
VII	Separation of hydrocarbon groups by methyl carbitol extraction	26
VIII	Summary of analytical results for aromatics sepa- ration	35
IX	Summary of analytical results from naphthene paraffin separation	36

INTRODUCTION

Although the problem of separating the components of a liquid solution is common to almost all of the chemical industries, it is of particularly great importance to the petroleum industry. Petroleum fractions contain a variety of compounds, many of which exhibit overlapping volatility or boiling points. This overlapping necessarily limits the degree of separation which can be obtained by distillation. While the separation of components according to molecular size by distillation continues to be a satisfactory and economical process, it needs to be supplemented. Improved methods for separating components according to type are desired. This need is becoming more critical as the demand for pure hydrocarbons, special chemicals, and high octane gasolines increases. Although several separation processes are available, the one which has commanded the most interest in recent years is that of liquid extraction.

Liquid extraction is not based upon physical properties such as boiling point but upon chemical characteristics. This makes separations feasible that would be impossible by any other means. Extraction is not new as a separation process but until recent years it was primarily confined to the laboratory. It was not until the 1930's that commercial units began to appear in appreciable number.²⁶ These units as well as present day units were designed with very little engineering background and there can be no doubt that the performance of liquid extraction units will be greatly improved as the process becomes better understood and as more engineering and operating data becomes available. In recent

years the amount of literature and published data concerning liquid extraction has steadily increased and despite the fact that the systems studied are generally of little interest to the petroleum industry it points out a developing trend.

The first successful commercial application of liquid extraction to the petroleum industry was initiated by Edeleanu^{6,7} in the early 1900's and involved the use of liquid sulfur dioxide as the solvent for upgrading kerosenes. Liquid sulfur dioxide is selective for aromatic hydrocarbons and is limited to making separations between aromatic and non-aromatic hydrocarbons. In general, sulfur dioxide is not used when olefins are present. During the second world war the Edeleanu process was adapted for the production of highly aromatic stocks to be used as aviation gasoline blending stocks.¹⁶ Other widely used extraction processes are adequately described in the literature^{17,27} but are mostly confined to sweetening and the treating of lubricating oils. The best known commercial solvent extraction processes include the Furfural,⁵ Duo-Sol,³⁰ Phenol,²⁵ Edeleanu,⁶ Chlorex,² and Propane.¹⁴ A general survey of such commercial processes was given by Morello and Poffenberger¹⁵ in 1950. Other solvents which have been used commercially are nitro-benzene,⁹ aniline and more recently, Di-ethylene glycol.¹

Although much work has been done on and with liquid extraction, a process has not yet been developed such that with one solvent different cuts can be made from a hydrocarbon feed with each cut being of high purity but containing a different type of hydrocarbon. For example, it would be very convenient if a given hydrocarbon feed could be completely

separated into groups of paraffins, naphthenes, olefins and aromatics. Each type of hydrocarbon could be used for a specific purpose. As an illustration, the paraffin cut could be reformed, the olefins polymerized, the aromatics used for aviation blending and so on. This would allow the original hydrocarbon to be utilized in a much more efficient manner and could be used to produce truly "tailor made" gasolines. The work presented in this report is an approach to this problem.

Many solvents have been used in extraction processes for both commercial and test purposes and many more are being currently tested.²¹ The solvent selected for the following tests was diethylene glycol, mono-methyl ether commercially known as "methyl carbitol". This solvent was chosen primarily because it is completely soluble with water thus making possible a wide range of hydrocarbon solubility and selectivity. Hydrocarbon solubility was varied by merely adding water to the solvent. Methyl carbitol also had the right density and viscosity characteristics to make it a good solvent for the system contemplated. Other factors studied in the selection of a solvent were surface tension, cost, availability, toxicity, boiling point and, of course, hydrocarbon solubility and selectivity.²⁸

Several types of equipment have been and are being used for liquid extraction processes. A few of the types of continuous countercurrent extractors which have been mentioned in the literature are--Scheibel spinner column,^{22,23,24} perforated plate towers,¹⁹ wetted wall columns,¹⁰ packed columns,³ bubble cap columns,²⁰ Podbielniak extractor,¹⁸ and the Koch tower.¹² These extractors have their individual merits but it is probable that more work has been done in the laboratory and pilot plant on spray

column extractors than on any other type. The equipment is simple and easily set up and the columns are easy to operate. For these reasons the spray-type extractor was selected for these tests.

After the equipment and solvent had been selected it was necessary to select a hydrocarbon feed which would offer a typical separation problem. A good feed should have the following characteristics:

- (a) It should have a fairly narrow boiling range in order that distillation would not be applicable.
- (b) It should contain several different types of components.
- (c) It should have a boiling range different from that of the solvent in order that the two could be separated by distillation.

The hydrocarbon finally selected had all of the above characteristics. The feed contained only aromatic, naphthenic and paraffin components since they served to illustrate the extraction process and the presence of olefins would have only complicated the process unnecessarily.

In the following text are presented the method of procedure, preliminary calculations, equipment description, and discussion of the performed extraction along with the experimental data. For the purpose of clarity each section is treated separately under its own heading.

MATERIALS

A. Hydrocarbon feed to extractor

A spectroscopic analysis of the hydrocarbon feed stream which was selected for these tests is given in Table I below.

TABLE I

INSPECTION TESTS OF HYDROCARBON FEED
STREAM TO EXTRACTOR

COMPOSITION			
<u>COMPONENT</u>		<u>WEIGHT PER CENT</u>	
Toluene		12.3	
Methylcyclohexane		67.8	
Iso-octanes		17.9	
N-Heptane		2.0	
API Gravity @ 60F		57.6	
ASTM Distillation, F			
IBP		206	
10 over		216	
50 "		218	
90 "		222	
EP		250	
Octane Numbers		<u>MOTOR</u>	<u>RESEARCH</u>
ml TEL/gal			
0		67.8	71.2
1		77.5	80.5
3		84.0	87.4

Small quantities of ethylcyclopentane, 3-ethylpentane and cis 1, 2-dimethylcyclopentane were also detected in the stream but were neglected for test purposes.

B. Solvent

The solvent used in these tests was diethylene glycol, monomethyl ether, which is referred to commercially as "methyl carbitol" and it will be so called in the remainder of this report. The solvent was originally obtained from the Carbide and Carbon Chemical Division of the Carbide and Carbon Corporation. It was purified by distillation and tap water added as specified.

Methyl carbitol in the pure state is a colorless liquid with the physical properties presented below. It has a molecular weight of 120.15

and the chemical formula $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$. It is completely soluble in water and its toxicity is low.

TABLE II

PHYSICAL PROPERTIES OF METHYL CARBITOL

Density	1.0354	20/4
Refractive Index	1.4264	27
Boiling point at 1 atm	193.2°C	

PROCEDURES

A. Operational

Because it was desired to separate a hydrocarbon mixture into its three molecular types, two extraction steps were required. The first separation desired was the extraction of the aromatics in the hydrocarbon stream from the naphthenes and paraffins. Since the aromatics present in the hydrocarbon feed stream are completely soluble in dry methyl carbitol, it was necessary to add water to the solvent to reduce the aromatic solubility and obtain the necessary two phases. Batch tests with toluene indicated that methyl carbitol plus 20 weight per cent water had the proper solubility characteristics and this mixture was used as the solvent for the aromatic separation. Since naphthenes are not completely miscible with dry methyl carbitol, a smaller amount of water was required in the solvent to make the naphthene separation. Again batch solubility tests were run and a solvent water content of 5 weight per cent was determined as suitable for making the naphthene-paraffin separation.

The two extraction runs were made simulating the operation of a commercial extractor. Schematic sketches of these two runs are presented in Figures 3 and 5, pages 22 and 25. The first run shown in Figure 3 was made in one step using methyl carbitol plus 20 weight per cent water as the solvent. Two 8-foot-tall spray columns were used as the enriching section of the extractor while the third spray column was used as the stripping section. This was feasible because 9 theoretical separation stages were estimated to be sufficient to make the desired aromatic separation. The raffinate from this run was used as hydrocarbon feed for the succeeding run.

The second extraction as shown in Figure 5 was made in two parts in order to simulate the operation of an 18-stage column. This was necessary because more stages were required for the naphthene-paraffin separation than for the less difficult aromatic separation. The enriching or top portion of the extractor was run first in which hydrocarbon was fed to the bottom of the 9-stage unit and fresh solvent to the top. The extract from this section was stored and during the stripping section run was fed to the top of the 9-stage unit with reflux hydrocarbon being fed to the bottom. The results were then combined to represent the operation of an 18-stage extractor with feed to the middle as shown in Figure 5. The solvent used for this separation was methyl carbitol plus 5 weight per cent water.

All tests were performed at 85 F. During stripping section runs extract samples were drawn from column 3 (see Figure 1) and the hydrocarbon solubility determined. This was done at hourly intervals and when the hydrocarbon solubility remained constant over several sample periods it was assumed that the extractor had reached steady state conditions. Periodically, samples were drawn to determine if all the hydrocarbon had been removed from the extract fractionator kettle bottoms. This analysis was the control test for the fractionator. After the column had reached steady state, timed samples of the extract and raffinate products were taken for material balance and analytical purposes. Feed samples were also taken and in some cases hydrocarbon samples were taken between the individual columns. Conditions were maintained in the distillation column such that some solvent and considerable water came overhead with the hydrocarbon. The water and solvent were allowed to settle in a chamber and were removed. Only the hydrocarbon phase was refluxed.

B. Analytical

The details of the analytical procedures used in these tests are given below.

1. Determination of the water content of the solvent feed.

In order that the water content of the solvent could be determined quickly a plot was made relating water content to refractive index. This curve was used for determining the water content of the solvent.

2. Determination of hydrocarbon content of the solvent phase.

A batch distillation procedure was developed for the separation of hydrocarbon from methyl carbitol in a quantitative manner. The apparatus consisted of a Claisen flask connected to a condenser which emptied into a calibrated burette. Cooling water was circulated through the condenser thus liquefying the overhead vapors. A small amount of methyl carbitol came over with the hydrocarbon and was drained out of the bottom of the burette. During the distillation, water was constantly added to the burette to cut down the hydrocarbon solubility in the methyl carbitol that came over. When the cut point was reached the volume of hydrocarbon that had come over was recorded and a Westphal density determined. The volume and the density of the overhead hydrocarbon plus the weight of the charge to the Claisen flask allowed the composition of the charge to be calculated.

3. Method for determining hydrocarbon composition.

The types and relative amounts of hydrocarbons present in a given hydrocarbon sample were determined by ASTM procedures. The aromatic content test was a sulfonation process given the ASTM designation of D875-46T as described in the 1948 edition of ASTM Standards of Petroleum Products and Lubricants. The differentiation of naphthenes and paraffins

was made by the "emergency test for hydrocarbon types in aviation gasolines" given the ASTM designation of ES-45a. This procedure is sometimes called a PONA analysis.

4. Method for removing solvent from hydrocarbon.

Although for calculation purposes it was assumed that the hydrocarbon or raffinate phase contained no solvent, the methyl carbitol was slightly soluble in the hydrocarbon. This impurity was removed by washing the hydrocarbon several times with water, the methyl carbitol being discarded with the water phase.

5. ASTM distillations.

The ASTM distillations as given in this report had the ASTM designation D86-46 in the 1948 edition of ASTM Standards on Petroleum Products and Lubricants.

6. Determination of Octane numbers.

Octane numbers were run by the standard research and motor methods known as ASTM Research D908-48T and ASTM Motor D357-48.

EQUIPMENT

The extraction equipment used for these tests consisted principally of three glass, 2-inch-diameter, 8-foot-tall spray type columns connected in series as shown in Figure 1. The columns were glass jacketed and cooling water was circulated through the jackets to keep them at a constant temperature. The solvent feed was pumped from the solvent feed tank through a rotameter and rate control valve into the top of column 1. The solvent feed tank was maintained at constant temperature by a steam heated water jacket. The solvent or extract leaving column 1 was pumped into the top of column 2 and then after passing through column 3 was finally preheated by means of steam and electrical heaters and flashed into the extract distillation column.

The hydrocarbon feed to the extractors was pressured by means of nitrogen pressure through a rotameter and hand control valve and then sprayed into the bottom of any one of the three columns as desired. Enough pressure differential was maintained between each column to force the hydrocarbon phase from one column to another. Thus column 3 had more pressure on it than did column 2 which in turn was maintained at a higher pressure than column 1. Column 1 was vented to the atmosphere.

The solvent phase was the continuous phase in each of the three extraction columns and it was necessary to maintain an interface or liquid level in each column in order to permit the hydrocarbon droplets to coalesce and separate from the solvent. Therefore, a liquid level controller was placed on each column. The controllers worked on an electrical contact which operated a solenoid valve on the extract line of each

column. The electrical contact type of interface controller was feasible because the solvent was an electrical conductor and the hydrocarbon was not. A relay box was used in conjunction with the electrical contact in order to provide the current to actuate the solenoid valve.

The extract distillation column consisted of a 4-inch-diameter, 7 1/2-foot-tall section packed with 1/2-inch berl saddles. The kettle capacity was approximately 1.5 gallons and was heated by means of two 500-watt electrical heaters. The feed was preheated by a combination of steam and electrical heaters. The column and kettle were wound with electrical heaters in order that adiabatic conditions could be maintained. The hydrocarbon came off overhead mixed with some water and solvent and after being condensed and cooled by cooling water went to a glass surge chamber. The mixed overhead stream was split into reflux and product streams by means of an intermittent reflux splitter combined with a flexopulse or electrical timer. The reflux portion went to a glass chamber where it was decanted and the water and solvent layer was drawn off through a constant level over-flow tube. The reflux hydrocarbon was then pumped into the bottom of column number 3.

An electrical contact type of liquid-level control was attached to the kettle of the extract fractionator in order to keep the solvent level from building up in the column. The solvent, now free of hydrocarbon, was cooled by a heat exchanger and was then pumped to storage. All pumps indicated were small Eastern-type centrifugals. All lines indicated were either 1/4-inch standard pipe or 1/4-inch copper tubing. A gas cap was maintained on the top of each extraction column in order to minimize the surge created by the on-off action of the solenoid valves on the extract

lines. Sample lines were provided at appropriate locations and iron-constantan thermocouples were located on all incoming and outgoing streams. A brown portable potentiometer, model 1117, with automatic cold junction compensation and accuracy within plus or minus one degree was used for reading temperatures.

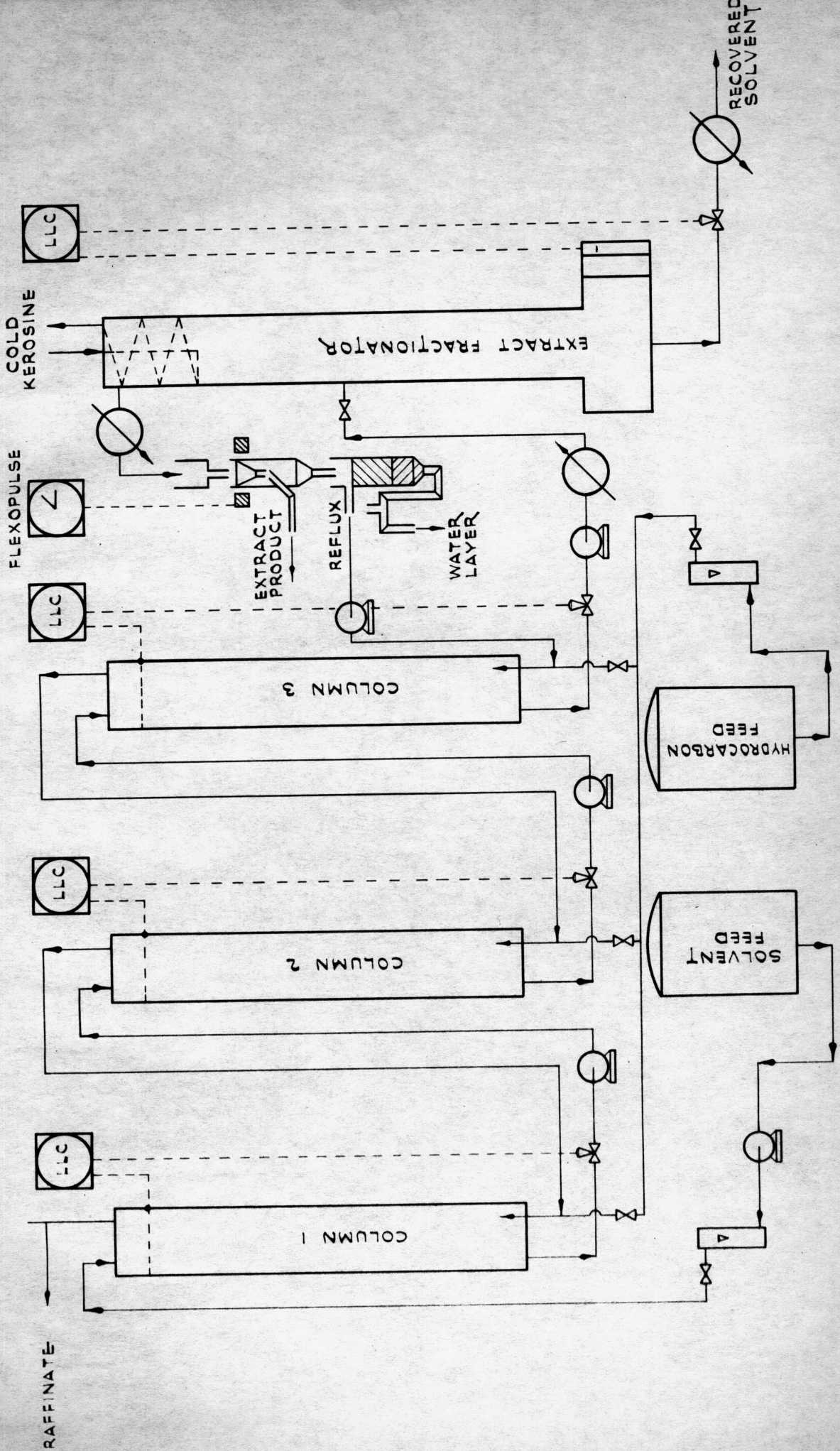


FIG. 1 METHYL CARBITOL EXTRACTION UNIT

CALCULATIONS

In order to be able to set up flow conditions for the extraction runs it was necessary that equilibrium data for the systems be estimated. This was particularly true in the case where the extraction run was made in two parts and the flows and compositions had to be matched in order to simulate a complete extraction column. Once equilibrium data was obtained and certain symplifying assumptions were made it was a relatively easy matter to make Ponchon type calculations to determine flow ratios and compositions.^{8,11,13}

The calculation of multi-component extraction is quite complicated if done in a more or less rigorous manner and it was considered that reasonable approximations was sufficient for the purposes of these runs. Therefore, whenever possible, symplifying assumptions were made and figures rounded off in order that the work should not become prohibitively time consuming. Most of the assumptions can be justified in view of the fact that the composition breakdowns were approximate in many cases.

Since the water content of the solvent used in these extractions was varied it was necessary to obtain equilibrium data for the system involving methyl carbitol plus 20 wt per cent water and for the system using methyl carbitol plus 5 wt per cent water. Ponchon type calculations are limited to two component systems, excluding the solvent, and such a system was simulated in one instance by classifying the aromatics as one component and the naphthenes plus paraffins as the other component. This can be justified in view of the fact that the solvent contained 20 per cent water and both the naphthenes and paraffins were relatively insoluble as compared to the aromatic components. When the solvent containing 5 per cent

water was used the aromatics plus naphthenes were classified as one component and paraffins as the second component. This is less easily justified because the solubility of the naphthenes and aromatics are considerably different. However, it was the original intent that the aromatic content of the feed to the second extraction be low and consequently have little effect upon the hydrocarbon solubility. As it turned out, the actual separation was close to the calculated separation thus justifying the original grouping.

In the estimation of equilibrium data it was assumed that the solvent was insoluble in the hydrocarbon phase. In reality this solubility is very low, probably of the order of one weight per cent. The equilibrium data for each solvent was estimated from pure hydrocarbon solubility data with an additional point or so which were run on hydrocarbon mixtures. Due to the number of hydrocarbons involved and the difficulty in obtaining accurate analyses, rigorous equilibrium data was out of the question. The approximate solubility of pure hydrocarbons in the solvents are given in the following table. These solubilities were obtained by running cloud points at 85 F.

TABLE III

Solubility of Hydrocarbons in Methyl Carbitol at 85 F

<u>Hydrocarbon</u>	<u>Water Content of Solvent</u>	
	<u>5 wt per cent</u>	<u>20 wt per cent</u>
Toluene	Miscible	13.3 wt %
Methylcyclohexane	6.5 wt %	0.75
N-Heptane	3.16	< 1
Iso-Octane	3.08	< 1

In the instances where hydrocarbon solubilities are listed as being less than one per cent the cloud point method of solubility determinations were inadequate and for calculation purposes those components were treated as though they were completely immiscible. Only a very slight error was introduced by this assumption.

Once the pure component solubilities had been determined, the solubilities of the hydrocarbon mixtures composed of two pseudo components were obtained from the known composition of the feed and from the assumption that each individual component would display the same solubility when in the hydrocarbon mixture as it did in the pure state. The solubility calculations for the hydrocarbons in methyl carbitol plus 20 weight per cent water is shown below.

TABLE IV

<u>Components</u>	<u>Weight Per Cent</u>	<u>Pure Component Solubility</u>	<u>Weighted Solubility</u>
Toluene	100	13.3	<u>13.3</u>
	Total Solubility		13.3
Methylcyclohexane	77.3	0.75	0.58
Normal heptane	2.3	0	0
Iso-Octane	20.4	0	<u>0</u>
	Total Solubility		0.58

From the two solubilities calculated above and from a series of batch tests that were run in order to give additional data the points given below were obtained and plotted as shown in Figure 2.

<u>Wt. per cent aromatics</u>	<u>Lbs solvent/lb hydrocarbons</u>
0	172
48.3	69.3
61.5	40.5
88.0	13.4
100.0	6.5

With the solvent phase solubilities established it was then necessary to obtain a conjugate line in order to complete the equilibrium data and allow stage calculations to be made. For illustration purposes equilibrium data for the three component system naphthenes plus paraffins - aromatics - methyl carbitol plus 20 wt per cent water will be calculated. Equilibrium data for a system is easily calculated if selectivity data is available but in this case such data was not readily available. Therefore,

a method for estimating selectivities and relating it to solubilities was desired. Selectivity and solubility data for the system furfural - N heptane - cyclohexane at 85 F was available and it was argued that this system was similar to the one in question and might be used in the estimation of equilibrium data. Selectivity in this case is defined as the following ratio

$$\frac{X_1/X_2}{Y_1/Y_2} \quad (\text{eq.1})$$

where X_1 = mole fraction most soluble component in extract.

Y_1 = mole fraction most soluble component in Raffinate.

X_2 = mole fraction least soluble component in extract.

Y_2 = mole fraction most soluble component in Raffinate.

The solubility ratio was defined as $\frac{\text{solubility of component 1 in solvent}}{\text{solubility of component 2 in solvent}}$

For the above mentioned furfural system the solubility ratio and selectivity was 2.58 and 2.00, respectively, and the solubility ratio for the methyl carbitol system was 13.3/0.58 or 22.9. As an approximate method for calculating selectivities the following equation was set up.

$$\frac{2.58 - 1}{22.9 - 1} = \frac{2.00 - 1}{Z - 1} \quad (\text{eq.2})$$

Z = Unknown selectivity

This simply states that the ratio of the selectivities of the two systems under discussion are equal to the ratio of the solubility ratios. It was reasoned that it might represent the fact more truthfully if the numeral one was subtracted from both sides because no separation is obtained when the selectivity is equal to one. The separation factor is represented by that portion of the selectivity which is greater than one. More recent work, however, has shown that this refinement has no appreciable effect on

the accuracy of equilibrium data calculated in this manner.

Equation 2 when solved gives Z a value of 14.9. Letting X equal the aromatic composition of the solvent free raffinate and substituting the selectivity value obtained from equation 2 into equation 1 the following equality results when it is realized that $Y_2 = 100 - Y_1$

$$X = \frac{100}{14.9 \frac{X_2}{X_1} + 1} \quad (\text{eq.3})$$

By assuming values of X_1 and substituting into equation 3, equilibrium data was calculated and is tabulated below as weight per cent.

TABLE V

X_1	X_2 or $100 - X_1$	X_2/X_1	$14.9 \frac{X_2}{X_1}$	$14.9 \frac{X_2}{X_1} + 1$	X
10	90	9	134	135	0
20	80	4	59.6	60.6	1.65
30	70	2.3	34.3	35.3	2.83
40	60	1.5	22.3	23.3	4.29
50	50	1.0	14.9	15.9	6.30
60	40	0.67	9.9	10.9	9.10
70	30	0.429	6.4	7.4	13.5
80	20	0.25	3.7	4.7	21.3
90	10	0.111	1.6	2.6	38.5
95	5	0.053	0.8	1.8	55.5
100	0	0	0	1.0	100.0

This data was then plotted in Figure 2 giving a complete Ponchon-type diagram.

Previous work using the extraction equipment had shown that the three columns in series were equivalent to approximately 9 theoretical separation stages and this figure was used in this calculation. Since the hydrocarbon feed was introduced at the bottom of the second column this gave the top or enriching section of the extractor six stages while the remaining three stages were in the bottom or stripping section of the extractor. The calculations will show that this was the proper place for the feed entry.

The actual stage calculations were made by the Ponchon method and were trial and error. The following assumptions were made in the trial and

error calculations:

(a) A 10/1 by weight reflux ratio.

(b) A total of 9 separation stages--6 in the top section and 3 in the bottom.

Extract and raffinate compositions were assumed and stages stepped off in the conventional graphical manner until the assumed compositions gave the correct number of stages. It was found by this method that a raffinate composition of 1 weight per cent aromatics gave 6 theoretical stages in the top section of the extractor while an extract composition of 97.5 weight per cent aromatics required 3 stages in the bottom section. The proposed separation was to take a hydrocarbon containing 12.3 weight per cent aromatics and separate it into products containing 1 and 97.5 weight per cent aromatics respectively.

Once the degree of separation was estimated the next step was the calculation of flow ratios and rates. This was done by means of an aromatic and an overall material balance. These material balances were straight forward and conventional so they will not be illustrated here but the results as based on 1.0 pound of hydrocarbon feed are presented graphically in Figure 3.

The calculations as described above were repeated on the system methyl carbitol plus 5 weight per cent water - aromatics plus naphthenes - paraffins. The results of these calculations are presented in Table VI below and in Figure 4. The curve of the solubility line on the Ponchon diagram was estimated from that of similar systems.

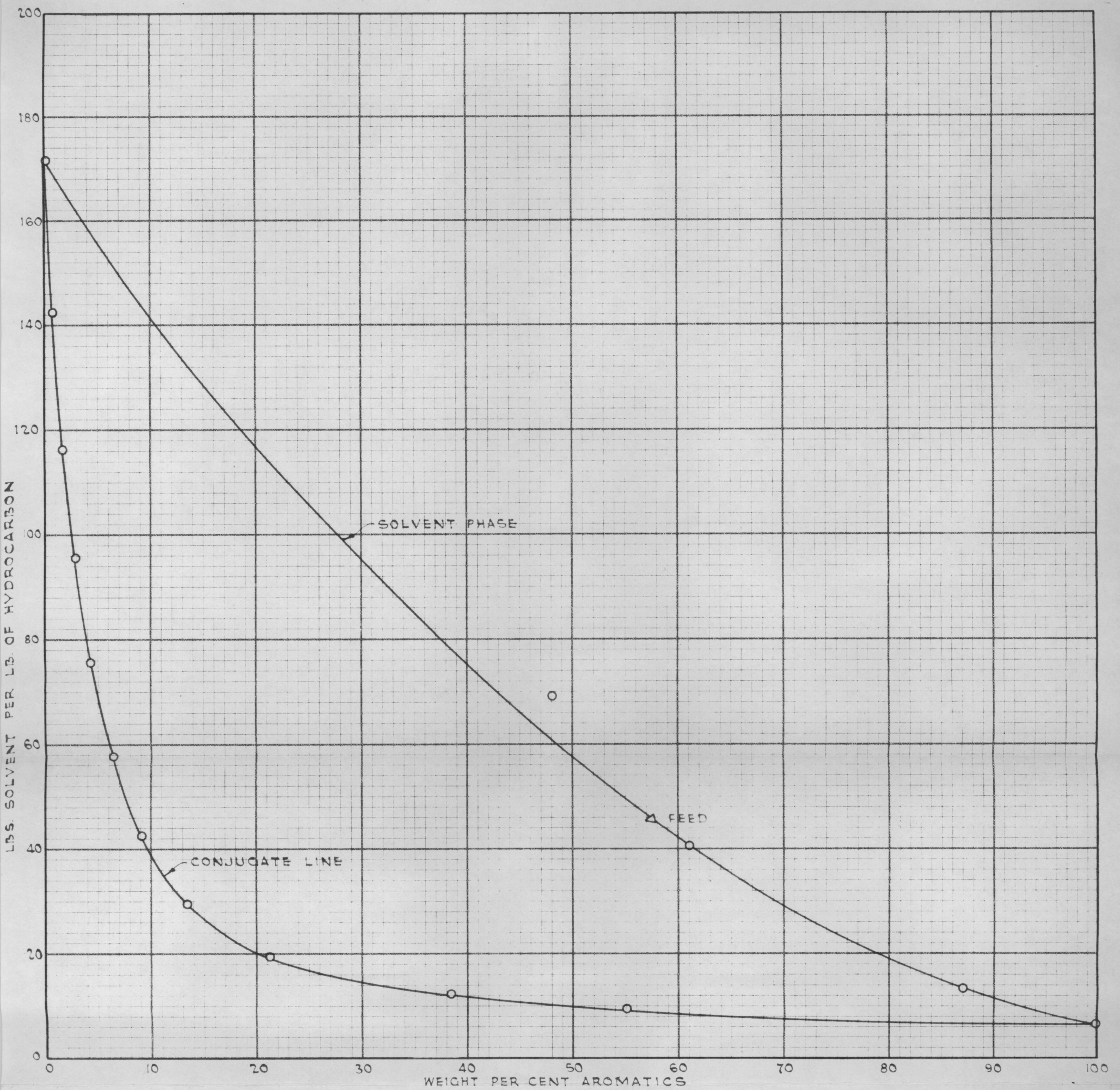
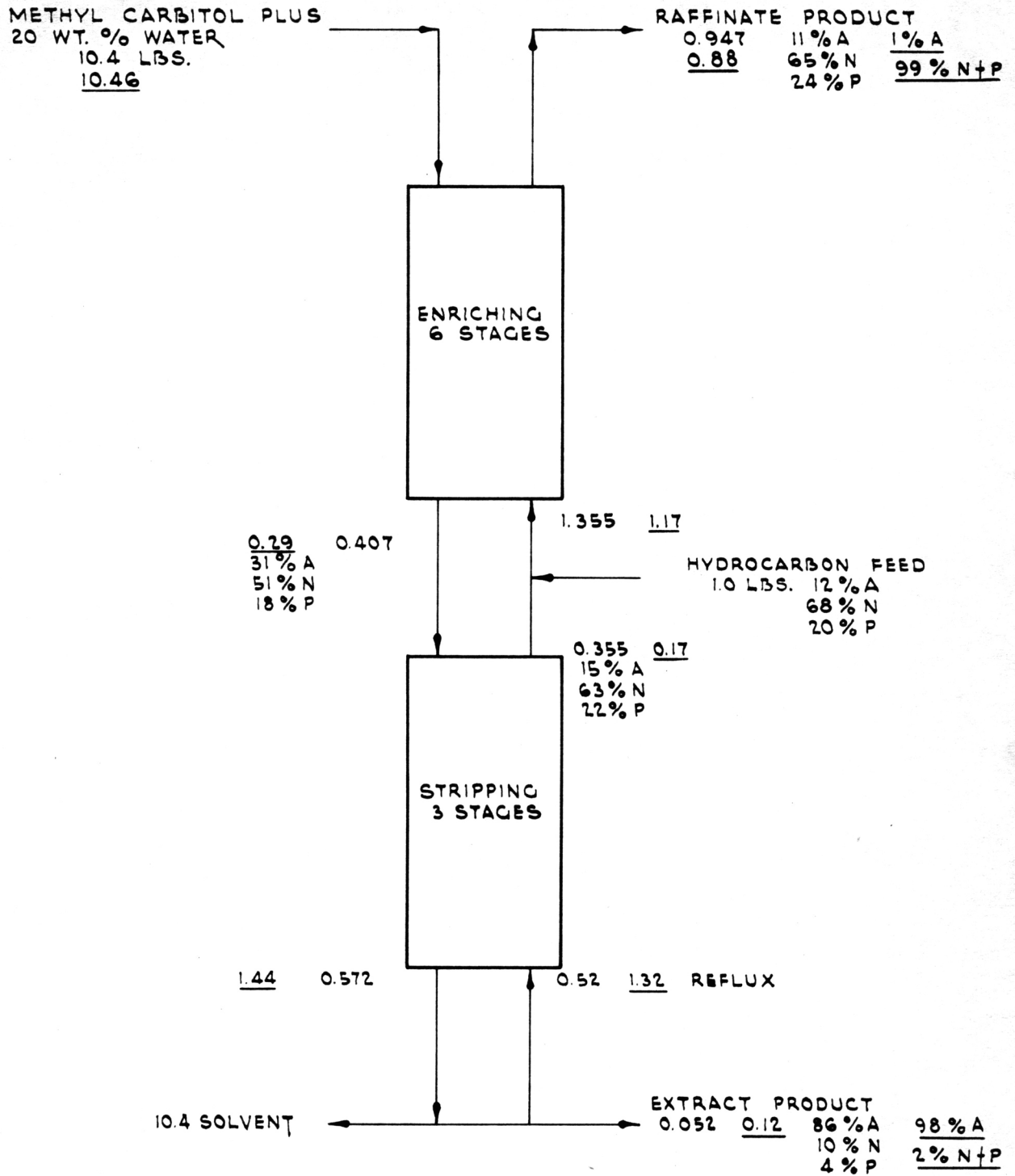


FIG. 2
 EQUILIBRIUM DATA FOR THE SYSTEM METHYL
 CARBITOL PLUS 20 WT. PER CENT WATER -
 AROMATICS - NAPHTHENES PLUS PARAFFINS
 AT 85°F



- NOTES: (a) RATES BASED ON 1.0 LBS. OF HYDROCARBON FEED.
 (b) RATES ARE ON SOLVENT FREE BASIS UNLESS INDICATED OTHERWISE.
 (c) RATES AND COMPOSITIONS NOT UNDERLINED ARE EXPERIMENTAL.
 (d) UNDERLINED COMPOSITIONS AND RATES ARE CALCULATED.
 (e) COMPOSITIONS ARE WEIGHT PER CENT.

FIG. 3 FLOWS AND COMPOSITIONS FOR AROMATIC SEPARATION

TABLE VI

ESTIMATED EQUILIBRIUM DATA FOR METHYL CARBITOL
PLUS 5 WT PER CENT WATER - HYDROCARBON SYSTEM

Solubility Ratio = 3.1
Estimated Selectivity = 2.33

Compositions, Wt Per Cent Aromatics Plus Naphthenes

<u>EXTRACT</u>	<u>RAFFINATE</u>
10	4.6
20	9.7
30	15.6
40	22.3
50	30.0
60	38.5
70	50.0
80	63.2
90	79.3
100	100.0

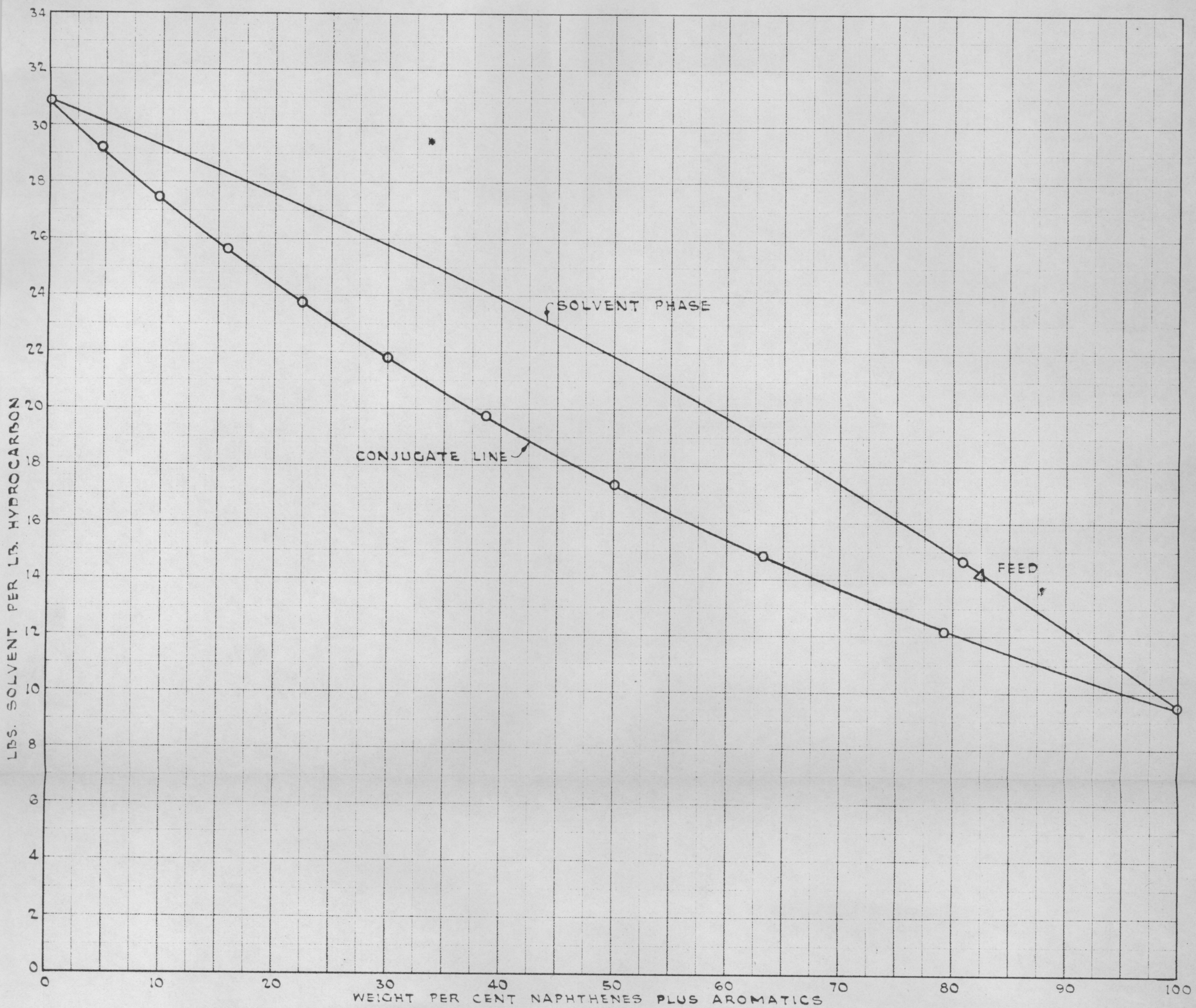
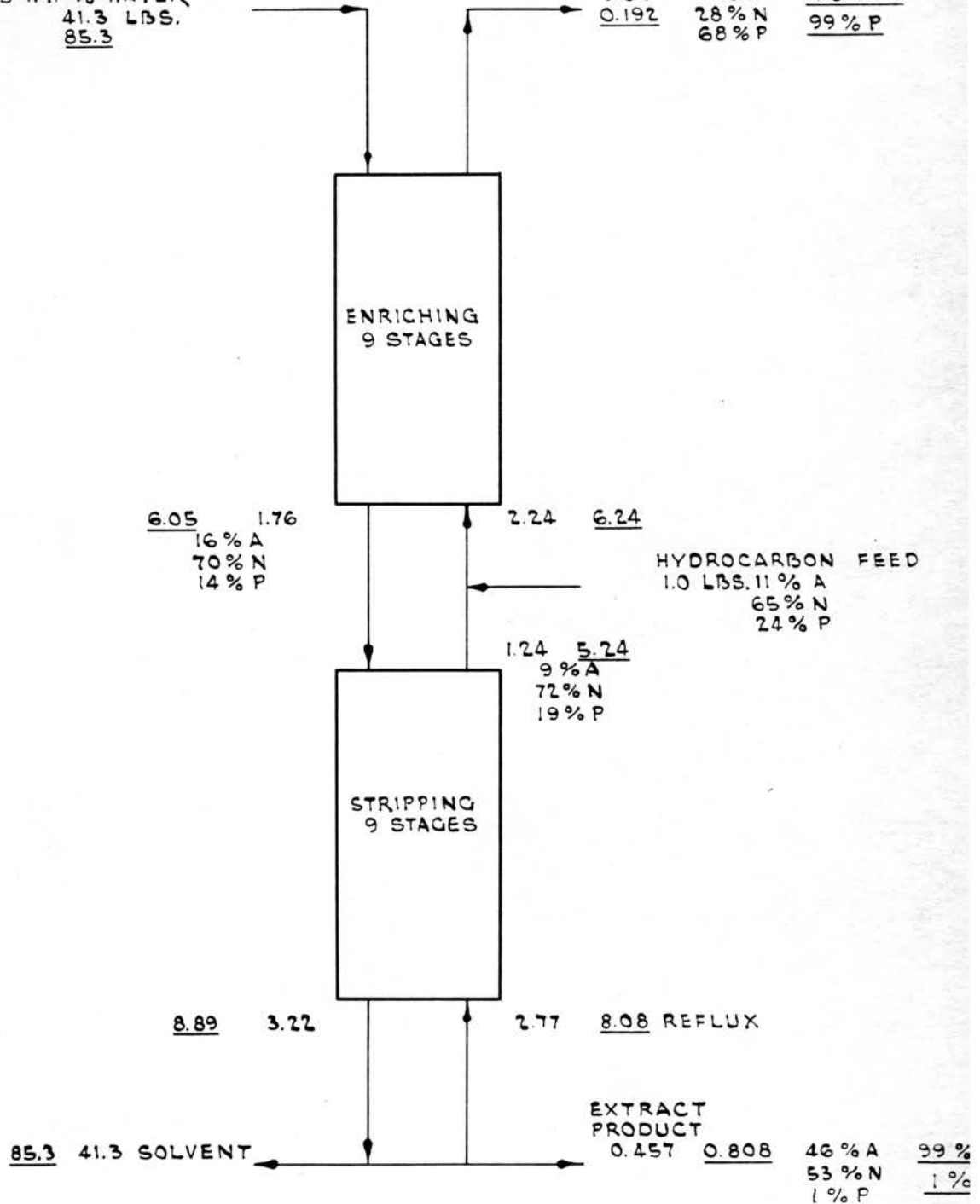


FIG. 4
 EQUILIBRIUM DATA FOR THE SYSTEM METHYL
 CARBITOL PLUS 5 WT. PER CENT WATER -
 AROMATICS PLUS NAPHTHENES - PARAFFINS
 AT 85°F

METHYL CARBITOL PLUS
 5 WT. % WATER
 41.3 LBS.
85.3

RAFFINATE PRODUCT
 0.50 4% A
0.192 28% N 1% A+N
 68% P 99% P



NOTES: (a) RATES BASED ON 1.0 LBS. OF HYDROCARBON FEED.
 (b) RATES ARE ON SOLVENT FREE BASIS UNLESS INDICATED OTHERWISE.
 (c) RATES AND COMPOSITIONS NOT UNDERLINED ARE EXPERIMENTAL.
 (d) UNDERLINED COMPOSITIONS AND RATES ARE CALCULATED.
 (e) COMPOSITIONS ARE WEIGHT PER CENT.

FIG. 5 NAPHTHENE PARAFFIN SEPARATION

DISCUSSION OF RESULTS

The results of these tests are summarized in Table VII below.

TABLE VII

Separation of Hydrocarbon Groups by
Methyl Carbitol Extraction

	<u>Feed</u>	<u>Aromatic Cut</u>	<u>Aromatic plus Naphthenic cut</u>	<u>Paraffinic cut</u>
Yield, Wt %	100	5.1	45.4	49.5
PONA Analyses, Wt %				
Aromatics	12	86*	46	4
Naphthenes	68	10	53	28
Paraffins	20	4	1	68
Motor Octane Numbers				
0 cc TEL/Gal	67.8	-	76.0	58.9
1	77.5	-	80.4	-
3	84.0	-	84.0	-
Research Octane Numbers				
0 cc TEL/Gal	71.2	-	84.9	50.4
1	80.5	-	91.2	-
3	87.4	-	96.4	-

Flow Rates Based on 1.0 Lbs of Original Feed Per hour

Naphthene-Paraffin Separation

	<u>Aromatic Separation</u>	<u>Enriching Section</u>	<u>Stripping Section</u>
Feed	1.0	2.24	1.76
Solvent	10.4	41.3	41.3
Extract Product	0.052	1.76	0.457
Raffinate	0.947	0.50	1.24
Reflux	0.52	-	2.77

As was previously stated, the purpose of these tests was to illustrate how a multi-component hydrocarbon mixture can be separated into molecular types by the use of liquid extraction. Table VII indicates that this was done although the various cuts overlapped to a certain degree. The aromatic cut, while not as rich as the preliminary calculations predicted, contained

* 75 Vol per cent toluene by ultra-violet analysis

86 weight per cent aromatics and represents considerable upgrading of a feed containing only 12 per cent aromatics. The low yield of the aromatic concentrate was a function of the amount of solvent fed to the extractor and the purity was a function of the number of separation stages available in the extraction unit. Thus it would have been possible to increase the yield of extract product by increasing the flow ratio of solvent to hydrocarbon and a greater aromatic purity would have been obtained if an extractor containing more stages had been used. More stages would have been available if the extraction had been made in two passes through the extractor as was the naphthene-paraffin separation.

Figure 3 graphically summarizes the calculated and experimental results for the aromatic extraction. It appears that the solubility in the upper portion of the extractor was greater than predicted thus allowing much more hydrocarbon to enter the lower section than was anticipated. This had the same effect that would have resulted from an increase in solvent rate, that is, a lower purity of aromatic product. The stripping section of the column produced less than the calculated separation which lowered the extract solubility and tended to give a low extract yield. In turn, the low extract yield necessarily produced a high raffinate yield giving a raffinate of a composition very close to that of the original hydrocarbon. This was unfortunate since a raffinate of low aromatic content was desired as hydrocarbon feed for the naphthenic-paraffinic separation. However, the degree of separation obtained in the aromatic extraction was gratifyingly close to the calculated separation. The feed tray composition was especially close to the calculated or hydrocarbon feed composition. In general, the material balances were fair for this separation though some inconsistencies

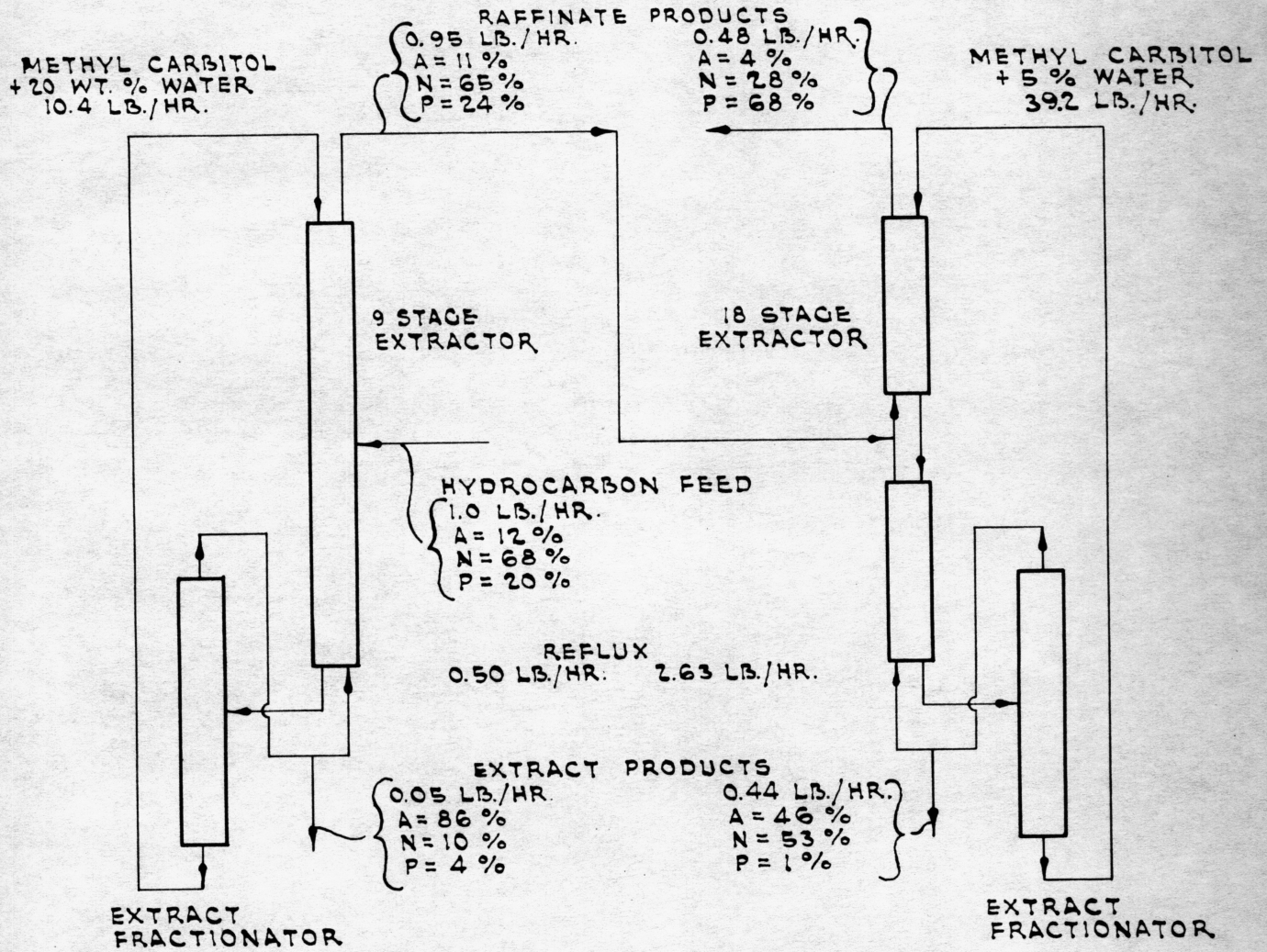
may be found in the component balances. This is probably a result of the inaccuracies inherent in the PONA method of analysis. In some instances the PONA analysis gives a very poor breakdown between the naphthene and paraffin components but the aromatic figure is usually reliable.

Figure 5 summarizes the naphthene-paraffin extraction giving both calculated and experimental results. This separation was more difficult than the aromatic separation requiring more separation stages and thus necessitating two passes through the extractor. With the exception of the raffinate product, experimental compositions agree closely with calculated compositions. The experimental flow conditions differed considerably from the calculated rates because the rates as originally set up were beyond the flooding rate of the column. When the rates were reduced to avoid flooding the extractor they were not cut back proportionately, resulting in a flow ratio quite different from that desired. It is probable that the preliminary calculations would have been more accurate if the feed to this run had been aromatic free. A small percentage of aromatics in a hydrocarbon has a large and unpredictable effect upon solubilities. Figure 6 presents the combined results of both separations described above as they would presumably be performed in a commercial operation.

Several physical tests were performed on the extracted hydrocarbon but the most significant tests were the octane numbers. Only a small amount of the aromatic concentrate was obtained and octane number were not run on this product. The octane numbers of the other streams are presented in Table VII. As could be expected, the naphthenic concentrate showed considerably larger octane numbers than the feed and the paraffinic concentrate exhibited low octane numbers. The relatively low lead

response of the naphthenic concentrate is probably due to its cyclic nature and probable higher sulfur content. It can be presumed that the aromatic concentrate would exhibit a high supercharge aviation fuel rating though no such test was performed. The other product tests are of no particular interest other than to illustrate that in both boiling range and density the raffinate is slightly lighter and the extracts slightly heavier than the hydrocarbon feeds.

It is apparent that the separation illustrated by these tests could not have been performed by a distillation process because the boiling ranges of the products overlap. Also, since the hydrocarbon feed had a boiling range of only 50°F, further separation by distillation would have required highly efficient equipment. This only emphasizes the fact that the two processes produce entirely different types of separation.



- NOTES: (a) RATES BASED ON 1.0 LB./HR. HYDROCARBON FEED.
 (b) HYDROCARBON RATES AND COMPOSITIONS ON SOLVENT FREE BASIS.
 (c) COMPOSITIONS ARE WEIGHT PER CENT.

FIG. 6 EXTRACTION OF HYDROCARBON WITH METHYL CARBITOL

CONCLUSIONS

The conclusions which may be drawn from this series of tests are as follows:

- A. A non-olefinic hydrocarbon stream can be cut up into the three groups, naphthenes, aromatics and paraffins, by the use of liquid extraction. This was illustrated by the extraction of a hydrocarbon using methyl carbitol plus varying amounts of water as the solvent.
- B. Liquid extraction will yield high-purity aromatics which are desirable as aviation fuel blending stocks. In this separation a concentrate was obtained which contained 86 weight per cent aromatics.
- C. Ponchon-type calculations can be adapted to multi-component systems in order to determine flow ratios and stage requirements. Estimated equilibrium data is accurate enough for these calculations.

SUGGESTED FURTHER WORK

This work as does nearly all research and development work answers a few questions but brings up several more. The investigation of liquid extraction for the separation of multi-component hydrocarbons should be continued. Further work is needed along the following lines:

A. The development of an accurate, "short-cut" method for the calculation of extractive separation of multi-component hydrocarbons when precise equilibrium data is unavailable.

B. The investigation of various solvents to determine both the properties of individual solvents and methods for predicting the performance of untested solvents.

C. The further development and testing of various types of extraction equipment should be carried out to determine or develop the most efficient type of apparatus. This is especially needed for large or commercial scale equipment.

D. The development of better and faster analytical methods for the determination of hydrocarbon compositions.

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APPENDIX

TABLE VIII

Summary of Analytical Results for Aromatic Separation

<u>Sample</u>	<u>HCF</u>	<u>Raff</u>	<u>Ext</u>
API Gravity @ 60F	57.6	57.7	54.9
<u>ASTM Distillation, F</u>			
IBP	206	206	200
5	214	213	218
10	216	215	220
20	216	216	221
30	216	216	222
40	217	216	222
50	218	218	222
60	218	218	222
70	218	219	223
80	220	220	224
90	222	222	225
95	225	226	227
EP	250	258	246
<u>PONA Analysis, Wt %</u>			
Aromatics	12	11	86
Naphthenes	68	65	10
Paraffins	20	24	4
<u>Motor Octane Numbers</u>			
0 cc TEL/Gal	67.8	-	
1	77.5	-	
3	84.0	-	
<u>Research Octane Numbers</u>			
0 cc TEL/Gal	71.2	-	
1	80.5	-	
3	87.4	-	

TABLE IX

Summary of Analytical Results from Naphthene Paraffin
Separation

<u>Sample</u>	<u>Enriching</u>			<u>Stripping</u>	
	<u>HCF</u>	<u>Raff</u>	<u>Ext</u>	<u>Raff</u>	<u>Ext</u>
API Gravity @ 60F	57.7	61.8	54.2	54.7	45.6
<u>ASTM Distillation, F</u>					
IBP	206	207	206	180	194
5 %	213	220	214	210	212
10	215	221	215	214	213
20	216	222	216	216	214
30	216	222	216	217	215
40	216	222	216	217	216
50	218	224	217	218	216
60	218	224	218	219	217
70	219	226	218	220	218
80	220	228	220	220	218
90	222	230	222	225	220
95	226	234	226	227	224
EP	258	268	251	257	248
<u>PONA Analysis, Wt %</u>					
Aromatics	11	4	16	9	46
Naphthenes	65	28	70	72	53
Paraffins	24	68	14	19	1
<u>Motor Octane Numbers</u>					
0 cc TEL/Gal	-	58.9	-	-	76.0
1	-	-	-	-	80.4
3	-	-	-	-	84.0
<u>Research Octane Numbers</u>					
0 cc TEL/Gal	-	59.4	-	-	84.9
1	-	-	-	-	91.2
3	-	-	-	-	96.4

DEFINITIONS AND ABBREVIATIONS

- Ext (Extract) - solvent phase or hydrocarbon contained in solvent phase depending upon usage.
- HCF (Hydrocarbon feed)
- IBP (Initial boiling point)
- Methyl Carbitol - commercial name for diethylene glycol, monomethyl ether.
- PONA - analytical procedure for determining composition of a hydrocarbon. The name was derived from the first letters of paraffins, olefins, naphthenes and aromatics.
- Raff (Raffinate) - hydrocarbon phase.
- Reflux: Hydrocarbon distilled from the extract phase and returned to the bottom of the extraction unit.
- Reflux ratio: Ratio of reflux returned to extractor to extract hydrocarbon withdrawn as product.
- SF (Solvent feed)
- TEL (Tetra-ethyl lead)

SYMBOLS

- X_1 Hydrocarbon composition of one component in the solvent phase on a solvent free basis. Subscript 1 refers to the component most soluble in solvent.
- X_2 Refers to composition of the least soluble hydrocarbon in the solvent phase.
- Y_1 and Y_2 Hydrocarbon compositions in hydrocarbon phase.
- Z Selectivity.

THESIS TITLE: SEPARATION OF MULTI-COMPONENT
HYDROCARBONS BY LIQUID EXTRACTION

NAME OF AUTHOR: RUSSELL O. SHELTON

THESIS ADVISER: DR. C. L. NICKOLLS

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