

SOLVENT EXTRACTION OF LUBRICATING OILS

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## I. INTRODUCTION

Solvent extraction, a comparatively unknown method of refining lubricating oils only a few years ago, is today one of the most, if not the most, important method of refining lubricating oils. It has largely replaced the older acid method of refining and has permitted the mid-continent and west coast refiners of lubricating oils to produce oils of better quality than that formerly made from the so called Pennsylvania paraffin base crudes. It was not possible to do this before the introduction of the solvent refining methods. Although the use of the method had been widely adopted, and many millions of dollars have been spent in the construction of plants for the solvent extraction of lubricating oils, the very complex problem of column design has been solved by purely empirical methods. The chemical complexity of petroleum crudes is responsible for this situation.

A great amount of research has been done on simple two and three component extraction systems such as toluene, benzoic acid and water. In these cases the calculation of the transfer coefficients has been comparatively simple since the chemical composition of the resulting phases was easily determined. Up to the present time, it has been difficult to determine the exact chemical composition of petroleum.

It was the object of this investigation to endeavor to apply the methods used on the simple two component systems to the extraction of lubricating oils by utilization of an empirical factor, the Viscosity Gravity Constant, which is an indication of the chemical composition of petroleum.

It was planned to carry out a number of operations in a spray column with different ratios of solvent to oil. The area of contact, quantity of flow of solvent, and the Viscosity Gravity Constant for the raffinate and extract of each run will be determined. It was hoped that the transfer coefficients as calculated from these data can be compared with the actual transfer coefficients.

It was also the object of this research to determine some of the improvements in the oil brought about by the use of solvent extraction.



## II. REVIEW OF LITERATURE.

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Sherwood has defined solvent extraction as a process or operation "that refers to the separation of the components of a liquid solution by treatment with an immiscible solvent in which one or more of the components of the solution are soluble". This operation has found its major commercial application in the refining of lubricating oils from petroleum crudes.

HISTORY. Although the use of petroleum and tar has been reported by Herodotus<sup>47</sup> (450 B.C.) and by other historians at dates prior to 1735, they did not tell how the oil was refined. The first real reference to the refining is that of the application of distillation to petroleum in Russia in 1775.<sup>47</sup> The first real refinery, as it is thought of today, was built by William Barnsdall and William H. Abbott in 1860 at Titusville, Pennsylvania.<sup>48</sup> It would seem then that this was the actual beginning of the petroleum refining industry.

The possibility of removing the undesirable constituents from petroleum oils by the purely physical action of a solvent has offered attractive possibilities since the very beginning of the petroleum industry.<sup>36</sup> Credit should be given to A. M. Butlerov for the first step in this direction.<sup>35</sup> He applied solvents to petroleum refining as early as 1870.



He was followed at later dates by Aisinman, Zuloaieche and Choritschkoff, but no commercially successful use resulted. The first commercially successful process was that of L. Edeleau who secured a British patent in 1908 on a process utilizing sulfur dioxide as a solvent.<sup>37</sup> The process was developed for the production and refining of kerosene which was the all important petroleum product at that time. These solvent extraction methods as applied to kerosene were soon extended to the refining of lubricating oils.<sup>38</sup>

From time to time other chemicals were investigated as to their uses as solvents. However, the first major investigation published was that of Ferris, Berkheimer and Henderson,<sup>23</sup> in 1931, who investigated the ability of 110 solvents to separate lubricating oils into two dissimilar fractions. At the same time the major oil refining companies were also investigating the possibility of solvent extraction with the result that when it became necessary to abandon the old refining methods, several competitive solvent refining processes were placed on the market and were successfully applied at the various refineries.<sup>38</sup>

The oldest plant designed especially for solvent extraction of lubricating oils was built in 1929 by the Imperial Oil Company of Canada.<sup>39</sup> This plant was built for the Phenol process. With the decreasing market for kerosene and the increasing market for lubricating oils that could meet certain specifications, some of the plants built for kerosene were converted to lubricating oil extraction plants.

TABLE I  
 Charging Capacity of Solvent Refining Plants Producing  
 Lubricating Oils

Plant Capacity in United States and Abroad

Year	Barrels 1933	Barrels 1934	Barrels 1935	Barrels 1936	Barrels 1937	Barrels 1938	Percentage Increase 1933-1938
United States	800	3400	18,742	45,572	48,572	48,572	5,071.5
Europe and Abroad	2000	5500	5500	7,980	13,250	20,786	939.3
Total	2800	8900	24,242	53,552	61,822	69,358	3,367.7

The growth of the plant capacities as shown in Table 1. illustrate the phenomenal growth of solvent extraction plants in the United States and Europe since 1930.

COMPOSITION OF PETROLEUM. The lack of knowledge of the chemical composition has been a lamentable fact for a number of years, and although there has been an enormous amount of work done on it, the problem is yet to be solved. However, we can group types of compounds found in petroleum as follows:

- 1- Asphaltenes. Dark-colored, high melting point, thermoplastic solids with a relatively low ratio of hydrogen to carbon.
- 2- Carbogens. Believed to represent, chemically high molecular weight, unsaturated compounds related to the aromatic or coal-tar series which in service are readily converted to sludge and carbon.
- 3- Naphthenes. Cyclic compounds of the polymethylene series recognized by a comparatively steep viscosity temperature curve and a relatively low flash point for a given viscosity.
- 4- Parathenes. The name given to the highest type of hydrocarbon lubricants, believed to consist largely of naphthenic rings with paraffin side chains in the same



molecule; they have been found to combine oiliness, flat viscosity temperature characteristics, high flash point, stability toward sludge formation and relatively low carbon forming tendency.

5- Paraffins. Ranging in consistency from soft petrolatums to hard, brittle waxes.

Crudes that contain a large percentage of parathenes, such as are found in the eastern part of the United States, are generally referred to as paraffin base crudes since they contain paraffin. In like manner, the crude found on the west coast of the United States are commonly referred to as naphthenic base crudes since they contain a large percentage of naphthenes. On this basis, the crude that are found in the United States may be classified according to their content of these two classes of compounds. Crudes from the mid-continent district possess properties intermediate between those of the so-called paraffin and naphthene base crudes. Hence, the terms intermediate and mixed base have been used to describe these oils. A classification of the crudes found in the United States on this basis may be as follows:

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A- Paraffin base:- Distillates paraffinic throughout.

B- Paraffin-intermediate base:- Light fractions paraffinic; heavy fractions intermediate.

C- Intermediate-paraffinic base:- Light fractions intermediate; heavy fractions paraffinic.



D- Intermediate base:- Distillates intermediates throughout.

E- Intermediate-naphthenic base:- Light fractions intermediate; heavy fractions naphthenic.

F- Naphthenic-intermediate base:- Light fractions naphthenic; heavy fractions intermediate.

G- Naphthenic base:- Distillates naphthenic throughout.

Generally speaking, the composition of the crudes from the east coast to the west coast progress from type A to type G as above. However, this is not entirely true since there are numerous crudes which might be called exceptions.

THE REQUIREMENTS FOR A GOOD LUBRICATING OIL. The requirements of an oil for good internal combustion engine lubrication have been determined by extensive research, and may be tabulated as follows:

- 1- Low carbon forming tendencies.
- 2- High viscosity index.
- 3- High resistance to oxidation or sludging
- 4- Low pour point.

To obtain these properties five types of constituents of ordinary lubricating oil fractions must be eliminated:

- 1- Wax, to obtain a low pour point.
- 2- Compounds with a very high viscosity, intermediate in molecular weight between the asphalts

and the heaviest lubricating fractions that have carbon forming tendencies.

- 3- Color bodies, primarily to make oil marketable.
- 4- Asphalt, for several reasons, primarily its carbon forming tendencies.
- 5- Naphthenic compounds which are generally responsible for low viscosity indices and low resistance to oxidation.

THE NECESSITY OF SOLVENT EXTRACTION. <sup>44</sup> Kwal has pointed out that in the last few years refiners have displayed an increasing interest in the development of improved lubricants that offer greater resistance to carbon deposition, oxidation and sludging, and are less susceptible to viscosity-temperature variations.

<sup>10</sup> Cannon and Fenske have pointed out that solvent extraction stands second only to distillation as a process for the separation of petroleum hydrocarbons. Distillation is, in general, limited to separation according to molecular size and is operable only below the cracking temperature; on the other hand, solvent extraction may be employed for separation according to either molecular size or type, and is operable over the complete range of hydrocarbons that occur in petroleum.

Before the development of the commercially successful solvent extraction process there was a method of refining lubricating oils based on the physical and chemical action

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of sulfuric acid. By modifying the conditions of the acid treatment, it is possible to control to a certain extent the predominance of these two major actions of sulfuric acid, but it is not possible to eliminate either completely. The chemical action causes the formation of polymerized, condensed and sulfonated compounds which for the most part are removed in the form of sludge. However, some of these colloidal compounds remain in the oil causing effects that are detrimental to the use of the oil as lubricating substances. In addition, some of the oil is lost in the sludge, and the sludge is in most cases a worthless byproduct of the refining process.

The existence of these undesirable effects and the losses led refiners to seek a means of refining lubricating oils that would not involve these losses and effects. From an investigation of the existing process, it was evident that a process based on physical action alone was the answer to the problem. It was obvious that this process should be  
44  
a solvent extraction process.

Two of these undesirable effects, corrosion and low viscosity index, were discovered by research and were brought to the attention of the public by advertising.  
49  
It was this that resulted in the phenomenal expansion of plant capacity over the short span of two years.

THE TESTING OF LUBRICATING OIL. Because of the lack of accurate and complete analytical information concerning



the composition of petroleum, it is impossible to determine just when the requirements for good lubricating oils is attained. However, a number of purely empirical relationships have been devised by investigators in order that some measure of the qualities might be realized.

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Hunter and Nash have approached the problem from a simplified point of view. They pointed out that the "oils are usually considered to be made up of two major groups of constituents generally referred to as 'naphthenic' and 'paraffinic', where the naphthenic is to be interpreted as denoting a mixture of hydrocarbons relatively poor in hydrogen, and the term 'paraffinic' as a mixture of hydrocarbon groups relatively rich in hydrogen".

17

Dean and Davis suggested the use of a "Viscosity Index Constant". From the standpoint of viscosity, the perfect oil has the same viscosity at all temperature. The viscosity index (V.I.) is an arbitrary, numerical index used to indicate the relative change in viscosity of oils for a given temperature change. Specifically, the viscosity index indicates the relation which the Saybolt Universal Viscosity of an oil at 100°F. bears to the Saybolt Universal Viscosity of an average paraffin oil and an average naphthene oil at that temperature, all three having the same viscosity at 210°F. The viscosity index of an average paraffin oil has arbitrarily been assumed to be 100, whereas that of an average



naphthene oil has been assumed to be zero.

According to Olower,<sup>11</sup> "the viscosity index serves not only to indicate viscosity changes with temperature but also to identify the base of the crude from which the oil is made, provided that a viscosity index improver has not been used". The calculation of the viscosity index has been simplified by the development of a series of alignment charts.<sup>11,29</sup>

Hill and Coats<sup>31</sup> have used a mathematical expression utilizing a relationship between viscosity and specific gravity to indicate the composition of crudes. When they plotted specific gravity against viscosity, they obtained straight line on semi-logarithmic coordinates. From this they derived the following mathematical expression:

$$V. G. C. = \frac{10 G - 1.0752 \log (V - 38)}{10 - \log (V - 38)}$$

Where:

V. G. C. = the viscosity gravity constant.

G. = the specific gravity at 60° F.

V. = the viscosity in Saybolt Universal  
Seconds at 100° F.

A similar expression for the viscosity at 210° F. is as follows:

$$V. G. C. = \frac{G - 0.24 - 0.022 \log (V' - 35.5)}{0.755}$$

Where:

V. G. C. = the viscosity gravity constant.

G. = the specific gravity at 60° F.

$V'$  = the Saybolt Universal Viscosity  
at 310° F.

The V.G.C. is an index of the chemical composition of the oil. It has a definite value, readily calculable for an oil. Oils of different viscosities but the same VGC are of similar chemical composition.

Ferris, Berkheimer and Henderson<sup>23</sup> have recognized the value of this constant in their work on solvent extraction of lubricating oils to indicate the degree of naphthenicity and paraffinicity of the lubricating oils. They also found the extreme Gulf Coast crudes have a V.G.C. of 0.807. A number of other investigators<sup>25,34,66,63,53</sup> have utilized this constant in their work.

Strang<sup>62</sup> has found that a naphthenic oil has a high V.G.C. and, at the same time, a low viscosity index, and that a paraffinic oil has a low V.G.C. and a high viscosity index.

Another type of gravity that is often used in the petroleum industry is the A.P.I. (American Petroleum Institute) gravity. It is related to specific gravity by the following mathematical expression:

$$\text{A.P.I. degrees at } 60^{\circ} \text{ F.} = \frac{141.5}{G} - 131.5$$

Where:

$G$  = specific gravity at 60° F.

However, gravity is an important quantitative factor, but bears no relationship to quality or usefulness of an oil.

2

The Conradson Carbon Residue<sup>2</sup> is another test of great importance in lubricating oils. Some oils upon vaporization leave a non-volatile carbonaceous residue which is undesirable. This test determines the amount of carbon residue and is a measure of the grade of oil that is tested.

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The Sligh Oxidation Number<sup>12</sup> is one of the most important tests that is applied to lubricating oils. All lubricating oils, when in contact with air, tend to oxidize forming undesirable compounds of a gummy, resinous, asphaltic, acid character. The Sligh Oxidation Number is a measure of the ability of a lubricating oil to resist oxidation. There are a number of other tests similar to the Sligh Test. However, the only other important test is the Indiana<sup>12</sup> test, which is very similar to the Sligh. Oils having high oxidation numbers as determined by these tests are readily susceptible to oxidation and produce soluble pitch like materials, commonly called asphaltenes, which are difficult to dissolve and are subsequently deposited in the oiling system as sludge.

A straight mineral oil when properly refined should show no acidity. However, if not properly refined, it may contain some substances that are undesirable such as naphthenic, or fatty acids, or traces of mineral acids used in the refining of oil and not entirely removed.

3

The Neutralization Number<sup>3</sup> is a measure of this acidity.



Lubricating oils before refining, or after long usage, may contain some so called asphalt or tar. The amount of this material is determined by centrifuging and is expressed as the Precipitation Number.<sup>4</sup>

Another test of great importance in lubricating oils is the Pour Point test,<sup>5</sup> which is determined as the temperature at which it will just flow under prescribed conditions.

Color tests<sup>6</sup> are very important from the standpoint of marketability of the oil.

REQUIREMENTS OF AN IDEAL SOLVENT. An ideal solvent for extraction of oils should possess the following properties:<sup>41</sup>

- 1- The solvent should be capable of extracting from petroleum oils the undesirable constituents so as to yield marketable products equal or superior to those obtained by other refining methods.
- 2- The solubility of the solvent in the oil layer should be low, while that of the impurities in the solvent must be high.
- 3- The solvent should be able to display its best solvent power at temperatures which do not require application of excessive quantities of heat or refrigeration, and at which the oil is sufficiently fluid to insure a good contact.

- 4- The boiling point of the solvent must be sufficiently low to insure its easy separation from the oil by distillation. It is also desirable that its vapor pressure at extraction temperatures should not be exceptionally high in order to avoid the use of pressure equipment.
- 5- The specific gravity of the solvent should be relatively high and interfacial tension low in order to obtain quick and complete separation into two liquid phases.
- 6- The freezing point of the solvent should be low in order to avoid complications in handling in cold weather.
- 7- The solvent must be stable and have no appreciable chemical action on the oil at temperatures encountered in separating the solvent from the oil.
- 8- The solvent must be available in large quantities at low cost.
- 9- The solvent should not exhibit exceptionally corrosive properties that would require the use of expensive corrosive resistant materials.
- 10- The solvent should not be of a poisonous or explosive nature in order to eliminate the danger

of handling it at the plant.

- 11- The quantity of solvent required for extracting the oil must not be excessive so as to insure a reasonable throughput in a plant of normal size.

SOLVENT REFINING PROCESSES. In extracting oils with solvents the following types of processes are feasible: <sup>42</sup>

- 1- Single solvent processes wherein the solvent consists of one chemical substance only.
- 2- Mixed solvent processes wherein the solvent consists of more than one chemical substance.
- 3- Double solvent processes wherein the oil is dissolved in a solvent not miscible with the solvent used for extracting the impurities, this solution being extracted with a single or mixed solvent.

There is probably no solvent in commercial use today that will fulfill all the requirements as enumerated in the preceding section. However, the solvents now in use approach these requirements closely enough to be commercially feasible.

Some of the solvents that are now in use or have been used are: <sup>49</sup>

- 1- Sulfur dioxide
- 2- Sulfur dioxide - benzol
- 3- Phenol
- 4- Dichlorethyl ether (Chlorex)
- 5- Furfural



- 6- Nitrobenzene
- 7- Propane - cresylic acid (Duo - Sol)
- 8- Nitrobenzene - Sulfuric acid
- 9- Crotonaldehyde - acrolein
- 10- Aniline
- 11- Propane
- 12- Acetic Acid

THE DEVELOPMENT OF THE FURFURAL PROCESS. Experi-  
<sup>45</sup>ments conducted by Manley, McCarty and Cross in the  
laboratories of The Texas Company in their search for a  
solvent that would best meet the requirements as outlined  
previously in this review, found that furfural would meet  
them very well. Furfural was selected by this company  
because of its relatively low cost, its availability in  
large quantities, high selective action on a wide variety  
of stocks, stability in the solvent, stability in the  
recovery operations. According to Manley et. al. <sup>45</sup> fur-  
fural compares favorably in price with practically all of  
the commercially available refining solvents. Further-  
more, furfural lends itself readily to the production of  
special oils such as high grade turbine oils, electric  
refrigeration oils, white oils, transformer oils, air-  
plane oils and the like. The properties of furfural are  
shown in Table II.

The raw material source in the manufacture of fur-  
fural is agricultural wastes such as oat hulls, straw,

TABLE II  
 Properties of Furfural<sup>1</sup>

Structural formula:	$  \begin{array}{ccccccc}  & & \text{H} & - & \text{C} & - & \text{C} & - & \text{H} \\  & & & & \parallel & & \parallel & & \\  \text{H} & - & \text{C} & & & & \text{C} & - & \text{CHO} \\  & & \parallel & & & & \parallel & & \\  & & \text{O} & & & & \text{O} & & \\  & & & & \diagdown & & / & & \\  & & & & \text{O} & & & &   \end{array}  $
Boiling point.....	158 - 162 °C.
Specific gravity.....	1.158 - 1.160
Flash point.....	55 - 57 °C.
Aldehyde content (Minimum).....	98.5 %
Organic acidity (As acetic acid).....	0.33 %
Color.....	Straw yellow to amber
Freezing point.....	-34.00 °F.
Viscosity at 100°F. in Saybolt	
Universal Seconds.....	28.7 Sec.
Specific heat (68 to 212°F.).....	0.416
Heat of vaporization (29.9 in. Hg.)	
in B.T.U. per pound.....	193.5
Vapor pressure at 100°F. (mm.).....	10
Solubility in water at 20°C. (per cent by volume).....	8.3 %

corn cobs, rice hulls, etc. Its production in commercial practice is comparatively simple, and good yields of solvent are obtained from relatively inexpensive waste materials. Furfural is prepared first by the hydrolysis of oat hull pentosan to pentose sugars, then by the dehydration of the latter.

It has been shown <sup>45</sup> that it is possible to obtain the same results in counterflow extraction with a little less than half of the solvent required in batch extractions.

It has also been shown <sup>45</sup> that furfural can be applied to lubricating oils at temperatures ranging from 100 to 250° F. This permits its use on high viscosity or high wax content oil. However, the oil is usually dewaxed before it is treated with furfural.

Manley et. al. <sup>45</sup> found that the selectivity of furfural begins to decrease around 250° F., and that recovery of the solvent by vacuum distillation permits operation at vacuum temperatures of 210 to 230° F. At these temperature it is possible to allow more complete removal of the furfural from the oil under moderate operating conditions. At oil temperatures of 375° F. or above and under 28 inches of vacuum, experience has shown that no furfural can be detected in the stripped oils; but provisions are made in plant operations to avoid losses in the stripped oils by steaming the remaining traces of furfural from the oil leaving the dry vacuum stripping unit.



In order that the solvent might be protected, it must be kept free from mineral acids, caustic alkali and ammonia, and against severe oxidation conditions. In general, it has been found preferable to recover the solvent under reduced pressures in order to keep solvent quantities in the stripped oil at a minimum and in order to prevent polymerization of the extract to a solid or semi solid condition due to excessive heat. Plant losses are not more than 0.2 per cent on the basis of total solvent used in the processing.

<sup>45</sup>  
Manley et. al. <sup>45</sup> have pointed out that one of the outstanding advantages in the use of furfural is its low toxicity. No ill effects whatsoever are encountered when the solvent is handled with reasonable care. They also have found that the cost of installation of a furfural plant amounts to about \$200 per barrel daily capacity; that cost of operation including overhead and fixed charges is about \$0.51 per 42 gallon barrel; that the furfural process is well adapted to the manufacture of 100 viscosity index and better oils from mid-continent crudes. In addition, they investigated the operating characteristics in high speed automobiles and found that furfural refined oils stand up just as well as the premium grades of lubricating oils, on the American market.

SOLVENT EXTRACTION METHODS. Three methods are employed in applying the solvent to the oil:

- 1- Single batch extraction, in which the solvent is applied to the oil in a single portion.
- 2- Multiple batch extractions, in which the solvent is applied to the oil in several doses, each of which consists of fresh solvent.
- 3- Countercurrent extraction, in which fresh solvent is mixed with the oil leaving the extraction system and partially spent solvent is mixed with the incoming oil containing many impurities.
- 4- Continuous countercurrent extraction is a modification of number three.

In solvent extraction processes that are, by definition, "the separation of the components of a liquid solution by treatment with an immiscible solvent" some designation must be given to these separated fractions in order that they may be easily distinguished one from the other. It is customary to designate the phase as the "Extract" phase. This phase usually contains the portion of the liquid solution that might be termed the impurity or the portion of the liquid solution

that is removed by the solvent. The other phase, the solvent poor phase, is called the "raffinate" phase. This phase contains the "purified" fraction of the oil.

In the case of the single batch extraction which is the simplest type of operation, the solute is transferred from one phase to the other, and the concentrations in the two phases approach equilibrium. A diagrammatical sketch of the equipment used in this type of extraction may be as that shown in Fig. 1. Because the efficiency permitted by the equilibrium involved is usually low, this type of operation is seldom employed for large scale work.

In the case of multiple batch extraction, as shown diagrammatically in Fig. 2, there is an obvious improvement over the single batch operation in which the extraction is repeated on the raffinate from the first contact. The reduction of the solute content of the raffinate may be improved to any desired extent by increasing the number of contacts, or stages. The concentration of the solute from the second and later separation is uneconomical of solvent.

The maximum efficiency is obtained when the total solvent to be used is divided in equal parts, that quantity being used in each stage.

In countercurrent multiple batch extraction it is obvious that fresh solvent added in the last stages will result in an extract leaving the last stages that is so



nearly all solvent that it could be used as such, a countercurrent, a countercurrent multiple batch or contact extraction method would result. Such a method is shown diagrammatically in Fig. 3. The system shown is for a three stage process. However, it is obvious that any number of stages may be utilized. It may be seen that the solution enters at one end of the apparatus and the solvent enters at the opposite end. The two streams flow countercurrently. All of the solvent passes through each stage and the overall efficiency for a given amount of solvent and number of stages is appreciably better than when part of the fresh solvent is used in each stage.

Until the past few years this type of operation with from two to five stages was the one most commonly used for commercial solvent extraction. The operation may be either batch or continuous, as exemplified by systems of batch mixers and settlers on the one hand, or by the bubble cap plate column on the other.<sup>57</sup>

Countercurrent extraction of the continuous type is an operation in which there is obtained intimate contact between phases in an apparatus, or in which the two phases are passed continuously in opposite directions producing maximum efficiency of extraction. Towers packed with Raschig rings or other filling may be employed. Such an apparatus is diagrammatically shown in

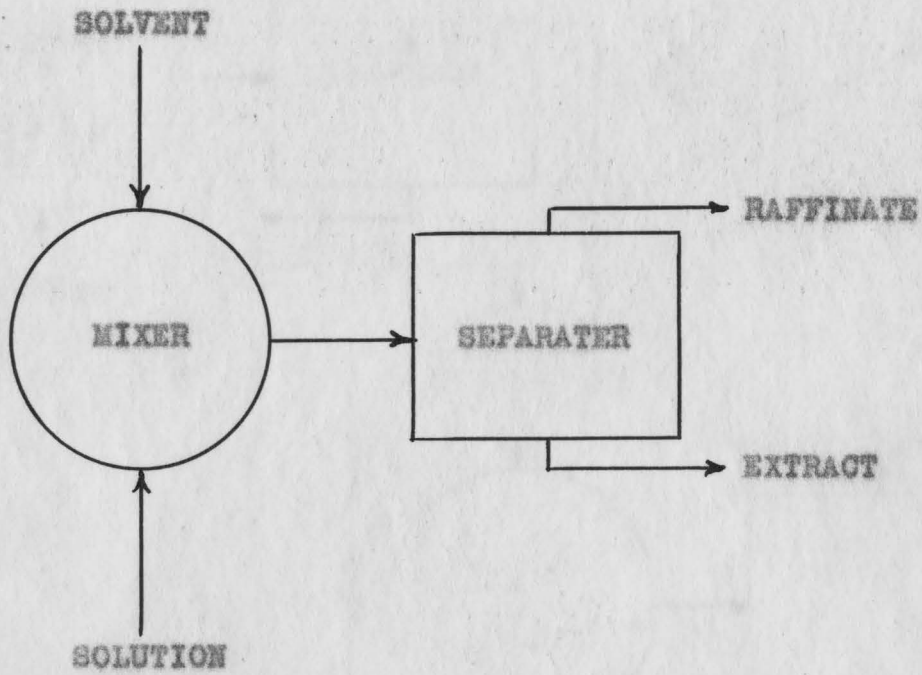


Fig. 1 - Single Batch Extraction

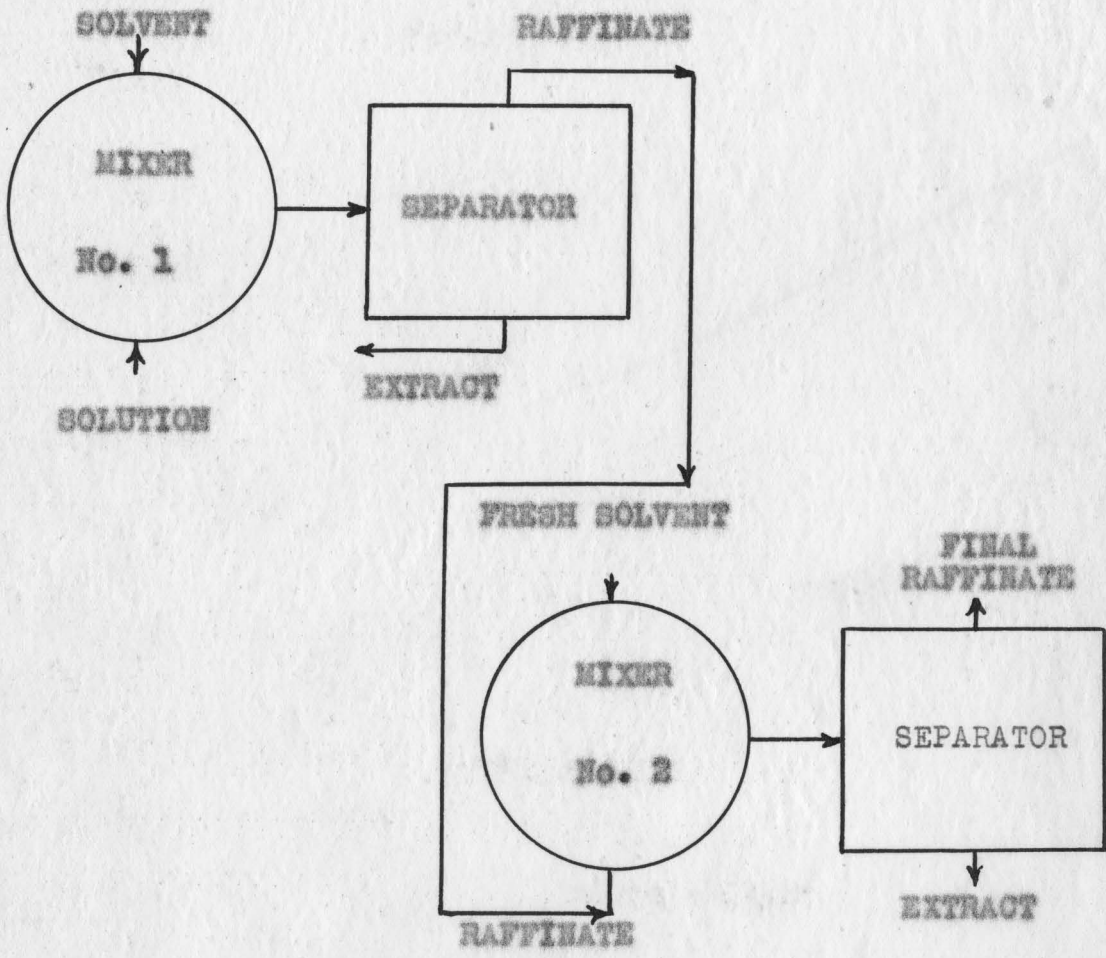


Fig. 2 - Multiple Batch Extraction Using Fresh Solvent In Each Case



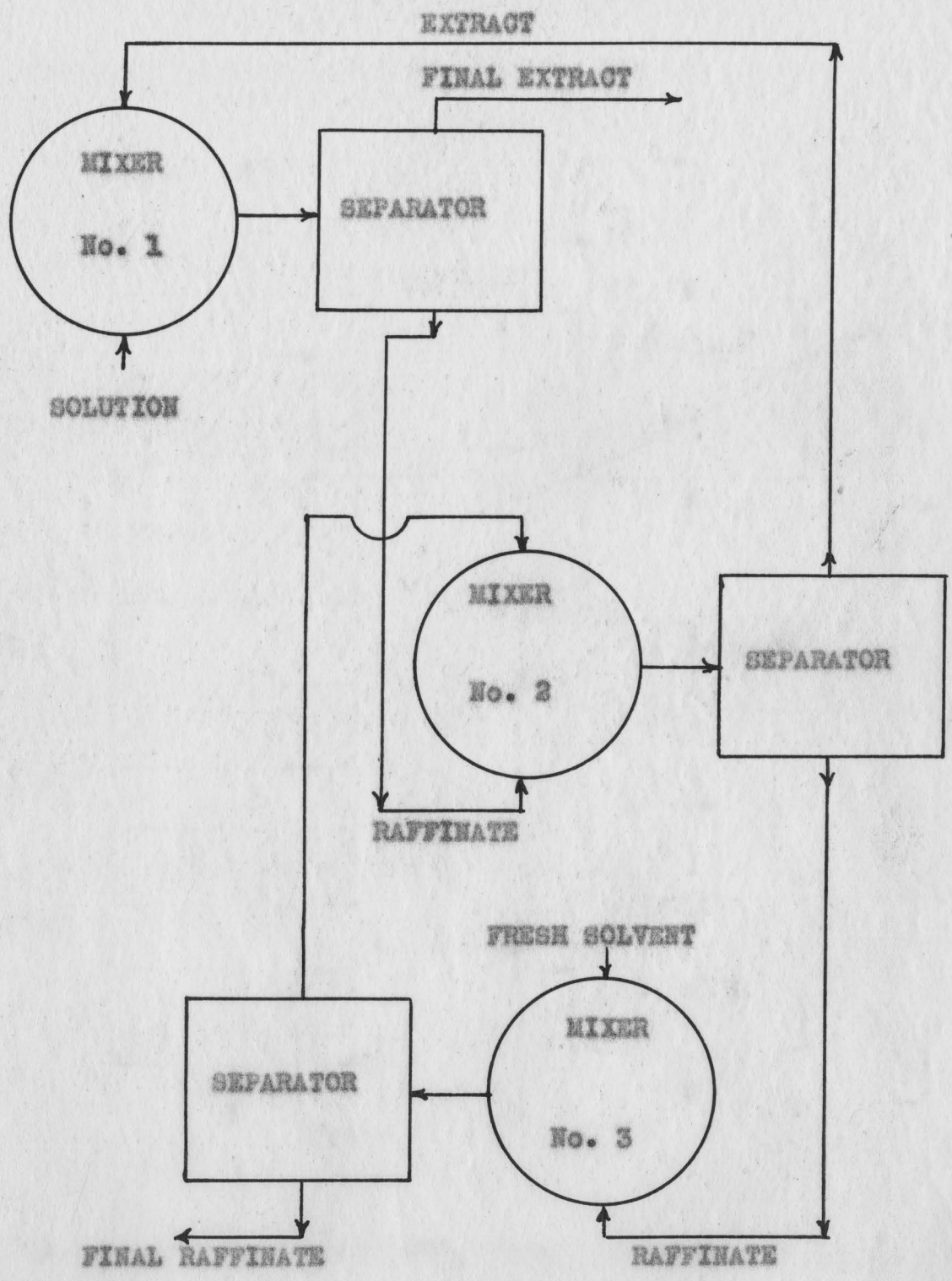


Fig. 3 - Three Stage Countercurrent Multiple Contact Extraction

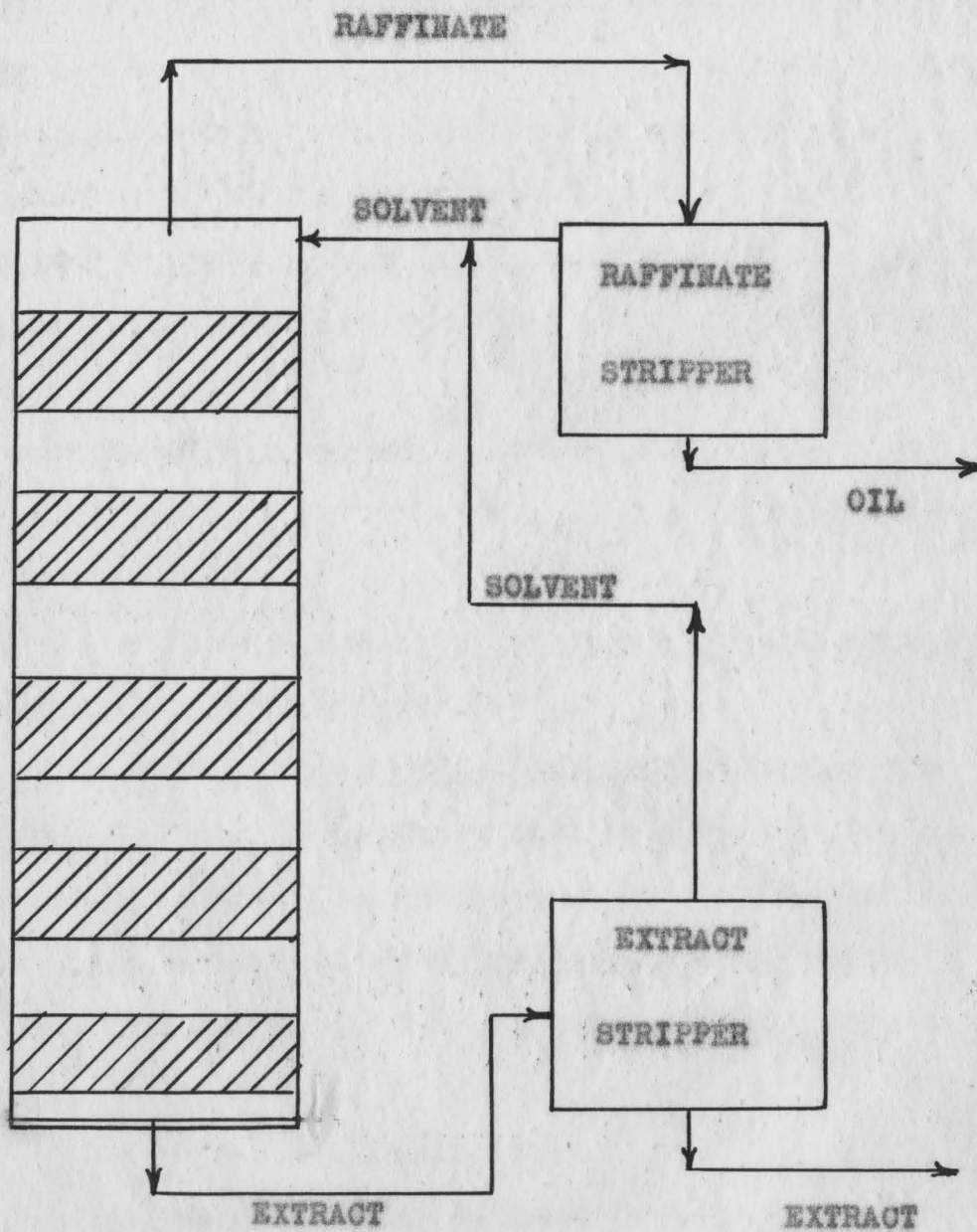


Fig. 4. - Packed Column for Solvent Extraction of Lubricating Oils

Fig. 4. In this case it can be seen that the oil and the solvent flow countercurrently due to the difference in density in the two streams. The intimacy of contact obtained in jet mixers is not possible in this case, but the apparatus is simple and reasonably cheap, and the theoretical maximum efficiency of this type of operation is higher than in the case of the countercurrent batch system.

57  
According to Kalichevsky <sup>35</sup> "One solvent extraction tower is better than an eight stage batch system - if properly operated".

There have been a number of patents issued on various methods of column construction. <sup>46,22,24</sup>

FACTORS AFFECTING COUNTERCURRENT SOLVENT EXTRACTION IN A SPRAY COLUMN. There are a number of factors that affect solvent extraction in a countercurrent column most of which seem to be of approximately equal importance depending, of course, on the operating conditions.

14  
They are:

- 1- Nature of solvent used.
- 2- Quantity of the solvent used.
- 3- Temperature of the extraction.
- 4- Time of contact between oil and solvent.
- 5- Time of settling.
- 6- Method of contacting the oil with the solvent.



## 7- Nature of the extract.

THEORETICAL CALCULATIONS OF SOLVENT EXTRACTION PROCESSES. In the case of batch extractions employing jet or agitator type mixers the contact is so good that equilibrium between phases is closely approached, and the rate of interphase diffusion does not govern performance. The efficiencies which may be obtained can consequently be calculated by stoichiometry from the equilibrium data and the so called "Distribution law":<sup>28</sup>

$$K = C_r / C_e$$

Where:  $K$  = The distribution coefficient.

$C_r$  = Solute concentration in the raffinate phase.

$C_e$  = Solute concentration in the extract phase.

However, in the case of countercurrent packed columns the solute can theoretically be completely extracted, but equilibrium is not reached because of the poorer contact between phases. Therefore, other methods of treatment must be used.

7

In 1937 Appel and Elgin pointed out that "although the theoretical aspects of liquid-liquid solvent extraction operations are becoming well developed, few of the data required for their application to the design of actual extraction equipment are yet available. This is

particularly true of the rate of extraction and the capacity of the column contacting equipment". However, Sherwood et. al.<sup>60</sup> suggested that the theoretical aspects of extraction as a unit operation have been developing relatively slowly.

Strang<sup>62</sup> has very adequately summed up the underlying theoretical principles when he states "that in solvent extraction processes, the solvent makes intimate contact with the oil thereby extracting the more soluble constituents. The essence of the process is the transference of this soluble portion from the oil stock to the solvent. The fundamental problem involved, therefore, is the transference of matter between two immiscible liquids in intimate contact with each other. This is the basis of all theoretical calculations on solvent extraction".

Colburn,<sup>15</sup> Strang,<sup>62</sup> Hunter and Nash,<sup>32,33,34</sup>  
 Poole,<sup>51</sup> Sherwood,<sup>54,59,60,61</sup> Appel and Elgin,<sup>7</sup> and  
 Elgin and Browning<sup>19</sup> have conducted the more important investigations on countercurrent extraction in spray and packed columns. Sherwood,<sup>60</sup> developed an equation for use in their work on extraction in spray columns. It is as follows:

$$K = \frac{L (C_2 - C_1)}{A \Delta C (\log \text{mean})}$$

Where:

L = Solvent rate, Cu.ft./hr.

$C_2$  = Concentration of solute in extract,  
Lb.Mols/cu.ft.

$C_1$  = Concentration of solute in entering solvent, pound mols/cu.ft.

$A$  = Area of contact at any one time, sq.ft.

$\Delta C$  l.m. = Log mean driving force in terms of concentration difference at each end of extractor.

In this work, the extraction was carried out with single and individual drops whose surface area, based on the assumption that the drops were spherical, was known. The area of contact was determined by determining the time of formation, the time that it took for a drop to rise to the top of the column and the number of drops introduced into the column per unit of time. In this manner, the investigators avoided the necessity of combining the area term with the transfer coefficients.

Elgin, et. al.,<sup>7,19</sup> developed another equation which is analogous to that of Sherwood. It is as follows:

$$K_w a = \frac{N/\theta}{V (\Delta C \text{ l.m.})}$$

Where:

$K_w$  = average overall extraction coefficient.

$V$  = effective volume of the column.

$N/\theta$  = number of mols of solute transferred/unit time.

This equation was developed as follows: The instan-



taneous rate of extraction from the water phase (W) to the ether phase (E) may be expressed by the usual two film relation:

$$\frac{dN_e}{Ad\theta} = k_w(C_w - C_{w1}) = k_e(C_{e1} - C_e)$$

Where:

$N$  = pounds mols of solute transferred per hour.

$w$  = water phase.

$e$  = isopropyl ether phase.

The significance of the terms and constants and their relationships to the variables involved are entirely analogous to the case of a gas absorption process.

Where the distribution law holds then:

$$\frac{dN_e}{Ad\theta} = K_w(C_w - C_w^*) = K_e(C_e^* - C_e)$$

Where:

$$C_w^* = BC_e, \text{ and } C_e^* = C_w/B$$

$B$  = Distribution coefficient, at equilibrium  $C_e/C_w$

The magnitude of  $B$  and the relative conditions of turbulence in the laminar films may be such that the rate of diffusion across one or the other, may be sufficiently slow to control the rate of the entire process. In this case,  $K_w = k_w$ , or  $K_e = k_e$ .

Integrating the above equation, assuming the  $B$  is constant (where the system does not depart widely from the

distribution law); and completed immiscibility; and the overall extraction coefficients constant thru the apparatus,

$$\frac{N}{\theta} = K_w A \text{ Log mean } \Delta C \quad \text{or} \quad \frac{N}{\theta} = K_w a V \text{ log mean } \Delta C$$

$$\text{and } K a = \frac{N/\theta}{V \text{ log mean } \Delta C}$$

Where:

$K_w$  = average overall extraction coefficient

$$\text{Log mean } \Delta C = \frac{\Delta C_{w1} - \Delta C_{w2}}{2.303 \log \frac{\Delta C_{w1}}{\Delta C_{w2}}}$$

Where:

$C_{w1}$  and  $C_{w2}$  = concentration difference at each end of the extractor, or  $C_{w1} - BC_{e1}$ , and  $C_{w2} - BC_{e2}$

In a later article, Elgin and Browning<sup>19</sup> obtained the following expression, analogous to absorption:

$$\int_{C_{w1}}^{C_{w2}} \frac{dC_w}{\Delta C} = \frac{K_w a S}{V_w}$$

Where:

$S$  = cross-section of column in feet.

$V_w$  = rate of flow of water phase, cu.ft./hr.

$C_w$  = overall concentration difference based on the water phase  $C_w - C_e/B$  in pound mols per cu. ft.

By definition, the number of theoretical plates

$$n = \int_{C_{w1}}^{C_{w2}} \frac{dC_w}{\Delta C}$$

Then the height equivalent to a transfer unit becomes.

$$\text{H.T.U.} = \frac{H}{n} = \frac{V_w}{K_w a S}$$

As the solutions are dilute and the distribution law is approximately valid, integration of the above equation gives

$$n = \frac{C_{w2} - C_{w1}}{\text{Log mean } \Delta C_w}$$

Colburn,<sup>15</sup> expresses the difficulty of a transfer operation in terms of a temperature or concentration change to be effected in either fluid stream, and of a driving force. This quantity is defined as a number of transfer units,  $N$ .

For equi-molar counter diffusion.

$$N = \int_{y_2}^{y_1} \frac{dy}{y - y^*}$$

For diffusion in one direction.

$$N = \int_{y_2}^{y_1} \frac{dy (1 - y) f}{(y - y^*) (1 - y)}$$

Where:

$y$  = solute mole fraction

$y^*$  = equilibrium value of  $y$  corresponding



to  $x$ .

$$(1-y)f = \text{Log mean } (1-y) \text{ and } (1-y^*)$$

The height of a transfer unit, H.T.U. is defined as the height of the column,  $Z$ , divided by the number of transfer units,  $n$ .

$$\text{H.T.U.} = \frac{Z}{n}$$

If  $y - y^*$  refers to equilibrium at interface, then  $n$  will be the number of transfer units where gas film is controlling. Usually it is more convenient to let  $y^*$  refer to the main liquid concentration, and define  $n$  as the overall transfer unit. This can be in terms of the change in gas concentration, or in terms of liquid concentrations.

$N_{OG}$  = number of overall transfer units based on gas concentration and defined by the above integral equations.

$N_{OL}$  = number of overall transfer units based on the liquid concentration.

$$N_{OL} = \frac{Z}{(\text{H.T.U.})_{OL}} \int_{x_2}^{x_1} \frac{dx}{x^* - x} \quad (\text{For equimolar counter diffusion})$$

and for diffusion in one direction only

$$N_{OL} = \frac{Z}{(\text{H.T.U.})_{OL}} \int_{x_2}^{x_1} \frac{(dx)(1-x)}{(x^* - x)(1-x)}$$

Given the value for the height of a gas film transfer unit,  $(H.T.U.)_G$ , and the height of the liquid transfer unit,  $(H.T.U.)_L$ , the height of the overall transfer unit, on the gas basis, is

$$(H.T.U.)_{OG} = (H.T.U.)_G + (H.T.U.)_L (m G_m/L_m)$$

Where:

$L_m/G_m$  = molar gas ratio

$m = dy^*/dx$  = slope of equilibrium curve

If Henry's law holds,  $M = y^*/x$

The terms in parenthesis in the above equation vary only moderately with widely different conditions. The values of  $(H.T.U.)_G$  and  $(H.T.U.)_L$  in general change but little with widely changing rates of flow, or even for different systems. The term  $mG_m/L_m$  is practically the same for any type of problem, whereas the individual values of  $m$  and  $L_m/G_m$  may vary a thousand fold, and the values of  $K_{Ga}$  and  $K_{La}$  may vary greatly with rates of flow.

$mG_m/L_m$  is essentially equal to the ratio of the slope of the equilibrium curve to the slope of the operating line at any point.

For the case where Henry's law holds, and where there is no solute in the entering liquid,  $y^* = mx$ , and

$$x (y - y_2) G_m/L_m$$

then

$$N = \int_{y_2}^{y_1} \frac{dy}{y-y^*} = \int_{y_2}^{y_1} \frac{dy}{y-(y-y_2)mG_m/L_m}$$

Integrating this:

$$N = \frac{2.3}{(1-mG_m/L_m)} \log (1-mG_m/L_m) (y_1/y_2) \frac{mG_m}{L_m}$$

The larger the value of  $mG_m/L_m$  is chosen, the larger will be the number of transfer units for a given ratio of  $y_1/y_2$ .

On the other hand, the lower the value of  $mG_m/L_m$  is chosen, the less the concentration will be the solute in the exit liquor. If the solute must be recovered by rectification, the cost of this is greater the weaker the solution. For this type of process, there will obviously be an optimum value of  $mG_m/L_m$  which gives a minimum sum of the absorption or extraction and rectification costs.

Although Colburn works out his treatment of the above for gas absorption on a packed column, it is obvious that it can be used for extraction in a spray column since the fundamentals are the same.

#### GRAPHICAL REPRESENTATION OF SOLVENT EXTRACTION PROCESSES.

In the solvent extraction of lubricating oils, <sup>10,20,21,</sup>  
it has been found by a number of investigators  
32,34,43,53,54

that triangular coordinates may be used to advantage to represent the process.



It is easy to show that the sum of the perpendiculars from any point within the triangle to the three bases is equal to the length of a perpendicular from any apex to the opposite base. The fact that the sum of the perpendiculars from any point to the three sides is equal to the altitude of the triangle makes it possible to represent compositions of ternary mixtures graphically and is one of two important properties of the triangle graph. Triangle diagrams have been adapted for use in a number of chemical engineering processes. They have proved to be particularly useful in the treatment of solvent extraction.<sup>19</sup>

In the solvent refining of lubricating oils, the object is to separate in the extract a high proportion of the undesirable "naphthenic" compounds, leaving a raffinate containing an increased proportion of "paraffinic" compounds. The improvement of the raffinate is measured by the change in any one of several criteria, such as the viscosity index (V.I.) and the viscosity gravity constant (VGC).

The problem is no longer that of a relatively simple ternary system, but involves a complex system of solvent and a large number of different and unknown hydrocarbons.<sup>32,33</sup> However, Hunter and Nash<sup>32,33</sup> proposed the use of the VGC which permits the use of triangular graphs.

It is first assumed that the VGC of two oils will be the weighted mean of the two values of the VGC for the two oils. This assumption does not appear to have been proved directly, but is borne out by comparison of experimental and calculated results for various cases of solvent treatment.

Fig. 5 shows a typical triangular representation of a solvent extraction process with lubricating oils. The ternary diagram is constructed by designating the three apexes as solvent, paraffinic oil, and naphthenic oil. A pure paraffinic oil may be assigned a VGC of say 0.80, and the naphthenic oil a VGC of 0.90. Laboratory extractions then serve to determine the solubility curves and the tie lines, as in the case of normal ternary systems. For example, suppose one volume of an oil having a VGC of A is shaken with an equal volume of solvent. The mixture will be represented by point F, located on a straight line AP and midway between A and P. A raffinate and extract are obtained, the solvent free layer is measured. Point E representing the composition of the extract is then located on the straight line connecting F and B, the VGC of the solvent free extract, at a position determined by measuring the solvent - oil ratio in the extract. Similarly, point D is located from the VGC of the solvent free raffinate C, and the solvent - oil ratio  $OD_2DP$  of the raffinate.

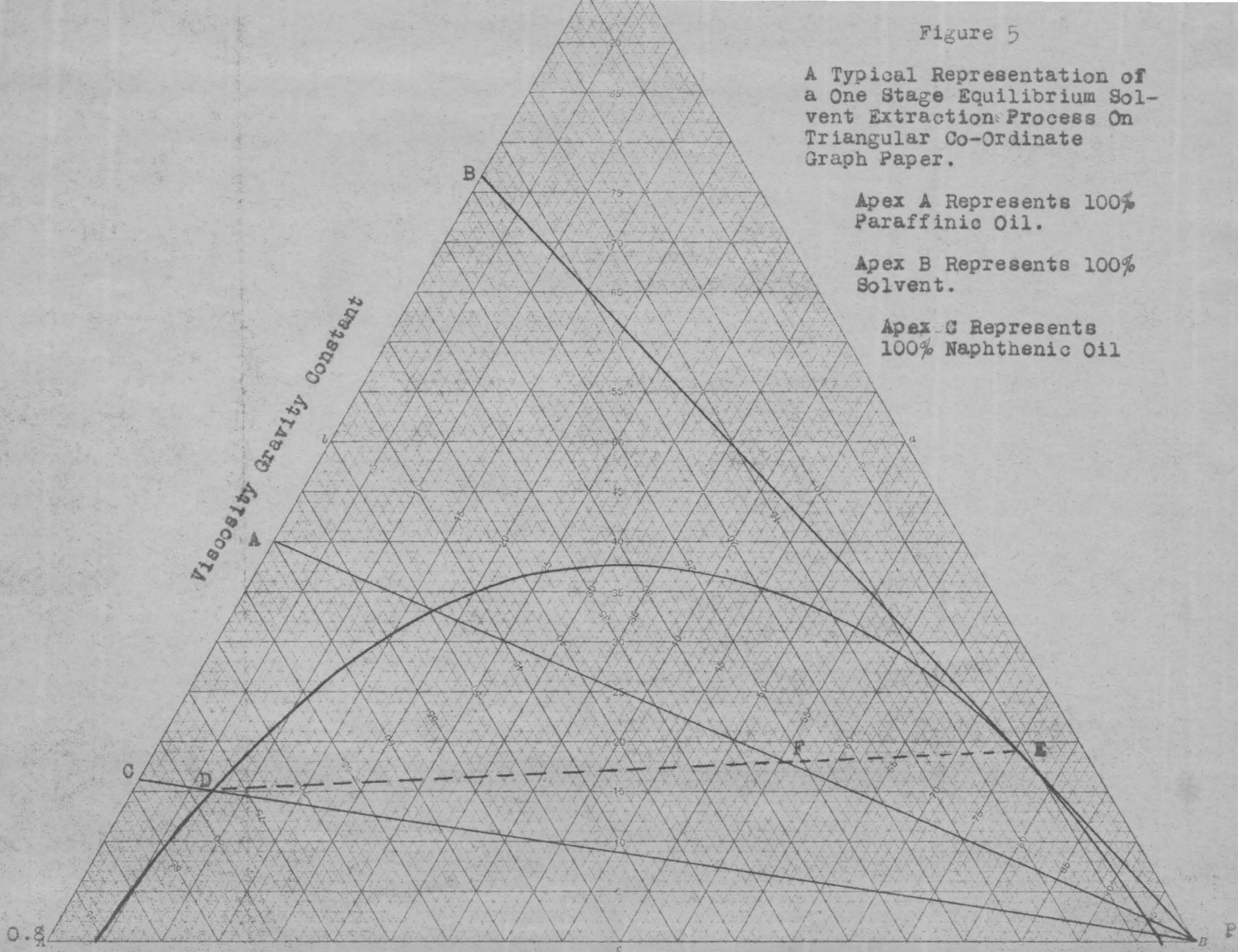
Figure 5

A Typical Representation of a One Stage Equilibrium Solvent Extraction Process On Triangular Co-Ordinate Graph Paper.

Apex A Represents 100% Paraffinic Oil.

Apex B Represents 100% Solvent.

Apex C Represents 100% Naphthenic Oil.





Thus one tie line and two points on the solubility curve are determined. Similarly other tests serve to locate other tie lines and other points on the solubility curve. It is also noted that extension of the tie lines meet at a common point outside of the triangle. This is the result of the geometry of the figure and is the basis of the method of graphically determining the composition of any number of desired stages of the extraction.

### III. EXPERIMENTAL

A- PURPOSE OF THE INVESTIGATION. The purpose of this investigation is to attempt to apply the basic mass transfer equation to the solvent extraction of lubricating oils, using furfural in a spray column. It is also the purpose of this investigation to study the effect of variable physical factors on the operating efficiency and the resulting effect in the quality of the product.

B- PLAN OF INVESTIGATION. Single drops of oil will be passed countercurrently to furfural in an unpacked column. The solvent rate in pounds per hour will be measured, and the area of contact of the oil drops will be calculated. The Viscosity Gravity Constant will be determined for the extract and the raffinate oil. A number of runs will be made at different ratios of solvent to oil and the same factors will be calculated. Equilibrium data at the same ratios of solvent to oil will be determined in terms of the Viscosity Gravity Constant and on a material balance basis. The transfer coefficients will be calculated by use of the equation and the corresponding value of H.T.U. will be calculated. The values of the transfer coefficients and the H.T.U. as calculated on the basis of a material balance,

Viscosity, Gravity Constant and contact area will be compared.

C- MATERIALS:-

FURFURAL was chosen as the solvent to be used because it is one of the very few of the large number of solvents used commercially that does not require pressure or refrigerating equipment, and it is not very toxic. A technical grade is to be used, the same as is used in the commercial refining of lubricating oils. It was supplied by the Quaker Oats Company, Chicago, Ill. The data on the properties of the furfural were furnished by the company and are tabulated in Table II.

OIL. The oil was cylinder stock supplied by the Ashland Oil and Refining Company, Ashland, Ky. The physical properties of the oil were supplied by the company and are tabulated in Table III. The lighter fractions such as gases, naphtha, kerosene, gasoline and other very volatile fractions have been removed. It is a non - dewaxed stock.

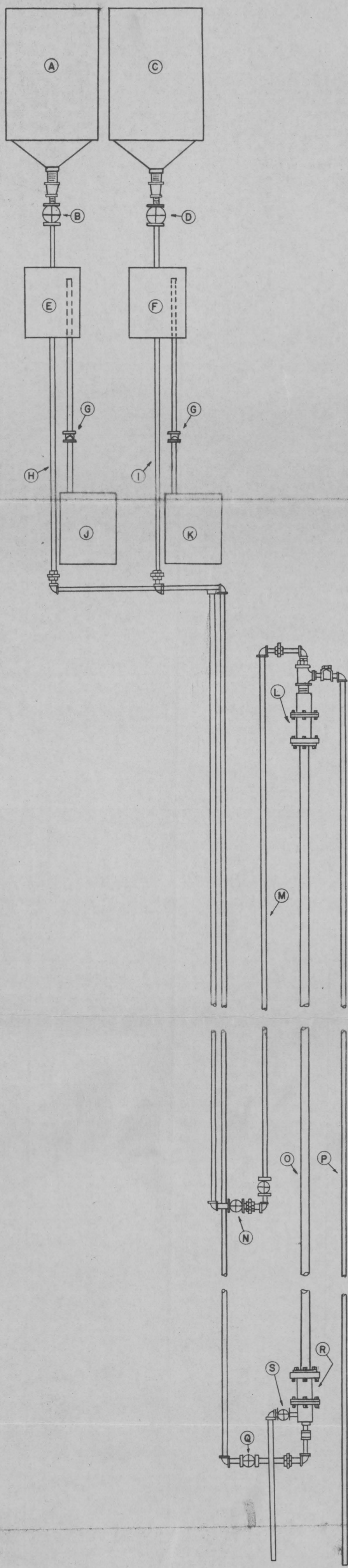
D- APPARATUS. The apparatus (Figure 6) consisted of a section of Pyrex glass piping (O) one inch in nominal diameter and ten feet long. Headers (L) and (R) constructed on a lathe from machine steel were attached to each end of the glass pipe which was supported vertically against an eight inch "H" beam by



TABLE III

## Physical Properties of the Charging Stock Used

Viscosity at 210°F. in S.U.S.....	145 Sec.
Viscosity at 100°F. in S.U.S.....	3165 Sec.
Viscosity Index.....	70
Flash Point, C.O.C.....	585°F.
Fire Point, C.O.C.....	635°F.
Flash Point, Penske Martin.....	515°F.
Four Point in Degrees Fahrenheit..	45°F.
Precipitation Number.....	0.1 cc
Conradson Carbon.....	2.77 Gr.
API Gravity.....	22.4
Specified Gravity.....	0.9194



LEGEND

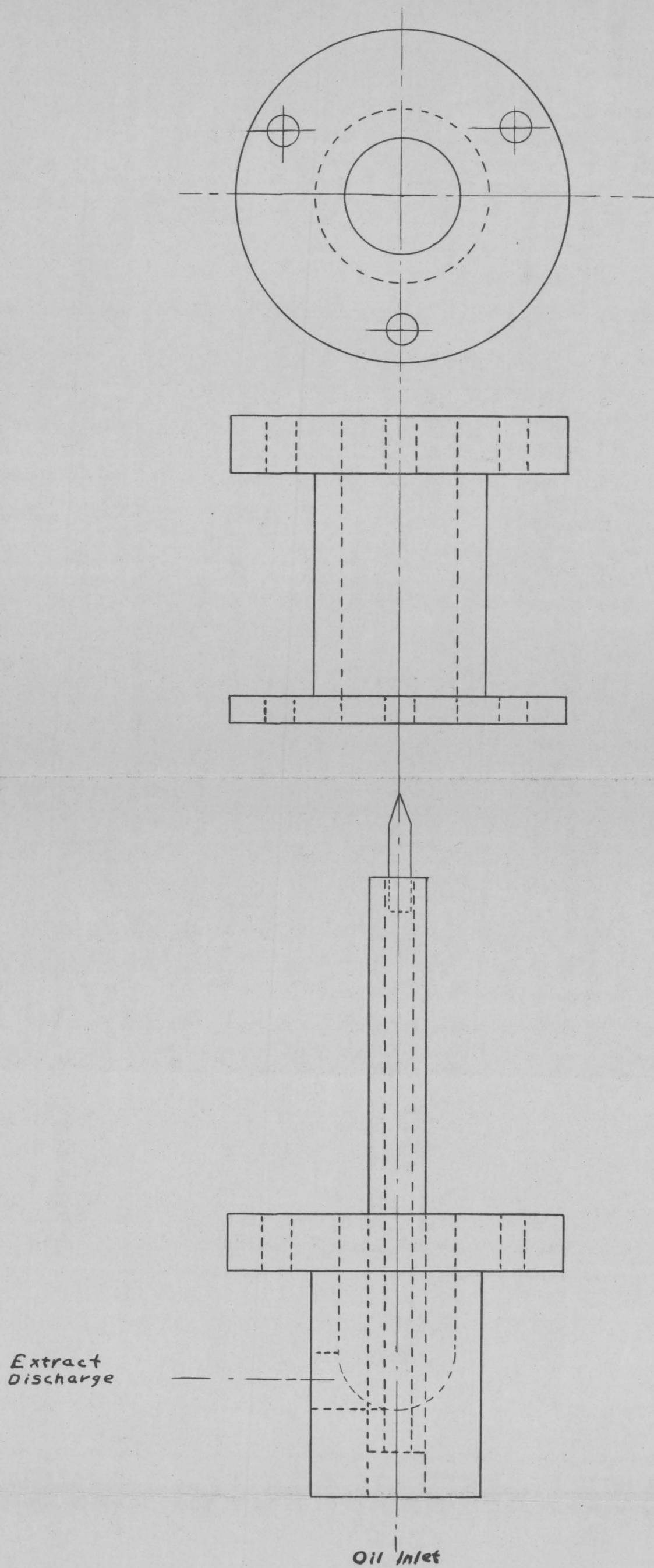
- A SOLVENT RESERVOIR
- B 1/2" BRASS GATE VALVE
- C OIL RESERVOIR
- D 1/2" BRASS GATE VALVE
- E SOLVENT CONSTANT HEAD FEED TANK
- F OIL CONSTANT HEAD FEED TANK
- G 1/2" GALV. IRON OVERFLOW PIPES
- H 1/4" GALV. IRON SOLVENT FEED LINE
- I 3/8" GALV. IRON OIL FEED LINE
- J SOLVENT OVERFLOW CATCH
- K OIL OVERFLOW CATCH
- L TOP COLUMN HEADER
- M 1/4" GALV. IRON SOLVENT FEED LINE
- N 3/8" BRASS COCK
- O 1" I.D. PYREX GLASS PIPE 10FT. LONG
- P 1/2" GALV. IRON EXTRACT DISCHARGE
- Q 3/8" NEEDLE VALVE
- R BOTTOM COLUMN HEADER
- S 1/4" NEEDLE VALVE

DEPARTMENT OF CHEMICAL ENGINEERING  
 VIRGINIA POLYTECHNIC INSTITUTE  
 BLACKSBURG, VA.  
**EQUIPMENT ASSEMBLY**  
**COUNTERCURRENT EXTRACTION**  
 LUBRICATING OIL WITH FURFURAL IN  
 A SPRAY COLUMN

DRAWN BY: *A. S. King*  
 APPROVED BY: *A. H. Cooper*

DATE: 5/15/70  
 SCALE: 1/8" = 1"  
 DWG: 1





DEPARTMENT OF CHEMICAL ENGINEERING  
 VIRGINIA POLYTECHNIC INSTITUTE  
 BLACKSBURG, VIRGINIA  
**SOLVENT REFINING**  
 FIGURE 7  
**HEADER DETAIL**

Drawn By: *A. S. King*  
 Checked By:  
 Approved By:

Scale: - 1" = 1"  
 Date: - 5/10/40  
 Dwg: - 2



means of brackets attached to the headers. The "H" beam was a support for the balcony in the Unit Operations Section of the Chemical Engineering Laboratory. The headers were attached to the piping by means of the special flanges supplied with the piping. The headers were constructed so that they would serve as a means of introducing the oil and solvent into the column and removing the extract and the raffinate from the column. A detail drawing of the headers is shown in Fig. 7.

Oil was fed to the bottom header (R) from a constant head tank and reservoir (C) and (F) respectively approximately 20 feet above through a 3/8 inch nominal diameter standard galvanized iron pipe (I). The solvent was fed through 1/4 inch nominal diameter standard galvanized iron piping (H) from a constant head tank on the same level as the oil tank to the top header. The extract was discharged from the column through the bottom header and a 1/4 inch nominal diameter standard galvanized iron pipe (S). The raffinate was discharged from the top header through a 1/2 inch nominal diameter standard galvanized iron pipe which extended down the side of the column to the floor (P). Each header was constructed so that it would fit the flanges supplied with the glass piping. They were made in two sections (Fig. 7) so that the nozzles on the inside of the

headers could be readily removed without disturbing the column itself. The oil lead-in pipe at the bottom header was reduced to 1/4 inch pipe by means of a bushing in the base of the header. The 1/4 inch pipe extended up through the header to a point 3/4 of an inch above the flange attached to the glass pipe. A fire polished glass nozzle was sealed in the end of this 1/4 inch pipe with molten sulfur.

The vacuum distillation apparatus consisted of two units each consisting of a 2 liter round bottom flask as the still to which was connected a water cooled condenser and a suction flask. An aspirator attached to the water line was used to create the vacuum. It was connected to the suction flasks by rubber tubing through a safety flask. Copper tees were inserted in the rubber tubing at the point where the suction flasks were connected.

Additional apparatus used was:

20 - one liter beakers.

20 - 250 cc. beakers.

Fairbanks platform scales.

Analytical balances.

Hydrometers.

Hot plates.

Westphal balance.

Eastman timer.

Stop watch.

Dual unit Tag - Saybolt viscosimeter and accessories.

Cleveland Open Cup Flash and Fire Tester and accessories.

Motor agitator.

Modified Ostwald Viscosimeter Pipet.

E- METHOD OF PROCEDURE. The oil and the solvent supply tanks were filled and weighed, as well as the cans used to catch the overflow from the constant head tanks. The valves in the solvent supply line were adjusted and the solvent allowed to flow through the constant head tanks into the column until the column was filled with solvent up to a point approximately 1/4 inch above the end of the solvent feed nozzle. The constant head tanks were then filled up to the top of the overflow pipes. The valves were then closed. The oil supply was started, and the time of starting recorded. The number of drops per minute entering the column, the time required for the drops to form and the time for the drop to rise to the top of the column were observed at one hour intervals throughout the run. At 15 minute intervals, the number of drops were checked. This became necessary because of the difficulty found in regulating the flow of oil.

A preliminary run was made to determine the approxi-



mate amount of extract oil extracted per pound of oil treated, and the pounds of solvent necessary to fill the column up to the predetermined point mentioned previously. When the weight of oil used became equal to the amount of oil required to attain the desired ratio of solvent to oil that was previously decided, the flow of solvent was started and adjusted to maintain this ratio by frequently weighing the supply tanks. The run was continued until approximately 2.5 pounds of oil had been treated. The column was then drained and the extract and raffinate collected. These two fractions were separated by vacuum distillation at from 24 to 27 inches of mercury, and at corresponding vapor temperatures of not more than 230°F. The weight of each fraction, the weight of solvent and oil separated from each fraction was determined and recorded. The specific gravity, Saybolt Universal Viscosity at 100°F. and at 210°F. for the raffinate, and at 210°F. for the extract oil, the flash and fire point and the A.P.I. of the raffinate oil were determined. The viscosity index and the Viscosity Gravity Constant were calculated for the oil from the extract and the raffinate.

The equilibrium curve and operating lines were constructed based on the no loss material balance and V.G.C. for the oil recovered from each extraction.

The transfer coefficients were calculated utilizing the contact area and the no loss material balance. They were also calculated utilizing the V.G.C. for the oil recovered from each extraction.

F. DATA AND RESULTS:

(1) Contact Area Data. The data necessary to calculate the area of contact between the oil and the furfural are presented in TABLES VI to VII inclusive. This data was taken on Runs A-1-D thru A-4-D only. These runs were column extractions. A summary of the data presented in these tables is presented in TABLE VIII.

The data are presented in the order of the increasing ratio of furfural to oil. The data are presented in this manner because that is the basis on which most of the comparisons are to be made.



TABLE VI

Treatment of 1.5 Pounds of Oil with 5.3 Pounds of Furfural.

Run A-1-D

Time	Rate, Drops of Oil Per Minute	Time in Extracting Section			Temperature ° F.
		Form Seconds	Rise Seconds	Total Seconds	
9:33 AM	51	1.00	34.50	35.50	72.0
10:33	50	1.00	34.25	35.25	73.0
11:33	57	1.00	35.00	36.00	72.3
12:33 PM	55	1.00	35.25	36.25	72.2
1:33	55	1.00	35.25	36.25	72.2
2:33	52	1.00	35.25	36.25	75.0
3:33	53	1.00	35.50	36.50	76.0
4:33	55	1.00	35.25	36.25	76.0
5:33					
6:33	31	1.00	35.50	36.50	76.0
7:33	50	1.00	35.50	36.50	76.0
8:33	50	1.00	35.25	36.25	76.0
9:33	48	1.00	35.00	36.00	76.0
10:03 PM	54	1.00	35.25	36.25	76.0
2:00 PM	55	1.00	35.25	36.25	76.0
3:00	52	1.00	35.25	36.25	76.0
4:00	63	1.00	35.25	36.25	78.0
5:00	50	1.00	35.00	36.00	78.0
6:00					
7:00	29	1.00	35.50	36.50	76.0
8:00	53	1.00	35.00	36.00	74.0
8:53 PM	53	1.00	35.25	36.25	74.0
1:30 PM	54	1.25	34.75	36.00	76.0
2:30	52	1.00	34.75	35.75	76.0
3:30	52	1.00	35.25	36.25	76.0
4:30	54	1.00	34.75	35.75	77.0
5:30					
6:30					
7:30	50	1.00	35.00	36.00	76.0
8:30	52	1.00	35.00	36.00	76.0
9:30	57	1.00	35.00	36.00	76.0
10:46 PM	35	1.00	35.00	36.00	76.0
9:55 AM	15	1.00	35.00	36.00	74.0
10:55	15	1.00	35.50	36.50	75.0
11:55	24	1.00	35.50	36.50	76.0
12:55 PM					
1:55	44	1.00	35.25	36.25	76.0
2:55	52	1.00	35.00	36.00	76.0
3:55	48	1.00	35.00	36.00	76.0
4:19 PM	28				

TABLE V

Treatment of 3.00 Pounds of Oil with 9.00 Pounds of Furfural.

Run A-3-D

Time	Rate, Drops of Oil Per Minute	Time in Extracting Section			Temperature ° F.
		Form Seconds	Rise Seconds	Total Seconds	
1:18 PM					
2:18	52				
3:18	45	1.00	35.25	36.25	73.0
4:18	43	1.00	35.25	36.25	73.0
5:18	40	1.00	35.25	36.25	72.0
6:18					
7:34	10	1.00	35.25	36.25	73.0
8:18	48	1.00	35.00	36.00	75.0
9:18	48	1.00	35.00	36.00	74.0
10:18	30	1.00	35.00	36.00	74.0
11:18	35	1.00	35.00	36.00	75.0
8:45 AM					
9:45	44	1.00	35.25	36.25	73.0
10:45	47	1.00	35.00	36.00	74.0
11:45	37	1.00	35.00	36.00	74.0
12:45 PM					
1:05	24	1.00	35.00	36.00	72.0
1:45	36	1.00	35.00	36.00	71.0
2:45	40	1.00	35.00	36.00	71.0
3:45	43	1.25	34.75	36.00	69.0
4:45	40	1.00	35.00	36.00	68.0
8:14 PM					
9:14	41	1.00	35.00	36.00	70.0
10:00	43	1.00	35.25	36.25	70.0
1:00 PM					
2:00	39	1.00	35.25	36.25	76.5
3:00	48	1.00	35.25	36.25	76.5
4:00	55	1.00	35.25	36.25	76.0
5:00	30	1.00	35.00	36.00	76.0
6:00	25	1.00	35.25	36.25	76.0
7:00	55	1.00	35.00	36.00	76.0
8:00	13	1.50	35.25	36.75	76.0
9:00	44	1.00	35.25	36.25	76.0
10:12	19	1.50	35.00	36.50	76.0
10:10 AM					
11:10	40	1.00	35.25	36.25	76.0
12:10 PM					
1:38	16				
2:54	55				
4:00	55				
5:00	47				
6:00					
7:00					
8:00	52				
9:00					
10:00	31				
10:40	43				
8:30 AM					
9:30	42				
10:30	45				
11:30	33				
12:30 PM					
1:20	30				
2:20	19				
3:20	34				
4:16	34				
9:15 AM					
10:15	45	1.00	35.00	36.00	71.0
11:15	44	1.00	35.00	36.00	72.0
12:15 PM					
1:15	50	1.00	35.50	36.50	72.5
2:15	43	1.25	35.00	36.25	74.0
3:15	42	1.00	35.00	36.00	75.5
4:15	47	1.00	35.00	36.00	76.0



TABLE IV

Treatment of 2.5 Pounds of Oil with 5.875 Pounds of Furfural.

Run A-2-D

Time	Rate, Drops of Oil Per Minute	Time in Extracting Section			Temperature ° F.
		Form Seconds	Rise Seconds	Total Seconds	
1:34 PM	54	1:00	35.00	36.00	75.5
2:34	53	1.00	35.25	36.25	76.0
3:34	52	1.00	35.25	36.25	75.0
4:34	50	1.00	35.25	36.25	76.0
5:12 PM					
8:55 AM	46	1.00	35.25	36.25	74.0
9:55	46	1.00	35.25	36.25	74.0
10:55	22	1.25	35.25	36.50	75.0
11:55	49	1.00	35.00	36.00	75.0
12:55 PM	22	1.25	35.25	36.50	75.5
1:55	48	1.00	35.25	36.25	77.0
2:55	46	1.00	35.25	36.25	78.0
3:55	48	1.00	35.00	36.00	78.0
4:55	50	1.00	35.00	36.00	78.0
5:55	58	1.00	35.25	36.25	78.0
6:55					
7:55	53	1.00	35.00	36.00	78.0
8:55	43	1.00	35.00	36.00	78.0
9:55	43	1.00	35.00	36.00	78.0
10:10 PM					
8:00 AM	42	1.00	35.00	36.00	78.0
9:00	55	1.00	35.00	36.00	78.0
10:00	52	1.00	35.00	36.00	78.0
11:00	55	1.00	35.00	36.00	78.0
12:00	39	1.25	35.00	36.25	78.0
1:00 PM	50	1.00	35.25	36.25	78.0
2:00	51	1.25	35.50	36.50	79.0
3:00	50	1.00	35.00	36.00	81.0
4:00	54	1.00	35.25	36.75	81.0
5:00	56	1.00	35.00	36.00	78.0
6:00	48	1.00	35.00	36.00	76.0
7:00	31	1.25	35.00	36.25	78.0
8:00	28	1.25	35.25	36.50	78.0
9:00	55	1.25	35.25	36.50	78.0
10:00 PM	40	1.00	35.00	36.00	78.0
9:50 AM	48	1.25	35.25	36.50	78.0
10:50	48	1.00	35.00	36.00	78.0
11:50	32	1.25	35.25	36.50	78.0
12:50 PM	10				
1:50	38	1.25	35.25	36.50	78.0
2:50					
3:50					
4:50					
5:02 PM	47	1.25	35.00	36.25	78.0
1:20 PM	48	1.25	35.00	36.25	78.0
2:20	47	1.25	35.00	36.25	76.0
3:20	56	1.00	35.00	36.00	76.0
4:20	44	1.00	35.25	36.25	75.0
5:20	55	1.00	35.00	36.00	74.5
6:20					
7:20	10	1.25	35.25	36.50	74.0
8:20	41	1.00	35.25	36.25	75.5
9:20	43	1.00	35.25	36.25	75.5
10:00					
1:10 PM					
2:10	53	1.00	35.25	36.25	75.5
3:10	57	1.00	35.00	36.00	75.0
4:10	57	1.00	35.25	36.25	75.0
5:10	56				
6:10					
7:47	11	1.50	35.25	36.75	75.0
8:47	34	1.00	35.25	36.25	76.0
9:10	36	1.00	35.25	36.25	75.0
10:12	36	1.00	35.25	36.26	75.0



TABLE VII

Treatment of 2.75 Pounds of Oil with 8.25 Pounds of Furfural.

Run A-4-D

Time	Rate, Drops of Oil Per Minute	Time in Extracting Section			Temperature ° F.
		Form Seconds	Rise Seconds	Total Seconds	
8:00 AM					
9:00	29	1.00	35.25	36.25	76.0
10:00	50	1.00	35.00	36.00	76.0
11:00	48	1.00	35.00	36.00	77.0
12:00					
1:00 PM	52	1.00	35.25	36.25	78.0
2:00	43	1.00	35.00	36.00	75.5
3:00	38	1.25	35.25	36.50	77.0
4:00	42	1.00	35.25	36.25	78.0
5:00	26	1.25	35.25	36.50	78.0
6:00					
7:20	21	1.25	35.25	36.50	78.0
8:54	20	1.25	35.25	36.50	78.0
9:54 AM					
11:10	28	1.25	35.00	36.25	76.0
11:54	38	1.25	35.00	36.25	76.0
12:54 PM					
1:34	54	1.00	35.00	36.00	76.0
2:34	41	1.00	35.25	36.25	76.0
3:20	40	1.00	35.00	36.00	77.0
4:20					
5:00	21	1.25	35.00	36.25	76.0
6:00					
7:00	17	1.25	35.25	36.50	76.0
8:00	43	1.00	35.00	36.00	76.0
9:00	34	1.00	35.00	36.00	76.0
10:03	37				
10:27 AM					
11:48	20				
1:00 PM	28	1.25	35.00	36.25	76.0
2:00	47	1.00	35.00	36.00	76.0
3:00	38	1.00	35.00	36.00	79.0
4:00 PM	36	1.00	35.00	36.00	78.0
4:45					
8:40 AM	42	1.00	35.00	36.00	75.0
9:46	41	1.00	35.00	36.00	76.0
11:00	35	1.00	35.00	36.00	74.0
11:40	30	1.00	35.00	36.00	74.0
1:00 PM					
2:00	38	1.00	35.00	36.00	76.0
3:00	39	1.00	35.00	36.00	73.5
4:00	41	1.00	35.25	36.25	74.0

TABLE VIII

Summation of Data Presented in TABLES IV to VII Inclusive.

Run Number	Time of Run (Hours)	Oil Used Pounds	Rate Average Number Drops Per Min.	Total Drops Based on the Average	Average Total Time in Zone Seconds	Drops in Zone at any Moment	Average Temp. ° F.	Contact Area in Square Feet
A-2-D	55.116	2.50	44.36	146,696	36.20	26.78	75.35	0.00583
A-3-D	55.200	3.00	39.32	130,127	36.10	23.62	76.77	0.00635
A-1-D	35.050	1.50	47.09	99,030	36.14	28.40	73.61	0.00572
A-4-D	37.250	2.75	36.15	80,795	36.15	21.80	76.00	0.00753

- (2) Physical Properties of the Oil Recovered from the Column and Batch Extractions. Data on the physical properties of the oil recovered from the raffinate and extract of the column and batch extractions are presented in TABLES IX to XII inclusive. This data indicates the improvement in the oil brought about by furfural refining. The Viscosity Gravity Constant of each fraction was also used in determining the transfer coefficients and the H.T.U. values based on the Viscosity Gravity Constant.



TABLE IX

Physical Properties of the Oil Recovered from the Raffinate of the Column Extractions.

Run Number	Viscosity			Flash Point °F	Fire Point °F	Sp. Gr. at 77°F	Sp. Gr. at 60°F	V.G.C. Based on 100°F	V.G.C. Based on 210°F	Average V.G.C.
	SUS 100°F	SUS 210°F	Index							
A-2-D	3131	143	71	560	615	0.9124	0.9186	0.8346	0.8396	0.8372
A-3-D	3099	143	72	565	625	0.9119	0.9181	0.8384	0.8389	0.8386
A-1-D	2867	138	73	545	625	0.9094	0.9156	0.8314	0.8362	0.8338
A-4-D	2916	140	73.5	565	620	0.9050	0.9111	0.8300	0.8243	0.8271
B-1-D	3120	145	73.0	560	625	0.9032	0.9094	0.8120	0.8271	0.8196
B-2-D	3087	145	73.5	565	625	0.8948	0.9010	0.8000	0.8161	0.8085

TABLE X

Physical Properties of the Oil Recovered from  
The Extract of the Column Extractions.

Run Number	Viscosity in SUS at 210°F	Sp. Gr. at 77°F	Sp. Gr. at 60°F	V.G.C. Based on 210°F
A-2-D	886	1.0107	1.0179	1.0258
A-3-D	490	0.9612	0.9674	0.8860
A-1-D	318	0.8163	0.8225	0.7000
A-4-D	467	0.9937	0.9940	0.9218
B-1-D	299	0.9440	0.9502	0.8701
B-2-D	301	0.9635	0.9697	0.8958

TABLE XI

Physical Properties of the Oil Recovered from the Raffinate of the Batch Extractions.

Run Number	Viscosity			Flash Point °F	Fire Point °F	Sp. Gr. at 77°F	Sp. Gr. at 60°F	V.G.C. Based on 100°F	V.G.C. Based on 210°F	Average V.G.C.
	SUS 100°F	SUS 210°F	Index							
A-2-E	2279	124	76.0	560	615	0.9023	0.9084	0.8151	0.8204	0.8177
A-3-E	2129	123	81.0	565	630	0.9013	0.9074	0.8239	0.8274	0.8256
A-1-E	2212	128	84.0	560	630	0.8999	0.9060	0.8120	0.8253	0.8232
A-4-E	1928	118	84.5	565	625	0.8898	0.8958	0.8080	0.8127	0.8104
B-1-E	1850	116	85.0	560	630	0.8775	0.8835	0.7830	0.8015	0.7923
B-2-E	1750	112	84.5	565	625	0.8773	0.8833	0.7825	0.7985	0.7905



TABLE XII

Physical Properties of the Oil Recovered from  
The Extract of the Batch Extractions.

Run Number	Viscosity in SUS at 210°F	Sp. Gr. at 77°F	Sp. Gr. at 60°F	V.G.C. Based on 210°F
A-2-E	3825	0.9794	0.9861	0.8839
A-3-E	3795	1.0179	1.0249	0.936
A-1-E	4025	1.0292	1.0362	0.9403
A-4-E	1195	0.9838	0.9905	0.8958
B-1-E	914	0.9865	0.9935	0.911
B-2-E	904	0.9870	0.9937	0.9141

- (3) Material Balances on the Column and Batch Extractions: Column and batch extraction data and calculated terms are presented in TABLES XIII and XIV. In each table the data are presented in the order of the increasing ratio of furfural to oil. The material balances are made up on a "no loss basis" so that the losses of material would not effect the results. The data in these tables serve as the basis of the calculation of the transfer coefficients and the H.T.U. values. A summary of calculated terms used in determining the transfer coefficients and the H.T.U. values based on the "no loss" material balance is presented in TABLE XV.



TABLE XIII

No Loss Material Balance Data and Other Calculated Terms from the Column Extractions Utilized in Determining the Transfer Coefficients and H.T.U. Values.

Run Number	A-2-D	A-3-D	A-1-D	A-4-D	B-1-D	B-2-D
Oil Used, pounds	2.500	3.000	1.500	2.750	2.500	2.500
Furfural Used, pounds	5.875	9.000	5.3000	14.300	23.100	35.500
Total Material Used, pounds	8.375	12.000	6.800	17.050	25.600	38.000
Ratio of Furfural to Oil	2.35:1	3.00:1	3.53:1	5.20:1	9.24:1	14.2:1
Furfural, % Charge	70.14	75.00	77.90	83.87	90.23	93.50
Oil, % Charge	29.86	25.00	22.10	16.13	9.77	6.5
Furfural Recovered:						
From Extract, pounds	5.397	7.167	4.870	11.100	21.963	34.210
From Raffinate, pounds	0.0881	1.559	0.558	0.882	0.416	0.970
Total Recovered, pounds	5.4851	8.7260	5.4280	11.9820	22.370	35.180
Loss, pounds	0.310	0.274	0.120	2.302	0.721	0.320
Loss, %	6.640	3.050	2.260	16.100	3.120	0.900
Oil Recovered:						
From Extract, pounds	0.0638	0.0859	0.1370	0.1420	0.1123	0.0705
From Raffinate, pounds	2.1780	2.9470	0.9280	2.1450	2.1560	2.2840
Total Recovered, pounds	2.2418	3.0329	1.0650	2.2870	2.2683	2.3545
Loss, pounds	0.260	0.030	0.440	0.4600	0.2400	0.1400
Loss, %	10.3	1.1	29.3	16.70	9.240	5.820
Total Furfural and Oil Recovered, pounds						
	7.7269	11.7589	6.4930	14.269	24.647	37.5345
Furfural:						
% of Total Recovery:						
In Extract, %	69.70	60.80	75.00	77.80	89.10	93.10
In Raffinate, %	1.4	13.3	8.60	6.20	1.7	2.58
No Loss Basis:						
Total Material Used Basis:						
In Extract, pounds	5.84	7.30	5.10	13.28	22.81	34.626
In Raffinate, pounds	0.117	1.592	0.585	1.05	0.43	0.98
Total, pounds	5.957	8.892	5.685	14.33	23.24	35.606
Total Furfural Basis:						
In Extract, pounds	5.760	7.390	4.760	13.260	22.670	34.525
In Raffinate, pounds	0.115	1.61	0.540	1.04	0.43	0.975
Total, pounds	5.875	9.000	5.300	14.300	23.10	35.500
Oil:						
% of Total Recovery:						
In Extract, %	0.8	0.7	2.1	1.0	0.45	0.02
In Raffinate, %	28.1	25.1	14.3	15.0	8.75	6.10
No Loss Basis:						
Total Material Used Basis:						
In Extract, pounds	0.067	0.088	0.143	0.170	0.120	0.076
In Raffinate, pounds	2.352	3.020	0.972	2.550	2.240	2.318
Total, pounds	2.419	3.108	1.115	2.720	2.360	2.394
Total Oil Basis:						
In Extract, pounds	0.0695	0.085	0.192	0.170	0.127	0.0795
In Raffinate, pounds	2.4305	2.9150	1.3080	2.5800	2.373	2.4205
Total, pounds	2.5000	3.0000	1.5000	2.7500	2.500	2.5000
Extract Composition:						
Total Weight, pounds	5.8293	7.4750	4.9520	13.4300	22.797	34.6045
Oil, %	1.2	1.1	3.9	1.3	0.56	0.23
Furfural, %	98.8	98.9	96.1	98.7	99.44	99.77
Operating Line Data:						
Extract:						
Weight, pounds	5.8293	7.4750	4.9520	13.430	22.797	34.6045
Furfural Separated, pounds	5.7600	7.3900	4.7600	13.260	22.670	34.525
Naphthenic Oil Extracted	0.0693	0.0850	0.1920	0.170	0.127	0.0795
Pounds of Naphthenic Oil Per pound of Furfural	0.0120	0.0116	0.0403	0.0128	0.0056	0.0023
Raffinate:						
Weight, pounds	2.5457	4.525	1.8480	3.620	2.803	3.3975
Oil Separated, pounds	2.4307	2.9150	1.3080	2.580	2.373	2.4205
Paraffinic Oil, pounds	1.525	1.830	0.915	1.680	1.525	1.525
Naphthenic Oil, pounds	0.9057	1.085	0.393	0.900	0.8480	0.8955
Pounds of Naphthenic Oil Per Pound of Paraffinic Oil	0.595	0.595	0.430	0.535	0.556	0.587
Raffinate Composition:						
Total Weight, pounds	2.5457	4.525	1.848	3.620	2.803	3.3975
Oil, %	95.5	64.5	70.8	71.3	84.6	71.2
Furfural, %	4.5	35.5	29.2	28.7	15.4	28.8



TABLE XIV

No Loss Material Balance Data and Other Calculated Terms from the Batch Extractions Utilized in Determining the Transfer Coefficients and H.T.U. Values.

Run Number	A-2-E	A-3-E	A-1-E	A-4-E	B-1-E	B-2-E
Oil Used, pounds	2.205	2.203	2.203	2.203	2.203	2.092
Furfural Used, pounds	5.176	6.609	7.930	11.455	20.355	29.330
Total Material Used, lbs.	7.381	8.814	10.135	13.660	22.560	31.422
Ratio of Furfural to Oil	2.35:1	3.00:1	3.60:1	5.20:1	9.24:1	14.02:1
Furfural, % Charge	70.14	75.00	78.26	83.87	90.23	93.343
Oil, % Charge	29.86	25.00	21.74	16.13	9.77	6.65
Furfural Recovered:						
From Extract, pounds	4.471	6.2545	7.170		19.625	28.650
From Raffinate, pounds	0.2853	0.2725	0.3820		0.3198	0.2290
Total Recovered, pounds	4.7563	6.5270	7.5520		19.9448	28.879
Loss, pounds	0.4197	0.0820	0.378		0.4102	0.451
Loss, %	8.1	1.24	4.77		2.02	1.54
Oil Recovered:						
From Extract, pounds	0.2312	0.2486	0.2466		0.4890	0.4760
From Raffinate, pounds	1.874	1.752	1.777		1.525	1.452
Total Recovered, pounds	2.1052	2.0006	2.0236		2.014	1.928
Loss, pounds	0.098	0.196	0.180		0.189	0.164
Loss, %	4.44	8.90	8.17		8.56	7.85
Total Furfural and Oil Recovered, pounds	6.8615	8.5381	9.5756		21.9588	30.8070
Furfural:						
% of Total Recovery:						
In Extract, %	65.2	73.3	74.9		89.3	93.0
In Raffinate, %	4.1	3.2	4.0		1.45	0.74
No Loss Basis:						
Total Charge Basis:						
In Extract, pounds	4.81	6.45	7.595		20.170	29.224
In Raffinate, pounds	0.30	0.28	0.405		0.325	0.232
Total, pounds	5.11	6.73	8.000		20.495	29.456
Total Furfural Basis:						
In Extract, pounds	4.872	6.335	7.529		20.032	29.009
In Raffinate, pounds	0.304	0.274	0.401		0.323	0.231
Total, pounds	5.176	6.609	7.930		20.355	29.330
Oil:						
% of Total Recovery:						
In Extract, %	3.4	2.9	2.6		2.23	1.54
In Raffinate, %	27.3	20.6	18.5		6.94	4.72
No Loss Basis:						
Total Charge Basis:						
In Extract, pounds	0.260	0.250	0.263		0.502	0.484
In Raffinate, pounds	2.01	1.83	1.872		1.562	1.482
Total, pounds	2.27	2.08	2.135		2.064	1.966
Total Oil Basis:						
In Extract, pounds	0.253	0.265	0.272		0.535	0.512
In Raffinate, pounds	1.952	1.940	1.933		1.670	1.580
Total, pounds	2.205	2.205	2.205		2.205	2.092
Extract Composition:						
Total Weight, pounds	5.125	6.600	7.801		20.567	29.611
Oil, %	4.9	4.0	3.5		2.6	1.7
Furfural, %	95.1	96.0	96.5		97.4	98.3
Raffinate Composition:						
Total Weight, pounds	2.256	2.214	2.334		1.993	1.811
Oil, %	86.6	87.6	82.9		83.8	87.3
Furfural, %	13.4	12.4	17.1		16.2	12.7
Equilibrium Curve Data:						
Extract:						
Weight, pounds	5.125	6.600	7.801		20.567	29.611
Furfural Separated, lbs.	4.872	6.335	7.529		20.032	29.099
Naphthenic Oil, pounds	0.253	0.265	0.272		0.535	0.512
Pounds of Naphthenic Oil Per pound Furfural	0.0519	0.0419	0.0362		0.0267	0.0176
Raffinate:						
Weight, pounds	2.256	2.214	2.334		1.993	1.811
Oil Separated, pounds	1.952	1.940	1.933		1.670	1.580
Paraffinic Oil, pounds	1.345	1.345	1.345		1.345	1.278
Naphthenic Oil, pounds	0.607	0.595	0.548		0.325	0.302
Pounds of Naphthenic Oil per Pound of Paraffinic Oil	0.451	0.442	0.408		0.241	0.237



TABLE XV

Summary of Calculated Terms Used in Determining the Transfer Coefficients and H.T.U. Values Based on the No Loss Material Balance

Run	Oil Transferred, pounds (W)	Time of Run, hours ( $\theta$ )	Pounds of Oil Transferred per hour (W/ $\theta$ )	Area of Contact Sq.ft. (A)	Rate, Furfural Cu.ft. Per hour $V_n$	$\Delta C_2$ lbs./lb.	$\Delta C_1$ lbs./lb.	$\Delta C_2 - \Delta C_1$	$\Delta G$ (log mean)	$K_n$ , Lbs./hr. sq.ft. Unit $\Delta C$	$K_{na}$ , Lbs./hr. sq.ft. Unit $\Delta C$	H.T.U. ( $K_n$ ), feet	H.T.U. ( $K_{na}$ ), feet
A-2-D	0.0693	55.116	0.001257	0.00583	0.001982	0.595	0.510	0.085	0.552	0.390	0.0427	1.080	1.15
A-3-D	0.0850	55.200	0.001530	0.00635	0.003930	0.595	0.515	0.080	0.553	0.437	0.0520	0.794	0.92
A-1-D	0.1920	35.050	0.005470	0.00572	0.002810	0.430	0.195	0.245	0.311	3.040	0.3310	5.94	6.32
A-4-D	0.1700	37.250	0.004570	0.00753	0.007140	0.535	0.500	0.035	0.518	1.168	1.6620	0.897	1.25
B-1-D	0.1270	7.500	0.016950		0.057300	0.630	0.556	0.074	0.597		5.430		4.98
B-2-D	0.0795	5.330	0.014850		0.124000	0.635	0.587	0.048	0.610		4.590		1.98

- (4) Column and Batch Extraction Data and Calculated Terms Based on the Viscosity Gravity Constant for Oil Recovered from Each Extraction. Data and calculated terms from the column and batch extraction based on the Viscosity Gravity Constant for oil recovered from each extraction are presented in TABLES XVI and XVII. This data is used as the basis of the calculation of transfer coefficients and H.T.U. values based on the Viscosity Gravity Constant. A summary of the calculated terms used in determining the transfer coefficients and the H.T.U. values based on the V.G.C. for oil of each extraction is presented in TABLE XVIII.



TABLE XVI

Column Extraction Data and Calculated Terms Utilized in Determining the Transfer Coefficients and H.T.U. Values Based on the Viscosity Gravity Constant for Each Extraction

Run Number	A-2-D	A-3-D	A-1-D	A-4-D	B-1-D	B-2-D
Furfural Used, pounds	5.875	9.000	5.300	14.300	23.100	35.500
Oil Used, pounds	2.50	3.00	1.50	2.75	2.50	2.50
Raffinate:						
Oil Separated, pounds	2.430	2.915	1.308	2.580	2.373	2.4205
V.G.C. of Separated Oil	0.8372	0.8386	0.8338	0.8271	0.8196	0.8085
Naphthenic Oil, % of Oil Separated	36.3	37.4	34.7	28.5	23.0	14.30
Naphthenic Oil, pounds	0.882	1.090	0.454	0.735	0.546	0.347
Paraffinic Oil, pounds	1.548	1.825	0.854	1.745	1.827	2.0735
Pounds of Naphthenic Oil Per Pound of Paraffinic Oil	0.570	0.597	0.532	0.422	0.299	0.167
Extract:						
Naphthenic, % in Original Charge	39	39	39	39	39	39
Naphthenic Oil in Charge, pounds	0.975	1.17	0.584	1.074	0.975	0.975
Naphthenic Oil Left in Raffinate, pounds	0.882	1.09	0.454	0.735	0.546	0.347
Naphthenic Oil Trans- ferred, pounds	0.093	0.080	0.130	0.340	0.429	0.628
Furfural Separated from Extract, pounds	5.76	7.39	4.76	13.26	22.67	34.525
Pounds of Naphthenic Oil Per Pound of Furfural	0.0161	0.0101	0.0274	0.0257	0.0189	0.0182

TABLE XVII

Batch Extraction Data and Calculated Terms Utilized in Determining the Transfer Coefficients and H.T.U. Values Based on the Viscosity Gravity Constant for Each Extraction

Run Number	A-2-E	A-3-E	A-1-E	A-4-E	B-1-E	B-2-E
Furfural Used, pounds	5.176	6.609	7.930	11.435	20.355	29.330
Oil Used, pounds	2.203	2.203	2.203	2.203	2.203	2.092
Raffinate:						
Oil Separated, pounds	1.952	1.940	1.933		1.670	1.580
V.G.C. of Separated Oil	0.8177	0.8256	0.8232	0.8104	0.7923	0.7905
Naphthenic Oil, % of Oil Separated	21.2	27.4	25.5	15.8	1.8	0.0
Naphthenic Oil, pounds	0.414	0.532	0.493		0.0300	0.000
Paraffinic Oil, pounds	1.538	1.408	1.440		1.640	1.580
Pounds of Naphthenic Oil Per Pound of Paraffinic Oil	0.270	0.379	0.342		.0183	0
Extract:						
Naphthenic, % in Original Charge	39	39	39	39	39	39
Naphthenic Oil in Charge, pounds	0.86	0.86	0.86	0.86	0.86	0.816
Naphthenic Oil Left in Raffinate, pounds	0.414	0.532	0.493		0.0300	0.000
Naphthenic Oil Trans- ferred, pounds	0.446	0.328	0.367		0.83	0.816
Furfural Separated from Extract, pounds	4.872	6.335	7.529		20.032	29.099
Pounds of Naphthenic Oil Per Pound of Furfural	0.0918	0.0520	0.0480		0.0413	0.0273



TABLE XVIII

Summary of Calculated Terms Used in Determining the Transfer Coefficients and the H.T.U. Values Based on the Viscosity Gravity Constant for the Oil from Each Extraction.

Run	Oil Transferred, pounds (W)	Time of Run, Hours (O)	Pounds of Oil Transferred Per hour (W/o)	Rate, Furfural Cu.ft. Per hour (Vn)	Rate, Furfural and Oil, Cu.ft. per hour	$\Delta C_2$ , lbs./lb.	$\Delta C_1$ , lbs./lb.	$\Delta C_2 - \Delta C_1$ , lbs./lb.	$\Delta C_{1-m}$ , lbs./lb.	$K_n^a$ (V.G.C.), Lbs./hr. Cu.ft. Unit $\Delta C$	H.T.U. (Kna), (V.G.C.), feet
A-2-D	0.093	55.116	0.00169	0.001982	0.002782	0.640	0.570	0.070	0.610	0.0520	1.400
A-3-D	0.080	55.20	0.00145	0.003930	0.004889	0.640	0.597	0.043	0.620	0.0440	0.778
A-1-D	0.130	35.05	0.00371	0.002810	0.003562	0.625	0.532	0.093	0.576	0.1210	2.300
A-4-D	0.340	37.25	0.00914	0.007140	0.00843	0.635	0.422	0.213	0.520	0.3310	2.480
B-1-D	0.429	7.50	0.0571	0.057300	0.06315	0.638	0.299	0.339	0.446	2.4200	2.260
B-2-D	0.625	5.33	0.1173	0.12400	0.13230	0.638	0.167	0.471	0.351	6.2800	2.700



- (5) Summary of Results. A summary of the H.T.U. values based on the transfer coefficient  $K_n$  in which the contact area and the material balance were used, based on the transfer coefficient  $K_n a$  in which the volume of the column and material balance were used and based on the transfer coefficient  $K_n a(VGC)$  in which the Viscosity Gravity Constant for the oil from each extraction was used is presented in TABLE XIX. This data is presented in the order of increasing ratio of furfural to oil.

TABLE XIX  
Summary of Results

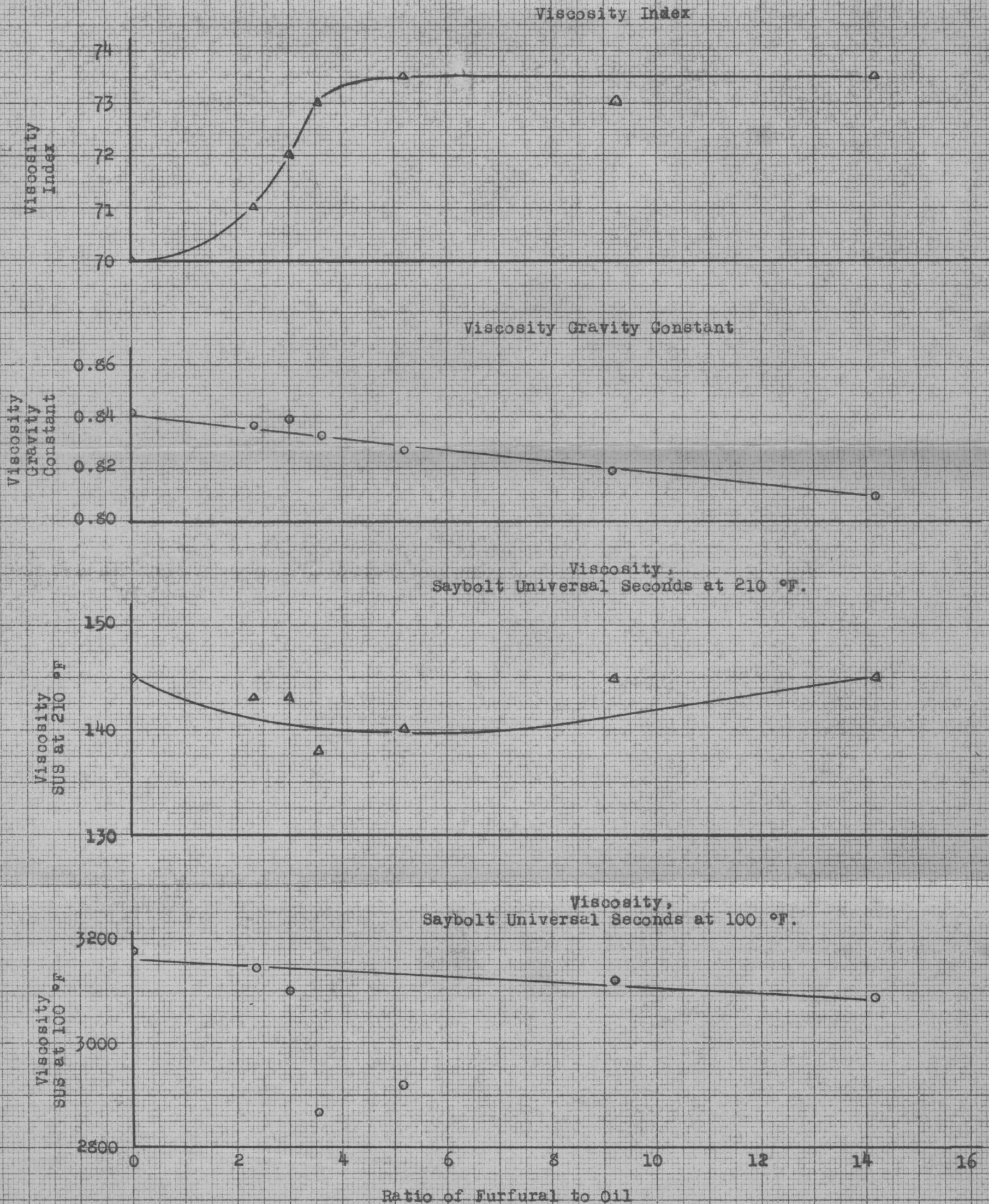
Run	H.T.U. $\cdot K_n$ , feet	H.T.U. $\cdot K_{na}$ , feet	H.T.U. $\cdot K_{na}$ (V.G.C.), feet
A-2-D	1.08	1.15	1.40
A-3-D	0.794	0.92	0.778
A-1-D	5.94	6.32	2.30
A-4-D	0.897	1.25	2.48
B-1-D		4.98	2.76
B-2-D		1.98	2.70

(6) Curves: The effect of varying the ratio of fural to oil on some of the properties of the oil recovered from the raffinate of the column extraction is presented in CURVE 1. The effect on the batch refined oil is presented in CURVE 2.



CURVE 1

Effect of Varying the Ratio of Furfural to Oil on Some of the Properties of the Oil Recovered from the Raffinate of the Column Extractions.

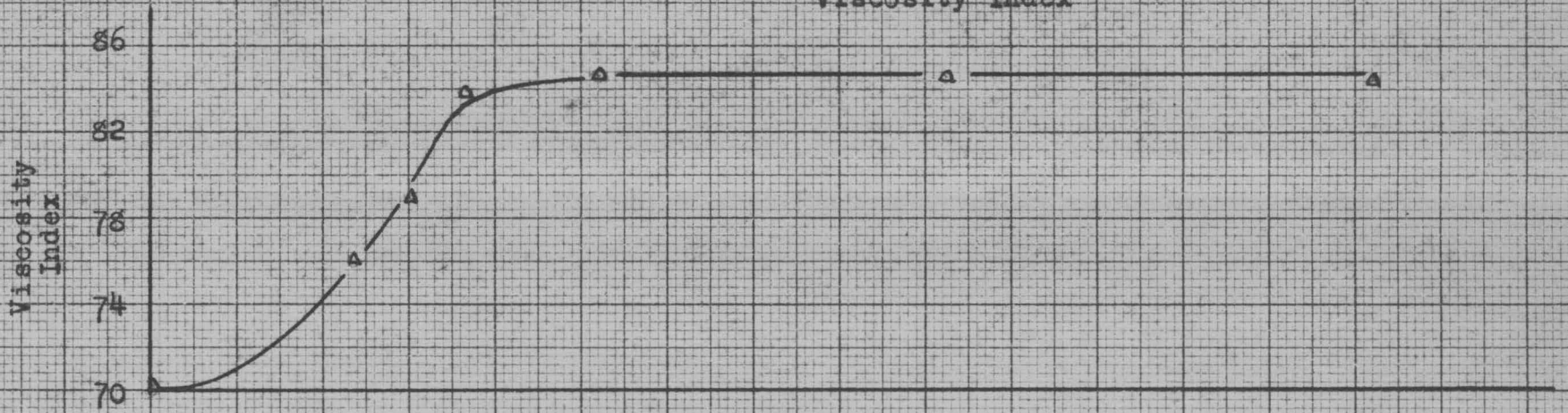




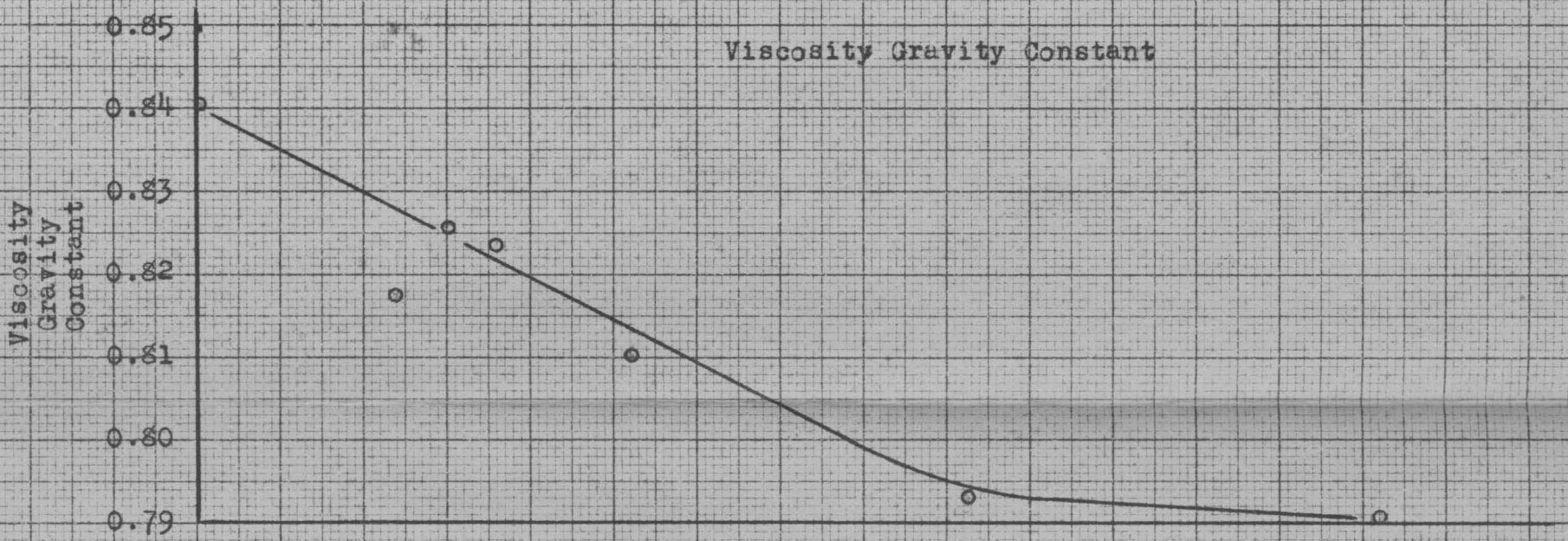
CURVE 2

Effect of Varying the Ratio of Furfural to Oil on Some of the Properties of the Oil Recovered from the Raffinate of the Batch Extractions.

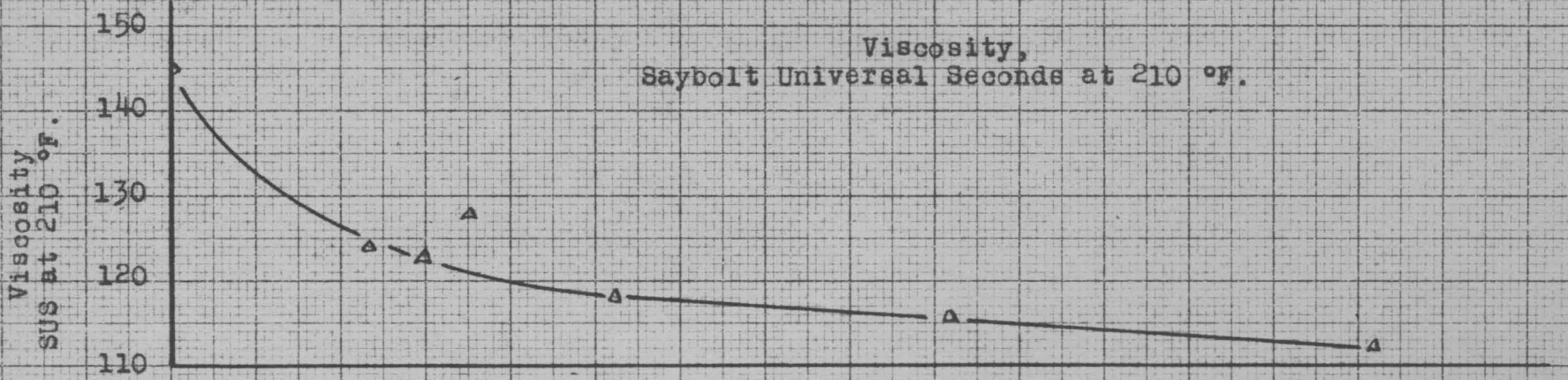
Viscosity Index



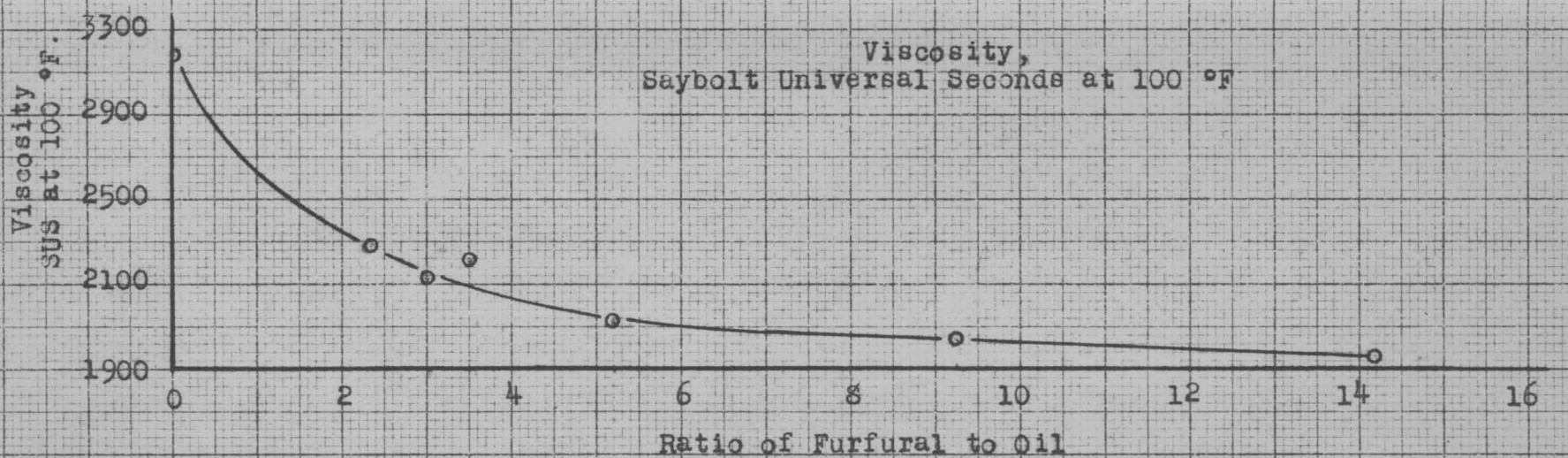
Viscosity Gravity Constant



Viscosity, Saybolt Universal Seconds at 210 °F.



Viscosity, Saybolt Universal Seconds at 100 °F.





G. SAMPLE CALCULATIONS.

- (1) Calculation of the Viscosity Gravity Constant based on the Viscosity determined at 100°F. in Saybolt Universal Seconds.

<sup>31</sup>  
FORMULA:

$$V.G.C. = \frac{10G - 1.0752 \log (V - 38)}{10 - \log (V - 38)}$$

Where:

V.G.C. = Viscosity Gravity Constant.

G = Specific Gravity at 60°F.

V = Viscosity, Saybolt Universal Seconds at 100°F.

Calculation for the raffinate oil of Run A-2-D.

$$G = 0.9186$$

$$V = 3131 \text{ seconds}$$

$$V.G.C. = \frac{10 (0.9186) - 1.0752 \log (3131-38)}{10 - \log (3131-38)}$$

$$V.G.C. = 0.8346$$

- (2) Calculation of the Viscosity Gravity Constant based on the viscosity in Saybolt Universal Seconds determined at 210°F.

<sup>31</sup>  
FORMULA:

$$V.G.C. = \frac{G - 0.24 - 0.022 \log (V' - 35.5)}{0.755}$$



Where:

V.G.C. = Viscosity Gravity Constant

G = Specific Gravity at 60°F.

V' = Viscosity, Saybolt Universal Seconds at 210°F.

Calculation for the raffinate oil from Run A-2-D.

$$G = 0.9186$$

$$V' = 143 \text{ Seconds.}$$

$$V.G.C. = \frac{0.9186 - 0.24 - 0.022 \log (143 - 35.5)}{0.755}$$

$$V.G.C. = 0.8396$$

(3) Calculation of Contact Area.

Note: In calculating the contact area, a number of assumptions must be made, some of which were shown by experiment to be only approximately correct.

These assumptions are as follows:

- (a) Drops that are formed are spherical.
- (b) Drops do not change in size as they move up the column.
- (c) Extraction taking place while the drop is forming at the nozzle is negligible in comparison with the extraction

taking place as the drop rises to the top of the column.

FORMULA: The formula used in these calculations is a composite formula derived as follows:

A.P.I. of Oil at 60°F. 22.4°A.P.I.

Specific Gravity at 60°F. = 0.9194

Conversion factor, A.P.I. Gravity to gallons per pound = 0.1306 at 60°F.

Let the volume conversion factor from the average operating temperature to the volume at 60°F. be "C". Then the cubic feet of oil in each drop of oil is

$$\frac{W \times 0.1306 \times 0.1337}{C \times D}$$

Where:

W = Weight of oil charged, pounds.

D = Total number of drops formed.

C = Volume conversion factor converting volume at operating temperature to volume at 60°F.

0.1337 = Conversion factor gallons to cubic feet.

Assuming the drops are spherical, then the radius of one drop is (Volume of sphere =  $\frac{4}{3} R^3$ )

$$R = \left( \frac{3 W \times 0.1306 \times 0.1337}{4 \times C \times D} \right)^{1/3}$$

Surface area of average drop with radius "R" is

$$A' = 4 R^2$$

Substituting R from preceding page.

$$A' = 4 \left( \frac{3 W \times 0.1306 \times 0.1337}{4 \times G \times D} \right)^{2/3}$$

The total area of contact at any one time is then

$$A = 4 N \left( \frac{3 W \times 0.1306 \times 0.1337}{4 \times G \times D} \right)^{2/3}$$

Where:

N = Number of drops in column at any instant.

Combining all constants the equation is reduced to

$$A = 12.5664 N \left( \frac{0.00416 W}{G \times D} \right)^{2/3}$$

Calculations for Run A-2-D.

$$N = 26.78 \text{ drops.}$$

$$W = 2.5 \text{ pounds.}$$

$$G = 0.9939$$

$$D = 146,696 \text{ drops.}$$

$$A = 12.5664 \times 26.78 \left( \frac{0.00416 \times 2.5}{0.9939 \times 146,696} \right)^{2/3}$$

$$A = 0.00583 \text{ square feet of contact area at any instant}$$

- (4) Calculation of the Transfer Coefficient based on the "no loss" weight balance and the contact area.



60  
FORMULA:

$$K_n = \frac{W/\theta}{A \Delta C} \text{ (log mean)}$$

Where:

$K_n$  = Mass transfer coefficient.

$W$  = Weight of naphthenic oil transferred, pounds.

$\theta$  = Time of run, hours.

$A$  = Area of contact at any instant.

$\Delta C$  = Log mean driving force expressed in terms of the difference in concentration at each end of the column and the equilibrium concentrations.

Calculation of the Transfer Coefficients  $K_n$  for Run A-2-D.

$W$  = Weight of Naphthenic Oil transferred, pounds.

= 0.0693 pounds.

$\theta$  = Time of run, hours. = 55.116 hours.

$A$  = Area of contact, square feet.

= 0.00583 square feet.

$\Delta C$  = Difference in concentration based on the log mean. See CURVE 3.

$$= \frac{(0.595 - 0) - (0.640 - 0.13)}{2.303 \log \frac{(0.595 - 0)}{(0.640 - 0.13)}}$$

$$= 0.552$$

Then

$$K_n = \frac{0.0693/55.116}{0.00583 (0.552)}$$

$$K_n = 0.390 \text{ lbs/hr./sq.ft./unit G}$$

(5) Calculation of  $K_{na}$  based on the "no loss" material balance.

19  
FORMULA:

$$K_a = \frac{W/O}{V \cdot G}$$

Where:

V = Volume of the column, cubic feet.

All other terms are the same as in part 4.

Calculation of the transfer coefficient  $K_{na}$  for Run A-2-D.

The average cross sectional area of a one inch nominal diameter Pyrex glass piping is 0.79 square inches. (Bulletin 814 - Corning Glass Works.) On this basis the Volume of the column is

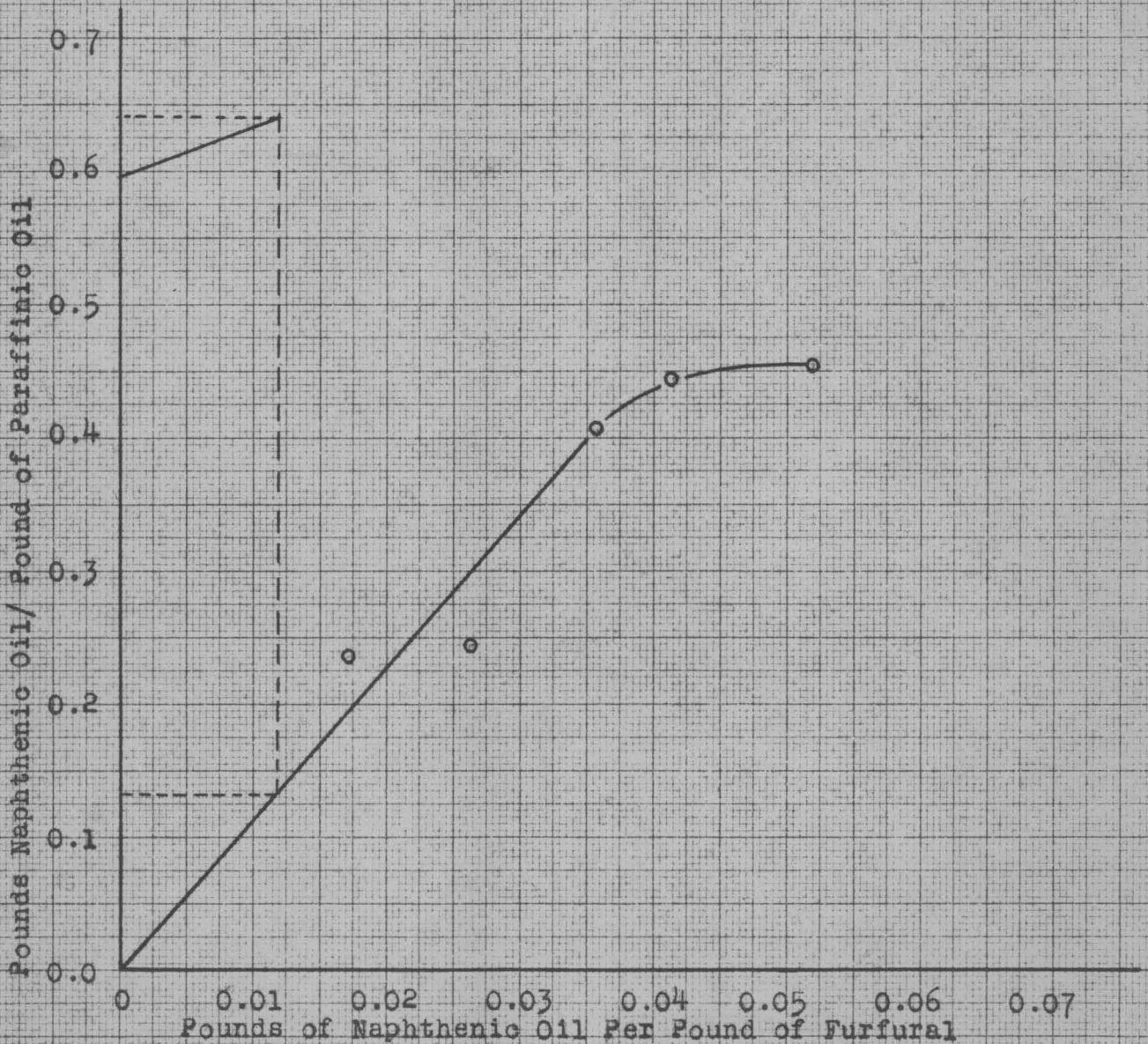
$$\frac{0.79}{144} \times 9.75 = 0.0532 \text{ cubic feet.}$$

$$K_{na} = \frac{0.0693/55.116}{0.0532 (0.390)}$$

CURVE 3

Graphical Determination  
of  $\Delta C$  Based on the No  
Loss Material Balance.

Run A -2- D





= 0.0427 lbs./hr./cu.ft tower  
vol./ unit G.

(6) Calculation of the H.T.U. $\cdot$ K<sub>n</sub>a based on the "no loss" material balance.

15  
FORMULA:

$$\text{H.T.U.} \cdot K_{na} = \frac{H}{n} = \frac{V_n}{K_{na} S}$$

Where:

H.T.U. $\cdot$ K<sub>n</sub>a = Height of the Theoretical Unit based on the Transfer Coefficient which in turn is based on the effective volume of the tower.

H = Effective height of the column.

n = Number of extraction stages.

V<sub>n</sub> = Solvent flow, cubic feet/hour.

S = Cross sectional area, square feet.

Calculation of H.T.U. $\cdot$ K<sub>n</sub>a for Run A-2-D.

$$K_{na} = 0.0427$$

$$H = 9.75 \text{ feet.}$$

$$V_n = 0.001982 \text{ cubic feet/hour.}$$

$$S = 0.00548 \text{ square feet.}$$

$$\begin{aligned} \text{H.T.U.} \cdot K_n a &= \frac{9.75}{n} = \frac{0.991982}{0.00548} (0.0427) \\ &= 1.15 \text{ feet} \end{aligned}$$

(7) Calculation of H.T.U.  $K_n$ . Based on the "no loss" material balance.

Note: In Colburn's <sup>15</sup> treatment of the H.T.U. (Formula Part 6.) no formula was developed for H.T.U.  $K_n$ . A modification of his formula was derived in order to calculate the H.T.U.  $K_n$ .

(a) Derivation of the modified formula.

Let

A = Contact area at any one time, square feet.

a = Contact area, square feet/cubic foot of effective column volume.

V = Effective column volume, cubic feet.

$$\text{Therefore: } A = aV \text{ or } a = \frac{A}{V}$$

$$\text{From Colburn: } \text{H.T.U.} = \frac{H}{n} = \frac{V_n}{K_n a S}$$

Where:

$V_n$  = Solvent flow, cubic feet/hour.

H = Effective column height, feet.

S = Cross sectional area of column,  
square feet.

n = Number of extraction stages.

$K_n a$  = Transfer coefficient based on  
contact area in terms of square/  
feet/cubic foot of column.

Therefore by substituting for (a) its equal

$\frac{A}{V}$

The following equation results:

$$\text{H.T.U.} = \frac{H}{n} = \frac{V_n}{K_n a S}$$

And since  $V = HS$ , the formula is reduced to:

$$\text{H.T.U.} = \frac{1}{n} = \frac{V_n}{K_n A}$$

(b) Calculation for Run A-2-D.

n = number of transfer units.

$V_n = 0.001983$  cubic feet/hour. (From  
part 6.)

$K_n = 0.390$  pounds/hour/square feet/  
unit C (From Part 4.)

A = 0.00583 square feet. (From Part 3.)

Then:

$$\text{H.T.U.} \cdot K_n = 1/n = \frac{0.001983}{0.390 \times 0.00583}$$



= 1.08 feet.

- (8) Calculation of the transfer coefficient based on data and calculations utilizing the V.G.C. for each extraction.

FORMULA:

$$K_{n^a}(V.G.C.) = \frac{W/\theta}{V \Delta C}$$

Where:

The terms in this formula are the same as in Part 4.

Calculation of  $K_{n^a}(V.G.C.)$  for Run A-4-D.

W = 0.093 lbs. naphthenic oil transferred.

$\theta$  = 55.118 hours.

V = 0.0532 cubic feet.

$\ln \Delta C$  = (Determined by the same graphical methods as used in Part 4. See CURVE 4.

$$= \frac{(0.640 - 0.005 - (0.422 - 0))}{2.303 \log \frac{(0.640 - 0.005)}{0.422 - 0}}$$

$$= 0.520$$

$$K_{n^a}(V.G.C.) = \frac{0.093/55.118}{0.0532 (0.520)}$$

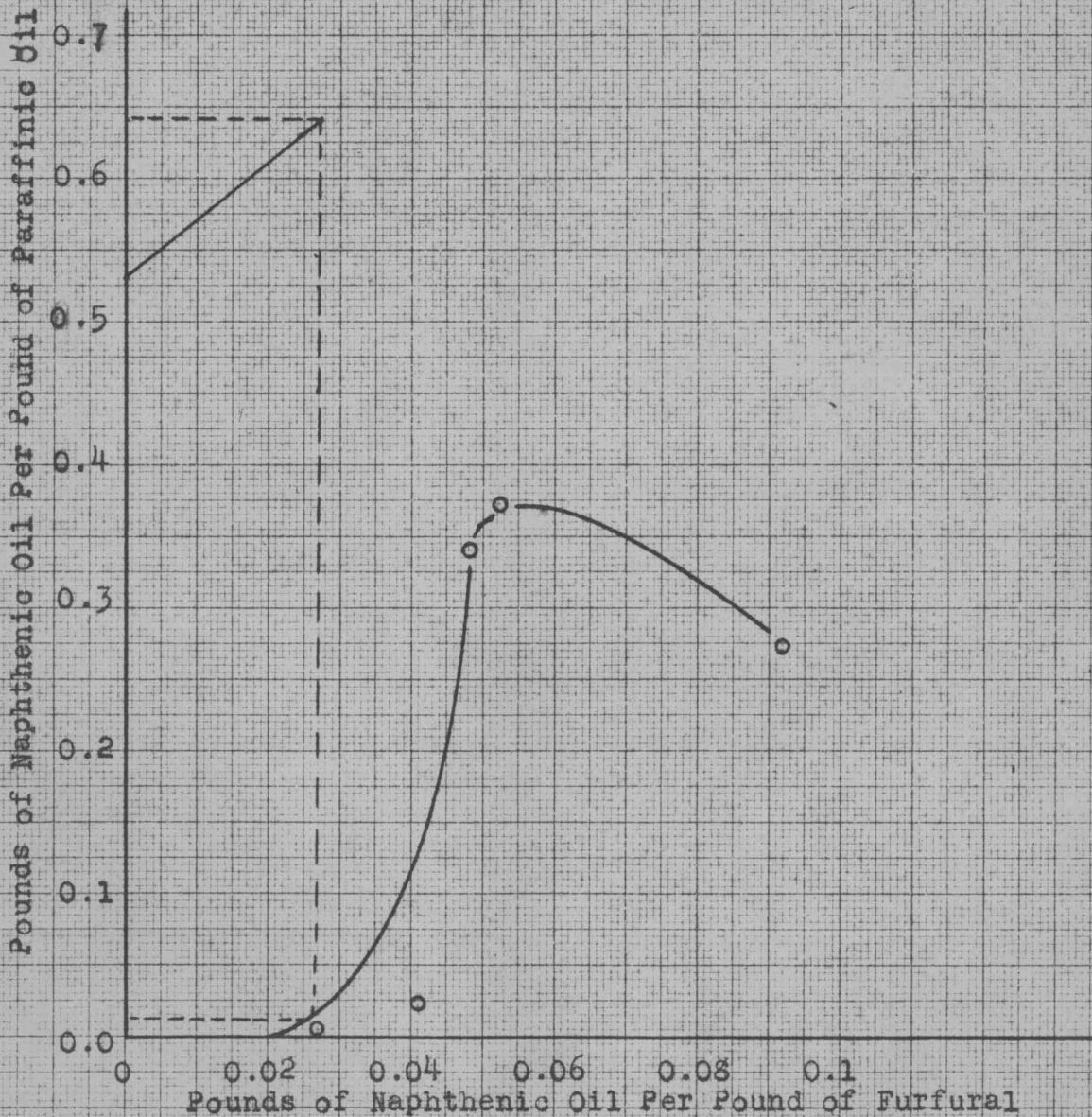
$$= 0.331$$

- (9) Calculation of H.T.U.  $K_{n^a}(V.G.C.)$  based on

CURVE 4

Graphical Determination  
of  $\Delta Q$  Based on Data and  
Calculations Utilizing  
the V.G.O. for the Oil  
Recovered from Each  
Extraction.

Run A-4-D



data and calculations utilizing the V.G.C. for each extraction.

15  
FORMULA:

$$H.T.U. \cdot K_n^a(v.G.C.) = H/n = V_n/K_n^a(v.G.C.)^S$$

Where:

Terms are the same as in Part 6.

$$K_n^a(v.G.C.) = 0.331 \text{ (From Part 6.)}$$

$$H = 9.75 \text{ feet.}$$

$$V_n = 0.00192 \text{ cubic feet/hour.}$$

$$S = 0.00548 \text{ square feet.}$$

$$H.T.U. \cdot K_n^a(v.G.C.) = \frac{9.75}{n} = \frac{0.00192}{0.331 \times 0.00548}$$

$$= 2.48 \text{ feet.}$$

(10) Calculation of the paraffinic concentration in the original oil.

In these calculations the V.G.C. of the purest paraffinic fraction is taken as 0.7900 and the V.G.C. of the naphthenic fraction is taken as 0.9200. The V.G.C. of the original oil was 0.84037. On this basis then the percentage paraffinic fraction in the oil is as follows:

$$\frac{0.9200 - 0.84073}{0.9200 - 0.79000} = 0.610 \text{ or } 61\% \text{ paraffinic.}$$

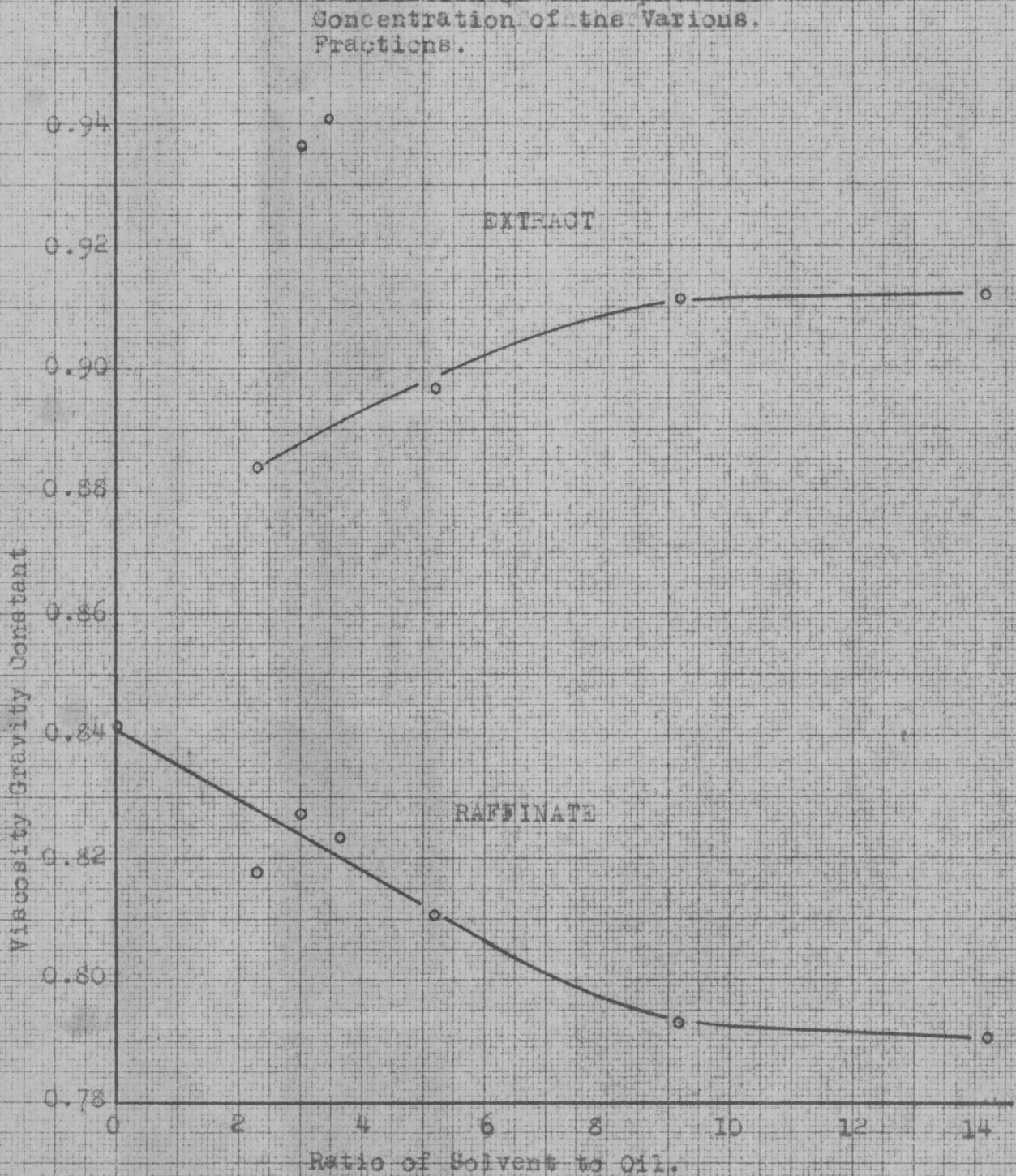
The above calculation method is based on the work of a number of investigators.



CURVE V was used to determine the limits of the V.G.C. It is evident from the graph that the two curves tend to become asymptotic at the V.G.C. of 0.7900 for the paraffinic (raffinate) and 0.9200 for the naphthenic extract.

CURVE 5

Determination of the Limits  
of the V.G.C. Used in the  
Calculation of the Naphthenic  
Concentration of the Various  
Fractions.



#### IV DISCUSSION OF RESULTS.

##### (A) Improvements in the Oil Brought about by Refining:

The results show that the batch extractions produced oil with properties far superior to those of the oil produced in the column extractions.

- (1) Effect of Varying the Ratio of Furfural to Oil on the Viscosity of the Oil. The viscosity of the unrefined oil was 3165 S.U.S. at 100°F. Batch refining with 2.35 parts of furfural to one part of oil by weight resulted in a viscosity of 2379 S.U.S. at 100°F. followed by an almost constant decrease of 100 S.U.S. each time the ratio was changed. Since the ratio was not increased by constant amounts but by increasing amounts, the result is a leveling off of the curve toward the higher ratios. The highest ratio (14.2:1.0) produced a viscosity of 1750 S.U.S. at 100°F.

The results show that the refined oil vis-



cosity determined at 210°F. in S.U.S. follows the same general pattern as the viscosities determined at 100°F. That is, the use of a ratio of 2.35:1.0 resulted in a decrease from the viscosity of the unrefined oil of 145 to 124 S.U.S. at 210°F. followed by a gradual leveling off at the higher ratios. The final batch extraction using 14.2 parts of furfural per one part of oil by weight produced a refined oil with a viscosity of 112 S.U.S. at 210°F. Therefore, the results show that solvent refining with furfural produced a far greater decrease in the viscosity determined at 100°F. than it did in the viscosity determined at 210°F.

In the case of the column extractions, the results show that there was little change in the viscosities in comparison with the batch extraction. In the batch extractions there was a drop in viscosity determined at 100°F.

from 3165 S.U.S. to 1750 S.U.S. Whereas, in the column extractions there was a drop from 3165 to 2867 S.U.S. only.

The same was true of the viscosities determined at 210°F. In the batch extractions, there was a drop from 145 to 112 S.U.S. However, in the column extractions the drop was only to 138 S.U.S. with the last two runs giving the same viscosity at 210°F. as the unrefined oil.

- (2) Effect of Varying the Ratio of Furfural to Oil on the Viscosity Index of the Refined Oil. The viscosity index of the refined oil produced by the batch and column extractions was effected in a similar manner by increasing the ratio of furfural to oil. Batch extractions with 2.35, 3.00, 3.53, 5.2, 9.24 and 14.2 parts of furfural to one part of oil by weight gave viscosity indexes of 76, 81, 84, 84.5, 85 and 84.5 respectively. The column extractions using the same ratios of furfural to oil as

above gave viscosity indexes of 71, 72, 73, 73.5, 73 and 73.5 respectively. Thus it can be seen that the batch extractions were far more efficient than the column extractions. The results also show that ratios above 5.24:1.0 produce little or no improvement in the viscosity index.

(3) Effect of Varying the Ratio of Furfural to Oil on the Specific Gravity of the Refined Oil.

The results show that the specific gravity decreases with an increase in the furfural to oil ratio. As in the case of viscosity, the decrease is more pronounced in the batch extractions. The specific gravity of the unrefined oil was 0.9194 at 60°F. Batch extractions with 2.35, 3.00, 3.53, 5.3, 9.24 and 14.2 parts of furfural to one part of oil by weight gave specific gravities of 0.9084, 0.9074, 0.9060, 0.8958, 0.8835 and 0.8833 respectively. Column extractions with essen-



tially the same ratios of furfural to oil gave specific gravities approximately 0.0100 higher in all cases. Here too, it can be seen that the effect is essentially the same as in the viscosity and the viscosity indexes.

- (4) Effect of Varying the Ratio of Furfural to Oil on the Viscosity Gravity Constant. Since the viscosity gravity is an empirical constant that is directly proportional to the specific gravity determined at 60°F. and the viscosity in Saybolt Universal Seconds determined at 100°F. or 210°F. it was expected that the variation with the ratio of solvent to oil would be similar to that of the viscosity and specific gravity variation. The results show that this is true. The V.G.C. determined for the refined oil produced by batch extractions is lower than those determined for the refined oil produced by column extraction. The difference between the batch and the column

V.G.C.'s is approximately 0.015 for all of the runs.

- (5) Effect of Varying the Ratio of Furfural to Oil on the Flash and Fire Points of the Refined Oil. According to the literature, the flash and fire points of the refined oil should be essentially the same as the original unrefined oil and very small amounts of furfural in the oil produces a very much lower flash point than the original unrefined oil. This is understood when it is noted that the flash point of the furfural was approximately 133°F. and the flash point of the oil was 565°F. On this basis the flash points of the refined oil samples was utilized as a check to determine whether or not the oil was essentially free of the furfural. The results show that the flash points of the refined oil was between 560 and 565°F. and the fire points were between 625 and 635°F. These values show conclusively that the oil was essentially free

of any furfural.

- (6) Effect of the Temperature of Extraction on the Properties of the Refined Oil. The fact that the batch extractions were more effective than the column extractions was due in part to the difference in the temperature of extraction. The column extractions were carried out at 75 °F. and the batch extractions at approximately 230°F. The viscosity index of the batch refined oil was from 5 to 10 points higher than the column refined oil. However, it should be noted here that this higher batch efficiency is not due entirely to the difference in the temperature but to the fact that in the batch extractions the temperature of extraction was higher than the miscibility point, and the area of contact between the furfural and the oil was infinite. Whereas, in the column extractions the area of contact at any



instant was between 0.00572 to 0.00753 square feet.

- (7) Effect of the Area of Contact on the Properties of the Refined Oil. The fact that the column extractions did not give as good results as the batch extractions is due in part to the small area of contact in comparison with the infinite area of the batch extractions.

In the determination of the contact area, it was necessary to assume that the drops of oil were spherical and that they would not change in size as they progressed from the nozzle at the bottom of the column to the top of the column. It was observed that these assumptions were not entirely true. It was noted that the drops were more nearly spherical when the rate was very low as in the first three runs. However, even then the drops were slightly distorted as they broke away from the nozzle. A portion of the tail

of the tear drop formed at the nozzle would break off forming tiny trailer droplets. The number of these droplets breaking off from each drop was not constant. It was observed that the number tended to increase and the size of these droplets tended to increase also as the rate of oil was increased.

In the last two runs, the oil and the furfural were passed through the column at very high rates in comparison with the rates used in the first two runs and no attempt was made to determine the area of contact. The distortion of the oil particles was very pronounced in these last two runs. Some of them were doughnut shaped and others collided in the column above the nozzle forming very irregular shaped bodies. It was thought that turbulent flow caused by the high rates was the cause of the distortions in the oil particles.

A number of attempts were made to take photographs of the drops so that a closer approximation of the contact area could be made but this proved impossible with the available apparatus.

The fact that no apparent improvement was made in the oil in the column extractions even though the ratio of the furfural to oil was increased from 5.2:1.0 to 14.2:1.00 is due in part to the very much smaller amount of contact area in the last two runs than in the first four. In these runs, no actual area of contact was determined. However, it was obvious from visual observation that the area of contact in these two runs was but a fraction of the area in the first four.

(B) Calculation of the Transfer Coefficients and the H.T.U.

- (1) On the Basis of a Material Balance. In order to prevent the losses that occurred from one step in the investigation to the next from effecting the results, the material balance was made up on



a "no loss" basis. The furfural and oil loss was due more than anything else to the handling of the materials between the various operations. The overall furfural loss was approximately four per cent, which does not appear to be excessive when the handling and the vacuum distillations are considered. The overall oil loss was approximately eight per cent and this too does not appear to be excessive when it is remembered that the oil was heavy and contained some wax.

The losses were prorated in order to make the material balance up on a "no loss" basis. The Viscosity Gravity Constant was used as an indication of the composition of the oil. In the "no loss" weight balance, the naphthenic concentration in the original oil was determined using the Viscosity Gravity Constant of the unrefined oil, the highest naphthenic extracted oil and the highest paraffinic refined oil. The percentage naphthenic fraction in the un-

refined oil was determined as the mean of the V.G.C. of the unrefined oil in respect to the V.G.C. of the highest naphthenic extracted oil and the highest paraffinic refined oil. This method of calculation is supported by the literature.

The results show that the values of the transfer coefficients  $K_{na}$  varied from 0.427 to 5.43 lbs./hr./cu.ft. of column volume/ unit  $G$ . as the ratio of furfural to oil was increased from 2.35:1 to 9.24:1. When the ratio was increased to 14.2:1 the transfer coefficient dropped to 4.59 lbs./hr./cu.ft. of column volume/ unit  $G$ . The H.T.U. value for a ratio of 2.35:1 was 1.15 feet. When the ratio was increased to 3.00:1, the H.T.U. value dropped to 0.92 feet. However, this was followed by a gradual increase in the H.T.U. values as the ratio was increased until a value of 4.95 feet was reached at a ratio of 9.24:1. When the ratio was increased to 14.2:1 the H.T.U. value dropped to 1.98 feet.

The results show that the values of the trans-

fer coefficients  $K_n$  in which the calculated area term was used followed the same trend as the  $K_{na}$  values when the ratio of furfural to oil was increased. It increased from 0.390 to 1.168 lbs./hr./sq.ft./unit  $\bar{C}$  as the ratio was increased from 2.35:1 to 5.2:1. However, a value of 3.04 for a ratio of 3.53:1 was far out of line. The H.T.U. values based on the transfer coefficients  $K_n$  and  $K_{na}$  check very well. The values for the first and third runs checked within 10 per cent but in the other two runs the percentage was slightly higher than 10 per cent.

- (2) Calculation of the Transfer Coefficients and the H.T.U. Values Based on the V.G.C. for the Oil Recovered from each Extraction. The transfer coefficients  $K_{na}(V.G.C.)$  followed the same general trend as those based on the material balance except there was no drop when the ratio was increased from 9.24:1 to 14.2:1. The ratio of 2.35:1



gave a transfer coefficient of 0.052 lbs./hr./cu. ft./unit C. When the ratio was increased to 3.00:1 the coefficient dropped to 0.044 lbs./hr./cu. ft./unit C. However, this was followed by an increase from 0.121 to 6.28 as the ratio was increased from 3.53:1 to 14.2:1. The H.T.U. values on this basis followed the same general trend as those calculated on the basis of the material balance alone. The ratio of 2.35:1 gave a value of 1.4 feet and was followed by a drop to 0.778 feet as the ratio was increased to 3.00:1. This was followed by an increase from 2.3 feet to 2.7 feet as the ratio increased from 3.53:1 to 14.2:1.

## V. CONCLUSIONS

1. Furfural refining of oil carried out at 75°F. in a column on drops of oil does not produce refined oil with properties equal to those produced by furfural refining in batches carried out at 230°F.
2. The ideal furfural to oil ratio for this oil is approximately 5.2:1.0. Higher ratios do not produce justifiable improvements in the quality of the oil.
3. A viscosity index of 85 is the best that can be produced in a single batch extraction with furfural.
4. The area of contact between the furfural and the oil is an important factor in furfural refining.
5. The transfer coefficient based on the "no loss" material balance increases from 0.0427 to 5.43 as the furfural to oil ratio is increased from 3.35:1.0 to 9.24:1.0.
6. The transfer coefficient based on the "no loss" material balance and the contact area increases from 0.390 to 1.168 as the ratio of furfural to oil is increased from 3.35:1.0 to 5.2:1.0.

## VI. SUMMARY

The object of this investigation was to determine the transfer coefficients based on a "no loss" material balance, Viscosity Gravity Constant for each extraction and the contact area in conjunction with the material balance when a cylinder stock out of midcontinent oil was subjected to furfural refining in a one-inch in nominal diameter pyrex glass spray column using various ratios of furfural to oil.

The oil was passed in tiny drops through the 9.75 feet high column countercurrent to the furfural flow which was down through the column. The average number of drops formed and the time of contact with the solvent was determined. From these values the average contact area in square feet at any moment was calculated. Two runs were made at high ratios of furfural to oil, and in these runs, no area of contact was determined. The column extractions were carried out at  $75 \pm 3^{\circ}\text{F}$ . In order to determine the equilibrium values necessary for these calculations, batch extractions using the same ratio of solvent to oil were carried out at  $230^{\circ}\text{F}$ .



- at which temperature the furfural and the oil were miscible. The ratios of furfural to oil used were 2.35, 3.00, 3.53, 5.20, 9.24 and 14.30. The values of the transfer coefficient based on the "no loss" material balance varied from 0.0427 to 4.59 lbs./hr./cu.ft. of column volume/unit  $\frac{1}{3}$  as the ratio was increased. The values of the transfer coefficients based on the Viscosity Gravity Constant varied from 0.0520 to 6.28 lbs./hr./cu.ft. of column volume/unit  $\frac{1}{3}$  as the ratio was increased. The values of the transfer coefficient based on the "no loss" material balance and the calculated contact area varied from 0.390 to 1.168 as the ratio was increased. The resultant values of the H.T.U.'s based on the three methods of calculation were good checks for the first two ratios and fair checks for the next two highest. For the ratio of 2.35:1.0 the H.T.U. based on the "no loss" material balance alone was 1.15, on the V.G.C. for each extraction it was 1.4 and for the method utilizing the contact area and the "no loss" material balance it was 1.08 feet.

The best batch refined oil had a viscosity index of

85. The best column refined oil had a viscosity index of 73.5. In both cases these values were reached using a ratio of 5.2 parts of furfural to one part of oil by weight and subsequent increases in this ratio did not improve the properties.

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