Physical and chemical factors contributing to the efficiency of separation units for the system naphthalene in coal tar oils

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THESIS

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PHYSICAL AND CHEMICAL FACTORS CONTRIBUTING TO THE EFFICIENCY OF SEPARATION UNITS. FOR THE SYSTEM NAPHTHALENE IN COAL TAR OILS.

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INTRODUCTION

Naphthalene is the most abundant single compound of coal tar. It occurs in about 7-8% concentration in horizontal retort tars, in about 3% concentration in vertical retort tars, while in coke oven tars, the concentration varies between 7% and 12% the average being about 9%. This large variation is due to the different sources of coke oven tars. Low temperature tars contain only traces of naphthalene and consequently are not of great importance from the point of view of naphthalene extraction.

The industrial demand for naphthalene has, in the past, been restricted and this has influenced the quality of naphthalene extracted, in that only the simplest forms of extraction were economically attractive. According to the Ministry of Power Statistical Digest, the total annual production of all grades of naphthalene in the U.K. for the years 1950, 1955, 1956, 1957, 1959 and 1960 was as follows. (See Table 1.)

TABLE 1

PRODUCTION OF NAPHTHALENE IN UNITED KINGDOM

Year	Total Production in Tons
1950	39,900
1955	50,000
1956	52,100
1957	49,600
1959	62,600
1960	74,200

In 1955, the total production figures for the year were as follows:- 574,931 tons of horizontal retort and intermittent vertical retort tar, 1,256,879 tons of continuous vertical retort tar and 1,101,294 tons of coke oven tar.

The total potential production of naphthalene was, therefore, nearly 180,000 tons as against an actual production of 50,000 tons. This vast difference between the potential naphthalene available and the actual amount extracted is mainly due to the restricted demand for naphthalene. Another factor which has contributed to the low production of naphthalene has been the attitude of industry to treat naphthalene as a by-product during the production of other materials. Consequently maximum plant efficiency has been directed towards production of the main material, such as light aromatic fractions for the manufacture of motor spirit. In recent years, the demand for phthalic anhydride for use in the manufacture of resins and plasticisers, and the demand for intermediates for dyestuffs and other fine chemicals, has increased considerably. In response, the demand for suitable grades of naphthalene has also increased, bringing with it a demand for better and more efficient forms of extraction from the crude coal tar.

Before discussing the more theoretical aspects of naphthalene extraction, it is considered appropriate to give a brief outline of the traditional methods of naphthalene extraction, in view of the fact that modern separation processes still follow the same general sequence of operations.

The traditional method consists firstly, in the distillation of the crude tar through a simple pot still or a continuous pipe still, to produce an oil containing approximately 50% naphthalene and boiling over the range 170°-250°C. The naphthalene containing oil is then allowed to cool to atmospheric temperature, generally in open, unlagged pans, and the crystals separated from the excess oil by gravity draining, or, alternately by mechanical pressing.

The solid naphthalene cake, which still contains some 25-30% adhering oils is then remelted and subjected to chemical washing in the following manner:-

Sulphuric acid of 94-96% concentration is employed to remove basic components such as pyridine and dimethyl pyridines and to remove others through condensation and polymerisation reactions. Water washing is then employed to remove excess acid and any water soluble products formed after the acid treatment, followed by a final washing with 10% sodium hydroxide solution to remove phenolic compounds and to neutralise the oil. The oil washed in this manner is then distilled through a pot still to produce naphthalene of approximately 94-96% purity, the grade required for phthalic anhydride manufacture.

The modern approach to the extraction of naphthalene still follows the same general outline, in that a naphthalene oil is first obtained from the crude tar. Further separation of the naphthalene oil is then achieved either by fractionation or by crystallisation followed by mechanical separation.

Mechanical separation involves either centrifuging, gravity draining or oil extrusion. Occasionally, a combination of both physical and mechanical processes are employed together.

The technique of sublimation is a further method of separation which could be applied to the naphthalene oil immediately after chemical washing. This method however, is not employed, since it tends to produce a naphthalene of purity higher than the specified phthalic anhydride grade (94-96% naphthalene) with a correspondingly lower recovery. The method does find occasional use in the further purification of phthalic anhydride grade naphthalene.

Referring to the former techniques of physical and mechanical separation, a loss of naphthalene inevitably occurs, and the problem facing the plant chemist or chemical engineer in the tar industry, resolves itself into the proper choice of the best sequence of operations to achieve, under the conditions peculiar to his refinery, the maximum economic yield of naphthalene of specification quality.

Chemical analysis of the naphthalene oil shows that only 50-55% of the oil is naphthalene, and that the remaining 45-50% contains a wide range of compounds which can be grouped into three categories, namely acidic, basic and neutral.

Acidic Group

Compounds belonging to this group are essentially phenolic in character, and can in theory be removed by washing the oil with caustic solution. However, it has been observed experimentally, that the solubility of phenols in caustic solution, decreases with the number of alkyl groups attached to the nucleus. Since increased molecular weight

Acidic Group (Cont'd)

is associated with increased boiling point, there are inevitably traces of high boiling phenols present in the oil even after washing with caustic solution.

Basic Group

Compounds comprising this group are pyridine, quinoline, and their associated homologues. Washing of the oil with dilute sulphuric acid will remove most of the low boiling bases, but the high boiling bases, such as quinoline and isoquinoline are not completely removed with dilute acid washing. Washing of the oil with concentrated acid is not practicable at this stage, since polymerisation occurs, resulting in the formation of unwanted resinous material, and loss of naphthalene occurs, through the formation of sulphoric acids.

Neutral Group

Compounds within this group are thionaphthene, methyl naphthalenes, dimethyl naphthalenes, indene, and other compounds not removed by treatment of the oil with acid and caustic solution. Their removal must, therefore, be achieved by alternate means.

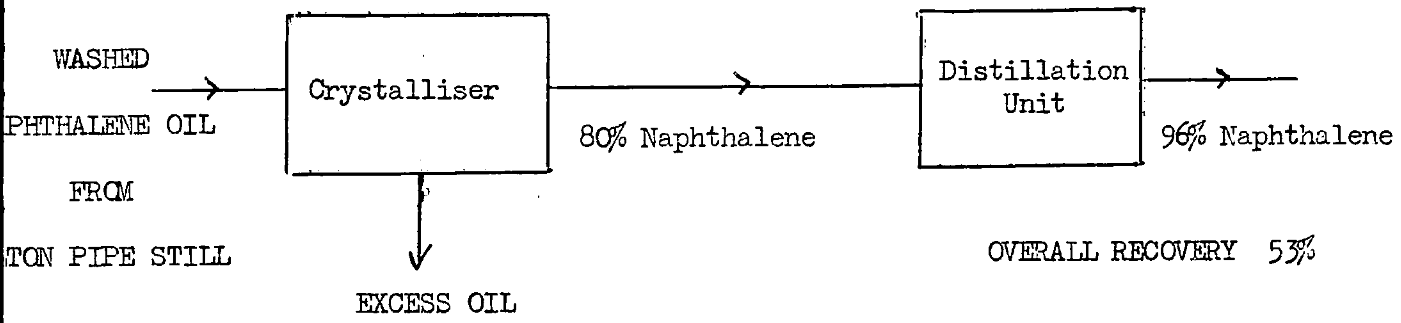
Within these three groups are compounds which can effect seriously the efficiency of any separation technique applied to this system.

The system of naphthalene extraction in operation at the works of North Eastern Tar Distillers, at the time of this investigation was capable of upgrading a naphthalene oil containing between 50% and 60% naphthalene, to give a product containing 96% naphthalene and with a 52% recovery figure. (Recovery is the term used to denote the quantity of available naphthalene recovered from the oil).

The system shown diagrammatically below consisted of:-

DIAGRAM 1

ORIGINAL SEPARATION SYSTEM



(1) Primary distillation of a crude tar mixture through a Wilton continuous pipe still (see Diagram 8 for description and flow diagram) to give a naphthalene oil boiling over the range 190-250°C. Since the Wilton still delivers five product sidestreams, of which the naphthalene oil is one, it was possible through adjustment of the sidestream temperature range, to concentrate the bulk of the naphthalene in the one fraction. A certain amount (approx. 15%) of the naphthalene is inevitably lost in the two sidestreams above and below the naphthalene oil sidestream.

(2) The naphthalene oil sidestream was then washed with a 10% caustic solution to remove phenolic compounds, after which, the washed oil was allowed to cool naturally in open unstirred crystallisers. After crystallisation, the excess oil was allowed to drain gravitationally from the bottom of the crystalliser.

(3) The crystallised product with a naphthalene content of approx. 80%, and a recovery figure of approx. 80%, was then fractionated through a continuous twin-column distillation unit (see diagram 7 - flow sheet) to give an overhead product containing 96% naphthalene, and with a recovery figure of 65%.

Thus the overall recovery of product containing 96% naphthalene, through the two separation stages, amounted to 52% of the available naphthalene in the naphthalene-oil system.

Although a product containing 96% naphthalene, satisfied the purity specification of "phthalic anhydride" grade naphthalene, a recovery figure of 52% was considered to be very low, and indicated poor efficiency at some stage or stages in the separation sequence. Thus an investigation was undertaken to increase the recovery figure from 52% to a minimum of 90%, whilst at the same time, maintaining the desired product purity of 96% naphthalene. Therefore, the investigation was based on a study of the physical and chemical factors affecting the efficiency of each of the available separation processes, with a view to developing a new or modified separation sequence capable of achieving the desired recovery and naphthalene purity.

The modified system developed as a result of this work has been operated successfully at the works of North Eastern Tar Distillers Limited, and has shown a substantial improvement over the original system.

THE PRODUCTION OF NAPHTHALENE OILS

Naphthalene oils are produced from crude tar by distillation in either a simple pot still, or in a continuous pipe still. The boiling range of the oil lies between 170°C and 250°C and the yield of oil on the tar varies between 8% and 15% according to the origin of the tar. This primary distillation process is very important in that it determines the chemical composition of the oil, and hence the relative ease of further separation. The amount of naphthalene present in the oil is approximately 50%, but this figure depends upon the degree of separation achieved in the distillation unit and on the type and nature of the crude tar. In general the separating power of a tar distillation unit is very low, and the main factor is the complexity of the tar being distilled.

It is known that certain phenolic compounds present in the tar are capable of forming azeotropes with naphthalene(1) and this causes a considerable "spread" of naphthalene throughout the distillation range. Thus for a tar containing phenolic compounds, the yield of naphthalene in the oil would be less than that obtained for a tar relatively free from phenolic compounds, when distilling over the same temperature range.

From the consideration of naphthalene recovery alone, it is better to operate the primary distillation stage to produce a larger quantity of a more dilute oil, thus ensuring a greater naphthalene recovery. Unfortunately this practice can lead to difficulties during crystallisation as will be shown later.

Table 2 shows the variation of naphthalene concentration with type of tar and type of distillation unit in operation.

TABLE 2

VARIATION OF NAPHTHALENE CONCENTRATION

Type of Tar	Naphthalene Content of Tar %	Type of Distillation Unit	Boiling Range of Naphthalene Oil (5-95%)°C	Yield of Naphthalene Oil on Tar %	Naphthalene Content of Oil %	Available Naphthalene in Oil %	Available Naphthalene in Drained Material %
Coke Oven	9.5	Pot Still	197-370	12.0	35.0	45.5	36.0
Coke Oven	8.0	Wilton Plant	208-240	14.0	50.0	87.5	79.3
Coke Oven	9.0	Koppers Plant	215-232	10.5	67.5	76.0	-
Horizontal Retort	7.5	Wilton Plant	205-240	10.0	47.0	62.6	-
Vertical Retort	3.0	Wilton Plant	201-222	8.5	14.0	40.0	27.8

NOTE: Drained material consists of naphthalene oil which has been allowed to crystallise and the excess oil drained off gravitationally.

THE CHEMICAL COMPOSITION OF THE NAPHTHALENE OIL

At the present time, some ninety compounds (2) having boiling points within the range 170°C to 250°C have been identified in high and medium temperature tars. From this number, 42 compounds are phenolic, 24 are basic and 6 are either nitriles, amides or acids. Treatment of the hot naphthalene oil with caustic solution to remove phenolic compounds and with acid to remove basic compounds, would leave 18 compounds to be removed by alternative means. These compounds together with their boiling points and crystallising points, where known, are shown in Table 3.

The list of compounds shown in Table 3 is intended to show the range of compounds which can be present in a naphthalene oil and the implication is <u>not</u> that all these compounds are present in every naphthalene oil.

TABLE 3

POSSIBLE COMPONENTS OF WASHED NAPHTHALENE OIL

Compound	B.Pt.°C	C.Pt.°C
6- Methyl Coumarone	190.0	-
Durane	191.0	80.0
5- Methyl Coumarone	192.0	-
Isodurene	195.0	(-) 24.1
Acetophenone	202.0	20.5
4- Methyl Hydrindene	203.0	-
Prehnitine	203.5	(-) 6.4
Tetralin	207.4	(-) 35.8
4- Methyl Indene	208.3	-
3.6 Dimethyl Coumarone	216.0	-
Dodecane	216.3	-
Naphthalene	217.9	80.3
Phenyl Ethyl Ketone	218.0	19.5
4.5 Dimethyl Coumarone	221.0	-
Thionaphthene	221.5	31.3
4.6 Dimethyl Coumarone	222.0	-
2- Methyl Naphthalene	241.1	34.5
1- Methyl Naphthalene	244.7	(-) 30.6

GENERAL METHODS OF SEPARATION

It has previously been stated that two types of separation are available for the naphthalene-oil system, namely fractionation and mechanical means. Fractionation can be either batch or continuous, whilst mechanical separation refers to centrifuging or oil draining.

FRACTIONATION

Continuous fractionation is encountered more frequently in industry than batch fractionation. This trend is in general due to:-

(a) reduced process costs resulting from continuous operation of the column at steady conditions.

(b) relative ease of operation arising from the constant feed quality and to the steady state conditions existing within the column.

The separation of a binary system is considered first since this is the simplest type of system encountered, and the principles involved during the analysis of such a system can be discussed more fully. Finally the separation and analysis of the multi-component system is discussed.

Binary Systems

To determine the separating power of the column or alternately, the degree of separation which can be expected from a given column, it is necessary to determine the change in composition of boty liquid and vapour from plate to plate, throughout the column. The degree of separation achieved depends upon four main factors:-

(1) the relative volatility of the components

(2) the ratio of reflux returning down the column to vapour rising up the column (reflux ratio)

(3) the height and cross sectional area of the column

(4) the degree of contact between liquid and vapour which can be attained within the column

Binary Systems (Cont'd)

Factor (1) is fixed by the nature of the components to be separated

Factor (2) is dependent upon operating conditions and can be varied within limits imposed by the column design.

Factor (3) is fixed, depending upon the column design.

Factor (4) is dependent upon the design of the column packing and on the relative amounts of the two phases present i.e. reflux ratio.

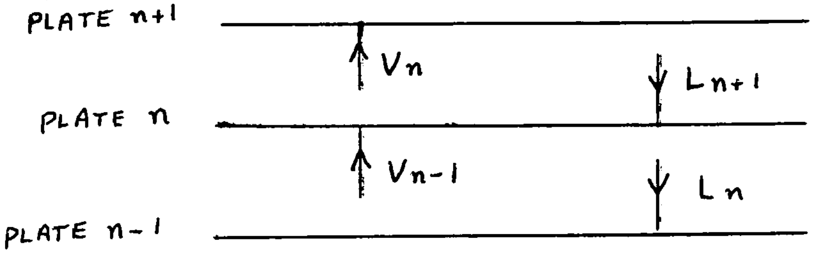
The classical methods available for determining column separating power can be considered under three general headings, namely:-

(1) plate to plate calculations

(2) graphical methods

(3) algebraic methods

The first plate to plate method developed by Sorel(3) consisted of calculating the enrichment from plate to plate, by equating the amount of energy and matter entering and leaving each plate and by assuming that complete equilibrium between liquid and vapour occurred on each plate.



In this manner Sorel was able to relate Y_n and x_{n+1} for each plate throughout the column, where Y_n - mole fraction of more volatile component in vapour on plate n.

x_{n+1} - mole fraction of more volatile component in liquid on plate n + 1.

Binary Systems (Cont'd)

Successive application of this treatment to each plate in turn rendered the method very tedious and involved a considerable amount of trial and error work, especially for cases where a large number of plates were involved.

Accordingly the method has been modified by later workers (4) in order to simplify the necessary calculations. Four assumptions are generally made namely:-

(a) Sorels' original assumption of complete equilibrium at each plate.

(b) the latent heat of vaporisation per mole of the components are the same, so that condensation of one mole of vapour releases sufficient heat to vaporise one mole of liquid.

(c) the components obey Raoults' law.

(d) the column is adiabatic and no heat of mixing occurs.

Conditions (b) and (c) are normally approximately true but condition (a) is never achieved in practice. Thus the separation achieved on an industrial column will be less than that expected from the number of theoretical plates upon which complete equilibrium is assumed. The percentage of the theoretical separation actually achieved is known as the plate efficiency of the column.

With the application of the above assumptions the relation between Y_n and x_{n+1} becomes a straight line with slope equal to $\frac{O}{V}$ where:-

O - total moles of overflow from one plate to the next per unit time.

V - total moles of vapour passing from one plate to the next per unit time.

On the basis of the necessary operating variables being fixed, the equation between Y_n and x_{n+1} is completely defined. Plate to plate calculations are thus made very much easier but still tedious for a large number of plates.

The observation that the relation between Y_n and x_{n+1} above the feed plate and Y_m and x_{m+1} below the feed plate, corresponded to the equations of two straight lines, led McCabe and Thiele(5) to suggest incorporating the two lines on the same diagram as the equilibrium curve, thus giving a graphical solution to the number of stages required. The main advantages of this graphical method are:-

(1) speed of manipulation, especially where a moderate number of plates are involved.

(2) the effects of equilibrium changes and operating conditions can be visualised.

(3) limiting operating conditions are easily determined.

Several mathematical equations have been developed for predicting column performance, such that in certain special cases an elementary substitution in a formula will give the desired result. The best known of these equations are probably the Fenske and Underwood equation(6), the Lewis equation(7) and the Smoker equation(8). The Fenske and Underwood equation relates the number of theoretical plates in the column to the relative volatility for ideal solutions, assuming the column to be operating under total reflux. The Fenske-Underwood equation can be expressed as:-

$$n + 1 = \frac{\log \left(\frac{x_A}{x_B}\right)\left(\frac{y_B}{y_A}\right)}{\log \alpha}$$

where x_A - mole fraction A in liquid
x_B - mole fraction B in liquid
y_A - mole fraction A in vapour
y_B - mole fraction B in vapour

The Smoker equation again involves the relative volatility but has been developed to enable the prediction of the plates necessary to effect a given separation between any desired concentrations and at any fixed reflux ratio. Although for a number of specific cases, these equations are useful for obtaining a quick result, in general, the complex form of the equations limits their application.

The above, brief discussion of the better known methods available for analysing and predicting column performance (binary systems) can be found fully discussed in a number of standard texts, such as, "Elements of Fractional distillation" - Robinson & Gilliland, and "Chemical Engineering" - Coulson & Richardson.

Multi-Component Systems

Fundamentally, the estimation of the number of theoretical plates required for the continuous separation of a multi-component mixture, involves the same principles as those given for a binary mixture. Thus the operating line equations for each component in a multi-component mixture are similar in form with those given for binary mixtures. However, in the case of the binary system, fixing the total pressure and the concentration of one component in either the liquid or vapour, immediately fixes the temperature and composition of the other phase, i.e. at a given total pressure, a definite relation exists between x and y, allowing the construction of the x, y equilibrium curve. In the case of a multi-component mixture of n components, in addition to the pressure, it is necessary to fix (n - 1) concentrations before the system is completely defined. Thus the x, y curve is a function not only of the physical characteristics of the other components but also of their relative amounts.

Multi-Component Systems (Cont'd)

To obtain experimentally the equilibrium relationships for such a system, requires considerable data, and one of two methods of simplification are usually adopted.

(a) For many systems, particularly those consisting of chemically similar substances, the relative volatilities of the components remain constant over a wide range of temperature and composition. Assume a mixture of components A, B, C, D, etc. to have mole fraction x_a, x_b, x_c, x_d etc. in the liquid and y_a, y_b, y_c, y_d etc. in the vapour, then

$$y_a + y_b + y_c + y_d + \ldots\ldots\ldots\ldots\ldots = 1.$$

and $$\frac{y_a}{y_b} + \frac{y_b}{y_b} + \frac{y_c}{y_b} + \frac{y_d}{y_b} + \ldots\ldots\ldots\ldots\ldots = \frac{1}{y_b}$$

Therefore $$\alpha_{ab}\frac{x_a}{x_b} + \alpha_{bb}\frac{x_b}{x_b} + \alpha_{cb}\frac{x_c}{x_b} + \ldots\ldots = \frac{1}{y_b}$$

Where α_{ab} denotes the relative volatility of components A and B.

Therefore $$\sum \alpha_{ab}.x_a = \frac{x_b}{y_b}.$$

and $$y_b = \frac{x_b}{\sum \alpha_{ab}.x_a}$$

since $$\frac{y_a}{y_b} = \alpha_{ab}.\ \frac{x_a}{x_b}.$$

then $$y_a = \frac{\alpha_{ab}.\ x_a}{\sum \alpha_{ab}.\ x_a.}$$

Thus the liquid and vapour compositions can be related through the relative volatility.

(b) An alternative method, particularly useful in the petroleum industry is to use the simple relationship:- $y_a = Kx_a$. Where K is a function of the pressure, temperature and component.

Multi-Component Systems (Cont'd)

(b) (Cont'd)

K values are known for a wide range of hydrocarbons and thus for special cases it is possible to use this relationship.

The above discussion assumes that the complete composition of the liquid at some position in the column is known, as a starting point for the calculation. This is not necessarily the case, and the difficulty arises from the fact that there are a limited number of independent variables which will define the distillation process, therefore, it is not possible to select arbitrarily the complete composition of a liquid or vapour at some position in the distillation system.

The estimation of the liquid or vapour composition at some position in the distillation system can best be considered by a study of the variables involved in the system. The number of variables involved is considerable and includes such factors as:- the number of compounds in the feed and products; the composition and quantities of feed and products; the quantities of interstage liquid and vapour flows; the number of plates or stages in each section of the column; the temperature and pressure on each stage; and the heat supplied to, and rejected by the system. Some of the variables are intensive in nature, and accordingly refer to the thermodynamic properties of the fluids, thus being independent of the quantities involved. The remaining variables are extensive in nature and refer to the relative quantities of material and energy, such as feed, products and heat supplied.

In a design calculation, it is necessary to determine the degree of freedom of the distillation system, or alternately, the number of independent variables which must be fixed in order to define the system completely. This has been discussed by Gilliland and Reed(9)

Multi-Component Systems (Cont'd)

who showed that for a rectifying column, consisting of a total condenser a reboiler, a feed plate, n theoretical plates above the feed plate, and m theoretical plates below the feed plate, the degree of freedom for a system involving C components is given by:-

$$F = C + 2n + 2m + 10$$

To derive this equation, it is necessary to determine initially the total intensive and extensive variables, by application of the laws of conservation of matter and energy and the second law of thermodynamics to each plate and section of the column. The determination of the intensive or thermodynamic variables involves, in addition, the use of the phase rule, which predicts the number of thermodynamic variables which must be arbitrarily set before an equilibrium system becomes invariant.

Although the phase rule is fundamental, it applies only to the thermodynamic variables, and accordingly, to obtain the total intensive and extensive variables, it is necessary to include the extensive quantity variables. Once the total variables for all sections of the system have been evaluated, the overall degrees of freedom of the system are given by the difference between the total intensive and extensive variables and the number of equilibrium relations involving these variables.

In a design calculation, it is usual to define the composition and conditions of the feed, the operating pressure of each plate, and the heat gain or loss to or from each plate and the condenser. Application of the above technique to these four items, gives a total of $C + 2n + 2m + 6$ variables, leaving four more variables still to be fixed. In the case of a binary mixture, the choice of two independent terminal concentrations will accordingly define the system completely, and thus give the complete compositions of the distillate and residue.

Multi-Component Systems (Cont'd)

In the case of the multi-component system, the complete composition of residue or distillate is still not determined, and it is necessary to estimate either the distillate or residue composition before proceeding with the calculation. If, after calculation, a component material balance is satisfied, then the estimate was correct. Thus a certain amount of trial and error work is necessary.

In the selection of two terminal concentrations it is convenient to select two key components, the light key component and the heavy key component. The former is the more volatile component whose concentration it is desired to control in the bottom product, and the latter is the less volatile component whose concentration is specified in the distillate. If attention is concentrated on the key components, it is often possible to simplify the handling of complex mixtures.

In the particular case of the naphthalene-oil system, the approach to fractionation must be essentially empirical since direct application of the standard technique is not possible because of lack of equilibrium data. If the complete quantitative analysis of the oil and the vapour pressure-temperature relationships of each of the components were known, it would be possible to calculate the degree of separation and thus the subsequent enrichment, of naphthalene oil on a column of given separating power. However, a complete analysis of a naphthalene oil is a difficult problem, and as yet, no such analysis is available. Furthermore the analysis obtained and the subsequent data on the individual components would be applicable only to the particular oil in question. Even if the analytical data were available, the time and amount of work required to determine the degree of separation achieved on a given column would be considerable.

Multi-Component Systems (Cont'd)

A further difficulty arising from the complexity of the naphthalene-oil, is that of azeotrope formation.

The formation of azeotropes from coal tar mixtures has been studied extensively in Poland in recent years. In fact, a Polish worker Swietoslawski(1), considers coal tar and its fractions as polyazeotropic mixtures. Naphthalene itself forms numerous azeotropes, both binary and ternary, during the distillation of the oil, and many of these azeotropes have boiling points very close to that of naphthalene.

Typical compounds which form these azeotropes are certain phenolic compounds such as cresols, and certain basic compounds. Whilst most of these compounds are removed by the initial chemical treatment of the oil, they are not all removed, and consequently, during fractionation, complete separation of the naphthalene is impossible. A higher degree of separation is of course possible by the use of a high separating power column, but the benefit gained is offset by the operating costs of such a column.

A list of the azeotropic mixtures formed with naphthalene is shown in Table 4.

TABLE 4

OBSERVED AZEOTROPIC MIXTURES FORMED WITH NAPHTHALENE

Compound	B.Pt. °C	B.Pt. °C of Azeotrope
Meta-cresol	202.2	202.08
p-ethyl phenol	218.8	215.0
Catechol	245.9	217.45
ethyl aniline	206.0	205.0

Thus to determine the degree of separation achieved by fractionation on a given column, it is necessary to consider more empirical methods, which in general, tends to reduce the system to a pseudo binary state.

Empirical Treatment

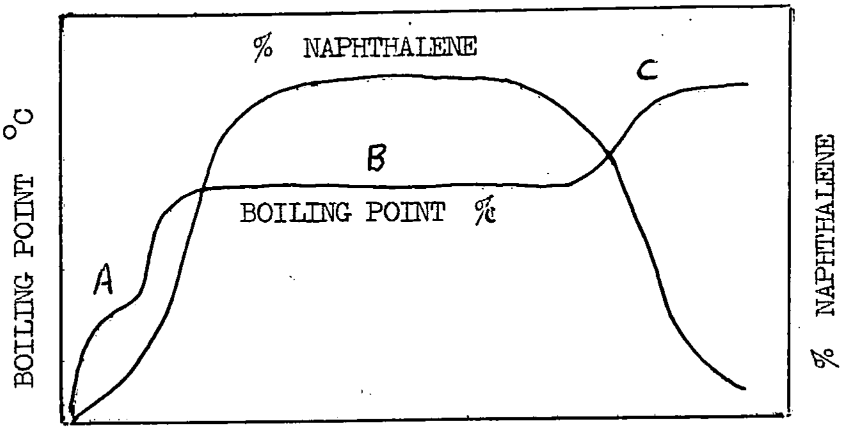
A method has been developed by Rose and Sweeney(10), for calculating the distillation curve for a phenol free naphthalene-oil system. The method has been applied to batch distillation only, and stipulates only one condition, namely, that pure or nearly pure naphthalene must occur at some stage in the distillation product.

The method considers a multi-component mixture as containing a number of binary mixtures, to which the McCabe Thiele technique can be applied. Thus for a three component mixture L, N and H, where L is the most volatile, H is the least volatile and N is the intermediate (naphthalene) component, two curves for distillate composition against percent distilled are calculated in the usual manner, one for the L, N binary and one for the N, H binary. These results are then combined consistent with the charge composition, to predict a similar curve for the ternary case.

The first stage in the procedure is to carry out two fractional distillations, one at atmospheric pressure and the other at some reduced pressure. From the boiling point curves, the relative volatilities of the three components can be calculated. The results of the atmospheric distillation are plotted as shown in Diagram (2), relating percent naphthalene with percent distilled and overhead temperature with percent distilled.

DIAGRAM 2

ATMOSPHERIC DISTILLATION OF NAPHTHALENE OIL



WEIGHT % DISTILLED

At atmospheric pressure, there is a constant-boiling material distilling at about 216°C indicated by point B. This material is approximately 96% naphthalene and is treated as the N component. There is a definite plateau in the boiling point curve (point C) and this component and everything that boils higher is treated as the H component. Similarly there is an inflection at point A, and this material is treated as the L component. The relative amounts of components L, N and H in the charge are determined from the area under the composition curve and the area outside the curve.

The L, N binary is considered first, and on the basis of a binary containing only L and N, the values of L and N can be calculated. From the above information and the calculated relative volatilities, a McCabe-Thiele diagram can be plotted for a given number of theoretical plates and fixed reflux ratio. The values of x_d can then be found for values of x_w, where x_d, and x_w represent the weight fractions of the L component in the distillate and residue respectively. The Rayleigh equation which relates the fraction of the original charge remaining in the pot, to the pot and distillate composition is then used to calculate x_d against percent L + N distilled. Values of x_d are then converted to weigh fractions of pure naphthalene, and the percent of L + N distilled is converted to percent of total charge distilled.

The N, H binary is taken to consist of all the H component and enough N component to give an x_d value close to 1.0. Using the McCabe-Thiele and Rayleigh methods as before, x_d is calculated to weight fraction of pure naphthalene (in this case x_d refers to the N component) and the percent of the last half of charge is converted to percent of total charge distilled.

The data resulting from the two binary calculations are then used to predict the curve of weight fraction of naphthalene in distillate against weight percent distilled. This is the essential information required for estimates of yield and purity for a given column.

As previously stated there is one necessary assumption to be made in order to calculate the N, H part of the curve, namely that pure N must appear in the overhead at some point. If this occurs, then it can be stated that :-

(1) all the heavy component in the charge remains in the pot.

(2) all the light component has been removed.

Thus there is actually a binary in the still at this point and the Rayleigh calculation procedure applies.

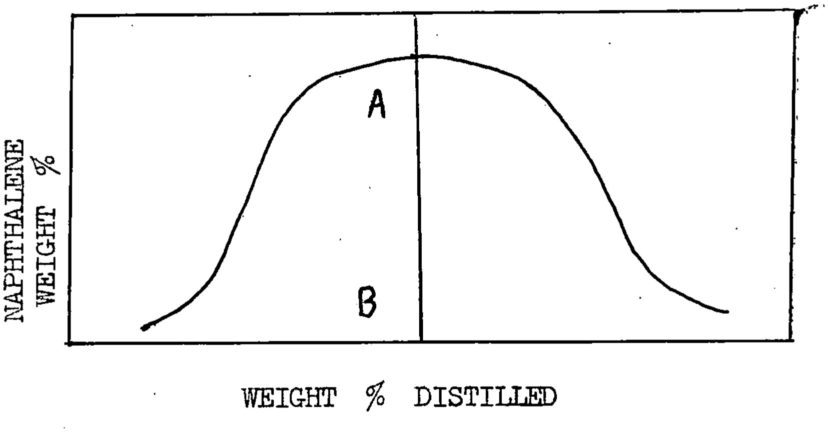
This assumption however, may apply for naphthalene oils derived from petroleum sources, but does not apply when the oil is of coal tar origin. It has previously been stated that naphthalene oils contain a number of compounds boiling very close to naphthalene (see table 3) and the overhead product must inevitably be contaminated. The extent of this contamination can be seen by a reference to Table 8a (page 61) where a naphthalene oil on fractionation through a 50 theoretical plate column, gave a maximum product purity of 93%. Thus the treatment will break down when applied to coal tar naphthalene oils. Practical application of this treatment to the recovery of naphthalene from coal tar oils has resulted in the "top" and "bottom" fractions containing the calculated amount of naphthalene, but the purity of the naphthalene fraction itself being 2-3% lower than the calculated purity(11).

A further empirical treatment has been developed by Briggs, Waddington and McNeil(12) whereby the purity and recovery of naphthalene are related mathematically to the separating power, expressed as plate equivalents, of a batch column, the procedure being based upon data obtained from a minimum of three laboratory fractionations.

The method is based upon the fact that when a phenol free naphthalene oil of coal tar origin, is distilled batchwise and the naphthalene content of the distillate plotted against the amount distilled, a curve symmetrical or nearly so, is usually obtained (see Diagram 3).

DIAGRAM 3

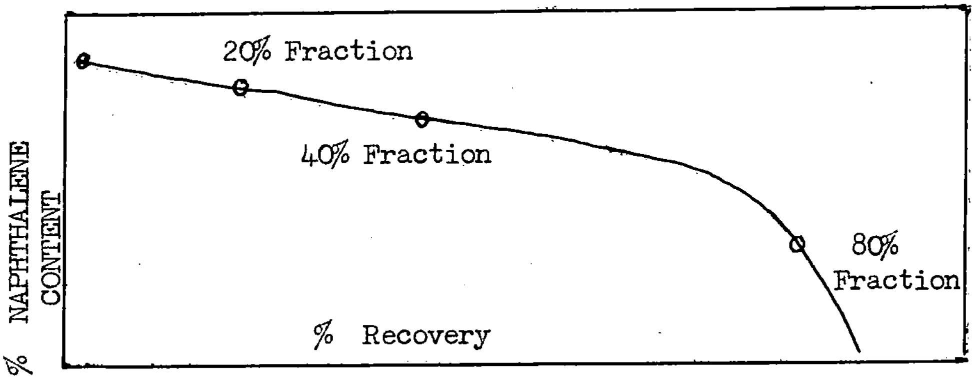
NAPHTHALENE DISTILLATION CURVE



The diagram shows that the maximum naphthalene content occurs close to the mid-point of the distillation. An alternative and more directly informative method of expressing the data for a fractionation is to plot percentage naphthalene content against percentage recovery of naphthalene, using data for fractions symmetrically distributed about the centre of the curve (line A.B. Diagram 3). For example, take the fraction boiling 10% before and 10% after the line AB, and call this the 20% fraction. Calculations based on consideration of the areas under the curve, give the recovery or percentage of the available naphthalene contained in the given fraction, and the average naphthalene purity of the fraction. This gives a point on a purity-recovery graph. Similarly points for the 40%, 80%, etc. fractions may be obtained and a line drawn on a plot such as Diagram 4 representing all data for a given degree of separation. Similarly other lines may be drawn representing data for different degrees of separation. Such a plot gives a visual picture of the relationships between numbers of plate equivalents, purity, recovery and fraction width for a given naphthalene oil. It is however, purely a chart expressing experimental data, though it is possible to extrapolate data in the following manner.

DIAGRAM 4

DESIGN CHART FOR A NAPHTHALENE OIL



EXTRAPOLATION OF EXPERIMENTAL DATA

If one takes the maximum purity of naphthalene obtained in a batch fractionation (y), the initial naphthalene content (x) and the number of plate equivalents (n) used to obtain this product, then the above terms can be related by an expression:-

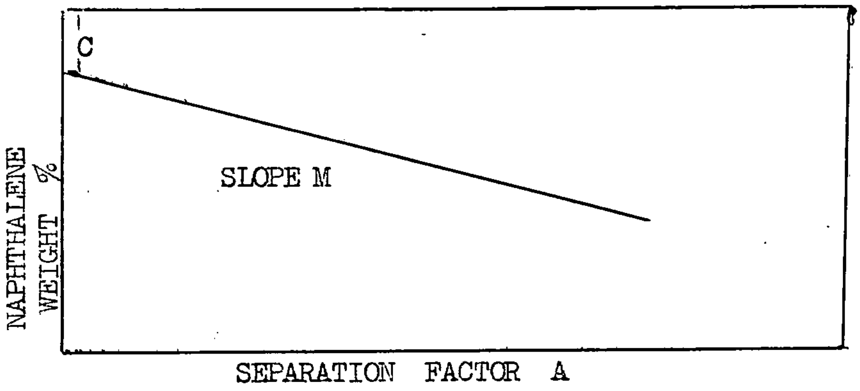
$$\frac{y}{100 - y} = A^n \frac{x}{100 - x} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where **A** is a separation factor whose value for a given oil depends on the relative volatilities of naphthalene and the remaining components in the overhead, and those in the pot, and on the degree of separation achieved. It is, therefore, an arbitrary constant dependent upon the characteristics of the naphthalene oil.

When the values for the maximum concentration of naphthalene obtained by subjecting the same naphthalene oil to batch distillation at different degrees of separation are plotted against the calculated values for A (derived from equation 1) a linear relationship is observed, as shown in Diagram 5.

DIAGRAM 5

RELATION BETWEEN PEAK NAPHTHALENE PURITY AND SEPARATION FACTOR



Thus an equation of the form:-

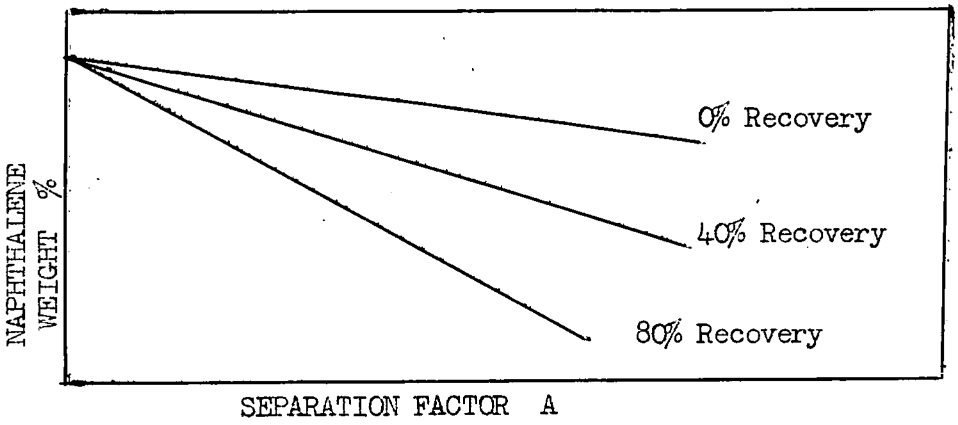
$$y = C - m\,(A - 1) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

may be used to represent the variation of A with y, and constant (m) being the slope of the line, and C being the intercept on the y axis when A = 1. i.e. the highest attainable naphthalene purity. If instead of the peak purity, which may be considered as the condition of zero recovery, the average naphthalene contents for some finite recoveries are taken and these values inserted instead of y in the equation, the values of A obtained at different plate equivalents are also found to be linear with y.

The lines relating the value of the separation factors to the naphthalene contents for the zero, 40% and 80% recovery are shown in Diagram 6. These values are derived from the curves in Diagram 4, the design chart.

DIAGRAM 6

AVERAGE PERCENTAGE NAPHTHALENE AGAINST SEPARATION FACTOR FOR VARIOUS PERCENTAGE RECOVERIES



It is interesting to note that the lines shown in the diagram, all converge at a maximum value of (y), when A is equal to unity. This maximum value of (y) represents the highest naphthalene purity which it is possible to obtain from the given oil, by fractionation, even at infinite numbers of plate equivalents. Thus this maximum value of (y) is in effect a measure of the amount of material in the oil which either forms azeotropes with naphthalene or boils at exactly the same temperature. Since all the necessary variables are now related, it is possible to calculate, the purity or recovery of naphthalene that can be obtained from a given batch column of known plate equivalents.

In this treatment it is implied that the separation is dependent on numbers of plate equivalents only and not on reflux ratio. This is not the case, and to achieve the separation required, the reflux ratio must be above the minimum value irrespective of the number of plate equivalents. With this proviso, the method has been found to be satisfactory for the design of columns for the recovery of naphthalene from naphthalene oils by batch fractionation (13).

This particular treatment of the batch fractionation of naphthalene oils is based upon the empirical finding that naphthalene oils gave symmetrical distillation curves. Continuous distillation, in which the oil is partially separated in a first column, to remove lighter boiling components with a minimum amount of naphthalene, and the bottoms from the first column then separated in a second column into a naphthalene fraction and a high boiling fraction, is a much more difficult problem. Rigorous plate by plate calculations are not at present possible owing to the lack of analytical and physical data concerning the individual components of the oil. A semi-empirical treatment for the continuous separation of naphthalene oils is at present being developed at the laboratories of the Coal Tar Research Association, but no data is at present available.

SUMMARY OF FRACTIONAL DISTILLATION AND ITS APPLICATION TO THE NAPHTHALENE OIL SYSTEM

Batch or continuous fractional distillation can be employed as a separation technique applicable to the naphthalene oil system. Its use, however, is very limited. The complex nature of the naphthalene oil and the subsequent lack of analytical and physical data concerning the oil, prevents a rigorous plate by plate calculation of the degree of separation to be expected from a given column, and any such estimation must, therefore, be based on a more empirical approach. The occurrence in the oil system of azeotrope forming components and other close boiling components indicates that a column of high separating power would be required to obtain both a high purity naphthalene and a high recovery of naphthalene. A calculation* based on the batch distillation approach of Briggs, Waddington and McNeil(12), shows that to obtain an 80% recovery of 96% naphthalene from a naphthalene oil of coke oven source, a column of nearly 200 plate equivalents would be required. Since the purpose of this thesis is to develop a method capable of producing a 90% recovery of 96% naphthalene, then batch fractionation or continuous fractionation is clearly unsuitable as a single operation.

Continuous fractionation however, does provide a satisfactory method for obtaining a high recovery of intermediate purity naphthalene (approximately 80%) prior to further separation by alternate means. A high recovery is possible in this case, since naphthalene purity and recovery are inversely proportional, and the column operating conditions can be adjusted to maintain a constant product purity.

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* Method described on page 25.

CRYSTALLISATION

Since crystallisation is employed as a preliminary operation to further oil separation, it is essential to be able to determine the type and nature of the crystals produced under varying operating conditions, such as rate of cooling, degree of agitation, final temperature attained in the crystalliser and to be able to determine the effect on crystal structure resulting from the different types of impurities present in the crystalliser.

The overall process of crystallisation can be considered to occur in two stages, namely, nucleation and crystal growth. In the case of a pure solution, nucleation must occur first, but in the case of an impure solution where solid particles are present, then crystal growth can begin immediately, utilising the solid particles as nuclei.

Nucleation

The formation of nuclei in the case of a pure solution or melt is generally considered to follow a sequence in which collision of two molecules occurs followed by collision with a third molecule and so on. Short chains or flat monolayers can then form, upon which the crystal lattice can then develop. This rapid construction process can only continue in regions of high supersaturation and even then the nucleus must first attain a certain critical size in order to achieve stability. A pictorial representation of the spontaneous nucleation regions is given by Miers(15), in the form of a temperature-concentration diagram.

A more rigorous treatment of spontaneous nucleation can be developed by considering the various energy requirements of the system. Utilising the Gibbs-Thomson equation for the vapour pressure of a liquid droplet, an expression can be derived which gives a measure of the work of nucleation in terms of the degree of supersaturation of the system.

i.e. $$W = \frac{16 \pi \sigma^3 M^2}{3 (R T \rho \, Ln.S)^2} \quad .... (1)$$

where W = work of nucleation

S = supersaturation of system

M = molecular weight

σ = surface energy of droplet per unit area

ρ = density of droplet

When the solution is saturated, S = 1 and Ln.S = 0, thus the amount of energy required for nucleation is infinite. Consequently, spontaneous nucleation cannot occur in a solution which is just saturated. Conversely, any supersaturated solution can nucleate spontaneously, since there is some finite work requirement associated with the process.

A further relationship between the excess free energy of the system and the size of the nucleus shows that nucleation can only continue when the nucleus attains a certain critical size.

The rate of nucleation can be expressed in the form of the Arrhenius reaction velocity equation:-

$$N = A \exp \left(\frac{-\Delta G}{R\,T}\right) \quad .... (2)$$

where ΔG = overall excess free energy of the particle

i.e. the work of nucleation W.

From equations (1) and (2) :-

$$N = A \exp. \left[\frac{16 \pi \sigma^{3} M^{2}}{3 R^{3} T^{3} \rho^{2} (\mathrm{Ln.}\, S)^{2}} \right]$$

Thus the rate of nucleation is shown to depend upon three main variables, namely, temperature, degree of supersaturation and interfacial tension.

The dependance of nucleation rate upon temperature is an important factor in determining subsequent crystal size. Reduced temperature results in increased supersaturation and consequently increased nucleation rate; thus rapid cooling will lead to the formation of a large number of nuclei and subsequent small crystals, whereas slow cooling produces relatively few nuclei and subsequent large crystals.

The effects of impurities upon nucleation are variable. Solid particles present in the system act as condensation nuclei thus initiating the process of nucleation. Soluble impurities can effect the rate of nucleation by acting as nucleation accelerators or inbibitors, depending upon the system in question and on the type of impurity.

<u>Crystal Growth</u>

The rate of crystal growth in a solution is dependent upon the concentration and temperature of the liquid at the crystal surface, on the degree of agitation, and on the type and nature of the impurities present.

On the basis of temperature-concentration dependence, the question of heat and mass transfer arises. The resistance to heat and mass transfer lies mainly in the laminar sub-layer close to the crystal surface, and thus increasing the relative velocity between liquid and crystal surface through the medium of agitation, will increase the transfer rate and consequently increase the crystal growth rate. In the case of a solution, mass transfer is more important than heat transfer, and thus a concentration gradient between liquid and crystal surface is necessary. Thus increased liquid concentration results in increased crystal growth rate.

In the case of a melt, heat transfer is the important factor, and thus a temperature gradient is required. Increasing the degree of supercooling, therefore, improves the heat transfer, and consequently increases the crystal growth rate.

The effects of impurities are variable. Certain soluble impurities will retard crystal growth by adsorption onto the crystal surface, whilst others are adsorbed onto one specific crystal surface only, thus modifying the shape of the crystal. A further type of impurity can interfere with the crystal structure as in eutetic and mixed crystal formation.

The mechanism of crystal growth is not at all clear. Many attempts have been made to explain the mechanism, and these can be broadly classified under three general headings, namely "Surface Energy", "Diffusion", and "Adsorption - layer" theories.

Surface energy theories are based on the postulation of Gibbs(17) and Curie(18), that a growing crystal assumes a shape, such that the surface energy is a minimum. The diffusion theories originated by Noyes(19), and Whitney(20), and Nernst(21), assume the continuous deposition of matter on a crystal surface at a rate proportional to the difference in concentration between the deposition point and the bulk of the solution. Adsorption - layer theories first introduced by Volmer(22) assume crystal growth to be a discontinuous process, proceeding by adsorption, layer by layer, onto the crystal surfaces.

The earlier surface energy approach has largely fallen into disuse, whilst recent modifications have been based on the adsorption-layer theory. Such a modification is the spiral growth theory of Frank(23) who has suggested that material deposition occurs at the site of a structural dislocation at the crystal surface.

In the case of the crystallisation of naphthalene from a pure melt, the variation of operating conditions such as rate of cooling, degree of agitation, final temperature attained etc. and their effects on the growth and size of crystals obtained are reasonably well established. However, for the naphthalene-oil system where there is a high degree of impurity, the effects of these variables are not so well known. The effects on the crystal structure arising from the presence of impurities is of particular importance during the crystallisation operation, since crystallisation is invariably followed by some form of mechanical separation such as centrifuging, and the overall degree of separation achieved is to a great extent, dependent upon the crystal purity obtained during crystallisation.

Crystal Contaminants

Recently it has been found that amongst the many compounds present in the naphthalene oil, are compounds capable of separating out with the naphthalene and recent work by Briggs(24) has shown that impurities in crystal naphthalene occur as:-

(1) Inter-crystalline, that is as mother liquor on the crystal surface or trapped in the crystal interstices.

(2) Intra-crystalline, that is as mixed crystals with naphthalene or impurities which have crystallised with the naphthalene as eutectics.

The first type of contaminant, i.e. inter-crystalline oils would be expected to increase in quantity with decreasing crystal size, and it has been found(25) that when a sample of naphthalene oil is crystallised under different conditions and the crystals filtered or centrifuged, the crystal purity decreased with increasing rate of crystallisation, corresponding to decreased crystal size.

If the crystals are washed during centrifuging with a detergent solution, there is a slight increase in crystal purity. It is apparent that surface oil is being removed by centrifuging, but when the crystal surface area increases, as with small crystals, the amount of surface oil increases.

However, beyond a certain point, continued detergent washing has no further effect. Thus, the detergent solution is able to remove surface oil but has little or no effect on inter-stitial oils.

The second type of contaminant consists of substances forming mixed crystals or high melting eutectics with naphthalene. A large number of naphthalene crystals of phthalic anhydride grade quality have been purified by zone melting techniques and the impurities analysed

Crystal Contaminants (Cont'd)

by gas-liquid chromatography(26). The major components of the impurities have been identified and are tabulated in Tables 5a and 5b.

Table 5a shows those compounds forming mixing crystals and Table 5b shows the compounds forming eutectics and the eutectic melting points.

TABLE 5a

Compounds forming Mixed Crystals
Thionaphthene
Quinoline
Iso-quinoline
Indene

TABLE 5b

Compounds Forming Eutectics	Melting Point of Eutectic °C
β-methyl naphthalene	25.5
2.6 dimethyl naphthalene	60.5
2.3 dimethyl naphthalene	54.2
diphenyl	39.2
acenaphthene	51.4
flourence	57.0

It is well known that if components capable of forming mixed crystals are present, then they will form continuously during crystallisation and be distributed throughout the crystal structure. Furthermore, the amount of components forming mixed crystals in the naphthalene crystal will depend primarily on the quantity of such material present in the naphthalene oil and the final crystallisation temperature. Rate of crystallisation, agitation, and detergent washing will have no effect on the crystal purity provided no super saturation occurs.

Similarly the amount of eutectic forming material will depend on the quantity of such compounds present in the naphthalene oil, and particularly on the temperature at which the crystals form. Crystals allowed to form above the melting point of any given eutectic will

Crystal Contamination (Cont'd)

contain much less of this impurity than crystals allowed to form below this temperature. The great importance of controlled crystallisation on the impurity distribution within the naphthalene crystal can be demonstrated, by an experiment carried out at the Coal Tar Research Association(27).

A sample of crystallised naphthalene was washed with successive portions of a solvent such as methanol and the material dissolved by each portion analysed. The analysis results shown in Table 6, indicate that the outer crystal layers are richer in impurities than the inner core. Thus, as nucleation begins at approximately 80°C, then impurities will build up successively as the falling temperature crosses each eutectic point (see Table 5b). Mixed crystal formation will commence however, from the point of nucleation.

TABLE 6

EFFECT OF SUCCESSIVE WASHING OF CRYSTAL NAPHTHALENE

	Wash					
	0	1st	2nd	3rd	4th	5th
Naphthalene Content of Undissolved Portion	91.3	96.1	97.0	97.2	97.4	97.8
Analysis of material removed by solvent extraction						
Wt. % Naphthalene	-	58.9	82.0	91.5	95.2	-
Wt. % Thionaphthene	-	3.3	2.6	1.6	1.4	-
Wt. % Quinoline	-	4.5	2.3	1.4	0.9	-
Wt. % -methyl naphthalene	-	15.1	7.0	2.5	2.9	-
Wt. % Diphenyl	-	1.7	NIL	NIL	NIL	-
Wt. % 2.6 and 2.7 dimethyl naphthalene	-	0.5	NIL	NIL	NIL	-

Crystal Contamination (Cont'd)

The concept of impurity deposition within the crystal as deduced from Table 6 is altered completely however if the crystallising conditions are such that super saturation or shock cooling of the oil can occur. In this case, naphthalene crystals come out of solution at a temperature lower than normal and the quantity of intra-crystalline impurities is increased.

The effect of stirring or agitation during crystallisation is that it tends to prevent supersaturation. An opposing factor however, is that agitation prevents the formation of large crystals and thus increases the quantity of interstitial impurities in the drained crystal.

The experimental evidence now acquired, enables some of the puzzling features of naphthalene crystallisation to be accounted for. In the case of the Pro-Abd(28) type process, in which naphthalene oil is crystallised in water cooled, stirred, tanks and the resulting slurry centrifuged, followed by hot water or dilute caustic washing on the centrifuge it is easier to produce phthalic anhydride grade naphthalene (78.0°C crystallising point) if the oil is of vertical retort origin, than if it is of coke oven origin. Oils derived from vertical retort tars, normally contain considerably less of the materials liable to form eutectics with naphthalene and thus yield crystals more amenable to further purification by washing.

Crystal Contamination (Cont'd)

Concerning the yield of naphthalene recovered by crystallisation, the amount recoverable will depend on the solubility of the naphthalene in the oil at the lowest temperature attained in the crystalliser. A number of isolated results for the solubility of naphthalene in various tar oils have been quoted by different workers. For example Warnes(29) has quoted results for two naphthas, cresylic acid and a heavy tar oil at an unspecified temperature; Thodes and Eisenhower(30) have given results for a heavy naphtha (boiling range 154°C - 188°C) and a high aromatic fraction (239°C - 303°C). Potashnikov(31) has given results for two acid and base free fractions boiling 195°C - 267°C and 224°C - 306°C.

Although there are a number of inconsistencies, the available data suggests that the solubility of naphthalene decreases the further the boiling range of the oil is removed from the boiling point of naphthalene. The data provided by Thodes and Eisenhower indicates that the solubility of naphthalene is increased by the presence of cresols in the oil.

Table 7 shows the results obtained by Potashnikov for the two given oils, and Figure 1 shows the results for the light oil fraction (naphthalene oil range).

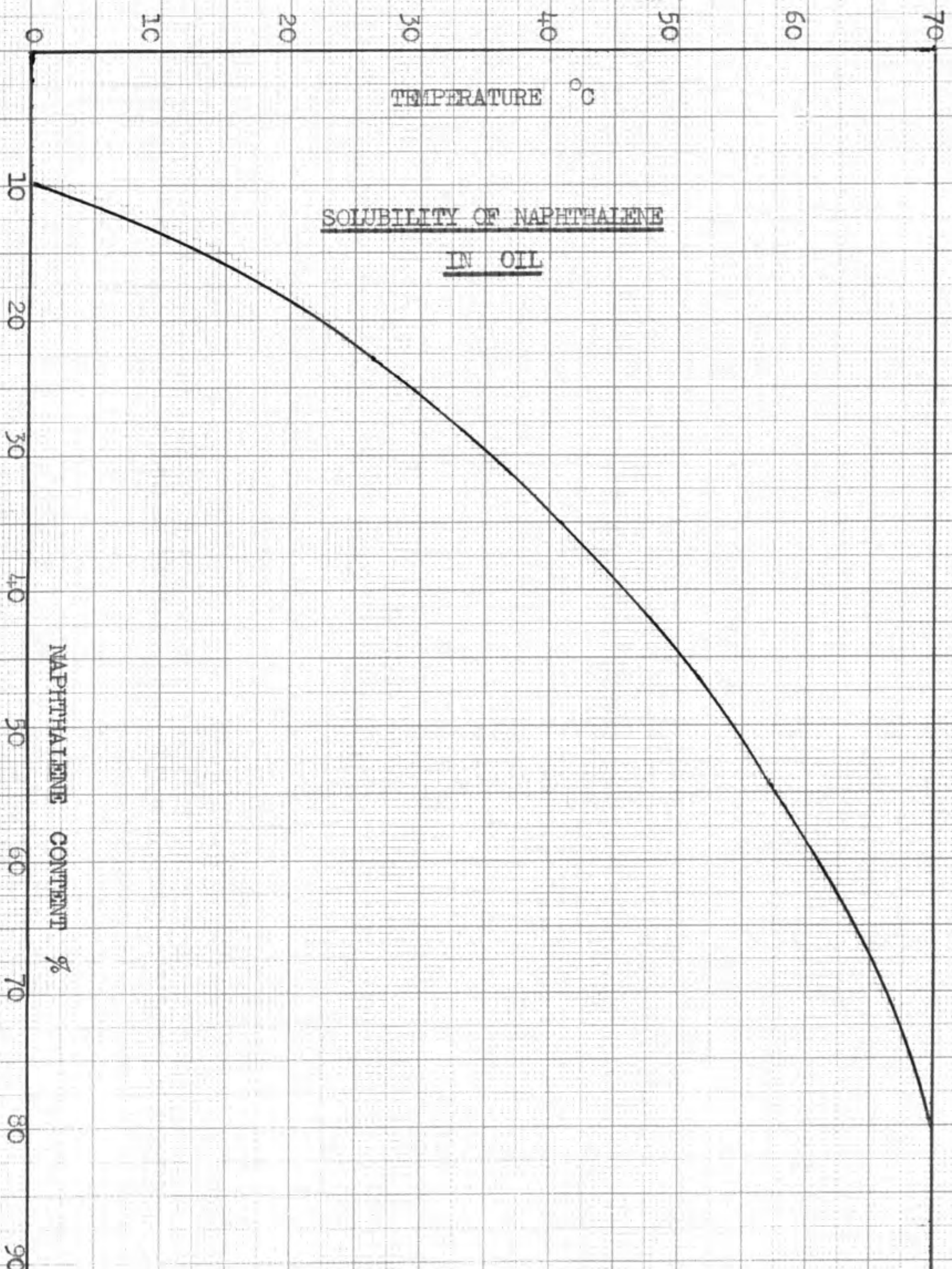
TABLE 7.

SOLUBILITY OF NAPHTHALENE IN LIGHT AND HEAVY OILS.

WT. %

	Light Oil 195 - 267°C.		Heavy Oil 224 - 306°C	
Temperature °C.	During Heating	During Cooling	During Heating	During Cooling
0	9.99	9.81	9.60	9.80
5	12.50	12.37	11.12	11.56
10	14.65	15.25	13.88	14.12
15	16.87	17.22	17.16	17.33
20	20.65	20.20	20.00	19.66
25	22.68	22.91	22.83	24.20
30	26.23	27.02	28.92	29.54
35	29.74	29.70	31.94	32.02
40	33.35	34.02	36.02	36.97
45	37.20	37.75	42.53	42.48
50	42.56	43.36	47.96	48.80
55	48.80	47.98	54.81	54.30
60	60.27	60.40	61.60	60.82
65	71.19	70.83	69.30	70.49
70	80.32	79.44	79.27	79.66
75	90.02	90.47	91.66	91.37

FIGURE 1



SOLUBILITY OF NAPHTHALENE IN OIL

Crystal Contamination (Cont'd)

The results obtained by Potashnikov are considered to be the most applicable and are used as the basis for all solubility determination

During the process of crystallisation, the final temperature attained in the crystalliser is generally 15-20°C. Cooling to temperatures below 15°C, requires the use of refrigeration equipment, and from Tables 2 and 7 it can be seen that the extra yield of naphthalene is not an economic gain in view of the extra equipment required.

Consider naphthalene oil No. 2 in Table 2. Cooling of this oil from 15°C to 0°C, would reduce the naphthalene lost in the oil from 8.2% to 4.7% i.e. it would increase the recovery of naphthalene as drained material from 79.3% to 82.8%.

Type of crystalliser in operation

Crystallisation of naphthalene oils can be achieved either in batch or continuous crystallisers. From the point of view of crystal purity the important factor is the degree of temperature control which can be achieved in the crystalliser. Thus the rate of cooling in any one crystalliser will depend on the heat transfer from the semi-solid mass, and as such, the design of the crystalliser must take into account the special requirements for minimum impurity deposition within the naphthalene crystal.

In general practice, crystallisation is frequently carried out batchwise in either unstirred, atmospherically cooled tanks, or in indirectly cooled, stirred tanks.

The former types of crystalliser has the advantage of:-

Type of crystalliser in operation (Cont'd)

(1) simplified process handling

(2) the formation of large crystals which can be easily freed from interstitial and surface oils

The disadvantages are:-

(1) large time interval to complete crystallisation cycle

(2) loss of naphthalene by evaporation

(3) fire and health hazards due to presence of vapour

The latter type of crystalliser has the advantages of:-

(1) shorter crystallisation cycle

(2) reduced evaporation losses and subsequently reduced fire and health hazards

The disadvantages being:-

(1) production of smaller crystals containing a greater quantity of contaminating oils

(2) greater complexity of process handling

From an overall point of view, the indirectly cooled, stirred type of crystalliser is the more efficient, and in fact forms the basis of the majority of naphthalene crystallisers used in this country.

A number of other devices have been patented, but as far as is known, are not actually used. Some of these devices are listed below:-

(1) A Russian patent(32) suggests continuous crystallisation by spraying a cooled slurry of naphthalene plus oil together with air at an elevated pressure, into a chamber with linen filters, allowing the oil to drain and removing the naphthalene continuously.

Type of crystalliser in operation (Cont'd)

(2) A simple type of continuous crystalliser patented by an Italian firm(33), allows oil to be fed continuously to a vertical container with a funnel shaped bottom and rotating discharger. The oil is cooled by means of a cooling fluid in the jacket, and crystals depositing at the bottom are discharged to a centrifuge, and the liquid is removed through an overflow pipe. The nature of the resulting crystals can be controlled by the temperature of the cooling fluid and the rate of crystal discharge.

(3) An early British patent(34) suggests cooling the naphthalene oil by passage through a series of water cooled tubes, the walls of the inner tube being kept free from crystals, and the crystals kept moving by a rotating shaft and worm conveyor.

(4) A more recent technique, consists of spraying the naphthalene oil, onto a rotating water cooled drum, the crystals being scraped off the drum continuously by a knife edge.

In the latter two devices, the crystals produced are very small, and consequently, the amount of surface and interstitial oil is increased.

CENTRIFUGING AND DRAINING

Following directly after crystallisation, the naphthalene crystals are separated from the excess oil either by a simple draining or centrifuging. The essential difference between the two techniques, apart from speed of operation, is that, whilst centrifuging further purification can be achieved by water or detergent washing of the crystals on the centrifuge.

In the case of straightforward oil draining, the separating force is entirely gravitational, and consequently a considerable amount of oil is left adhering to the crystal surface.

In the case of the centrifuge, the force developed by centrifugal action is given by the equation:-

$$F = \frac{WV^2}{gR}$$

where F = force developed in lbs.

W = weight of rotating assembly plus load (lb. mass)

V = peripheral velocity of assembly (f.p.s.)

R = radius of rotating assembly from axis of rotation (ft)

If N = speed of R.P.M., then $V = \frac{2\pi R N}{60}$

Substituting for V and 'g'

$$F = \underline{0.00341\ WRN^2}$$

From this equation it can be seen that the separating force developed by the centrifuge, is directly proportional to:-

(1) the speed of rotation

(2) the distance of the mass to be centrifuged from the axis of rotation

Centrifuging and Draining (Cont'd)

Increasing the speed of rotation will increase the purity of the crystal by removing more of the surface oil on the crystal. Occluded oils or oils trapped within the crystal and impurities of the intra-crystalline type will not be removed however great the speed of rotation.

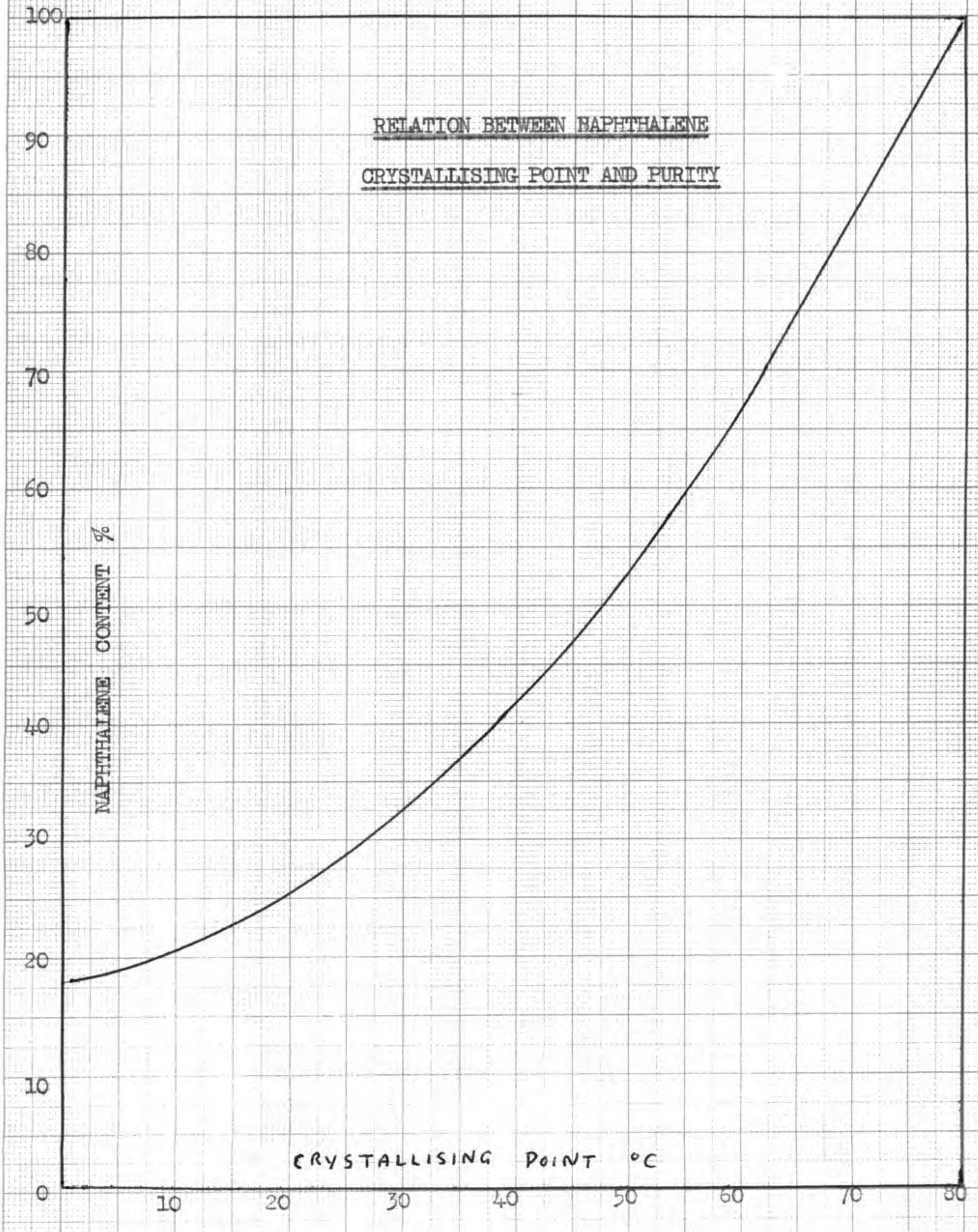
Present day centrifuges employ a perforated basket to hold the crystal slurry and the cake of naphthalene builds up from the outer wall of the basket in towards the axis of rotation. Consequently, in a system of this type, there will be an impurity gradient across the crystal cake. The highest degree of naphthalene purity will occur on the edge of the cake furthest removed from the axis of rotation.

When discussing centrifuging or draining, it is necessary to consider the yield of naphthalene obtained or alternately, the loss of naphthalene in the drained oil.

Centrifuging or draining is normally carried out at atmospheric temperature and although when centrifuging, there may be a slight temperature rise within the crystal slurry due to friction effects, for purposes of calculation, the drained oil is assumed to be at atmospheric temperature.

The calculation for naphthalene yield and recovery is based on determining the loss of naphthalene to drained oil, when upgrading a naphthalene of given purity to one of higher purity. It is necessary to know the solubility of naphthalene in oil at the given temperature and also the initial and final naphthalene purities. Solubility values are obtained from the solubility curve of Potashnikov, and naphthalene purities are obtained from the curves drawn up by Curtis (Figure 2), relating naphthalene crystallising point with purity(35).

FIGURE 2



RELATION BETWEEN NAPHTHALENE CRYSTALLISING POINT AND PURITY

Centrifuging and Draining (Cont'd)

A calculation of this type is given in Appendix 3.

OIL EXTRUSION

Oil extrusion is a method of oil separation, now practically obsolete. The method consists of applying pressure to crystallised naphthalene at normal of elevated temperatures. Although the degree of separation is high, the product recovery is low due to the oil saturation. Thus this method is not discussed further.

EXPERIMENTAL WORK

INTRODUCTION

The original system of naphthalene separation in operation at the time of this investigation was known to be inefficient at some stage or stages in the process.

Accordingly, the investigation was designed to study the processes available for the separation of naphthalene from naphthalene oils, in order to gain a better understanding of the physical and chemical factors involved, and to ultimately improve or modify the system so as to increase the overall efficiency.

Owing to the presence of certain specific plant equipment, namely, a twin column, continuous distillation unit, a naphthalene oil crystalliser and a Pilot scale centrifuge, the scope of the investigation was limited to the above Plant equipment.

An outline of the investigation is given below:-

Fractionation

(1) Naphthalene oil (from the Wilton Tar Still) fractionated through Laboratory column - to study naphthalene distribution, recovery and purity.

(2) Naphthalene oil washed free from phenolic compounds and fractionated through Laboratory column - to study the effects of phenolic compounds during fractionation.

(3) Naphthalene oil washed free from phenolic compounds and fractionated through Plant Distillation Unit - to study recovery and purity of naphthalene product - at Plant scale.

EXPERIMENTAL WORK (CONT'D)

Crystallisation and Centrifuging

(1) Naphthalene oil washed free from phenolic compounds, crystallised and centrifuged at Laboratory scale - to study effects of operating conditions on recovery and purity of naphthalene.

(2) Laboratory crystallisation and centrifuging of Plant distilled naphthalene oil - to study effects of combination of two separation p processes.

(3) Plant scale crystallisation and centrifuging of Plant distilled naphthalene oil - to study combined separation process at Plant scale.

EXPERIMENTAL WORK (CONT'D)

DESCRIPTION OF EQUIPMENT USED

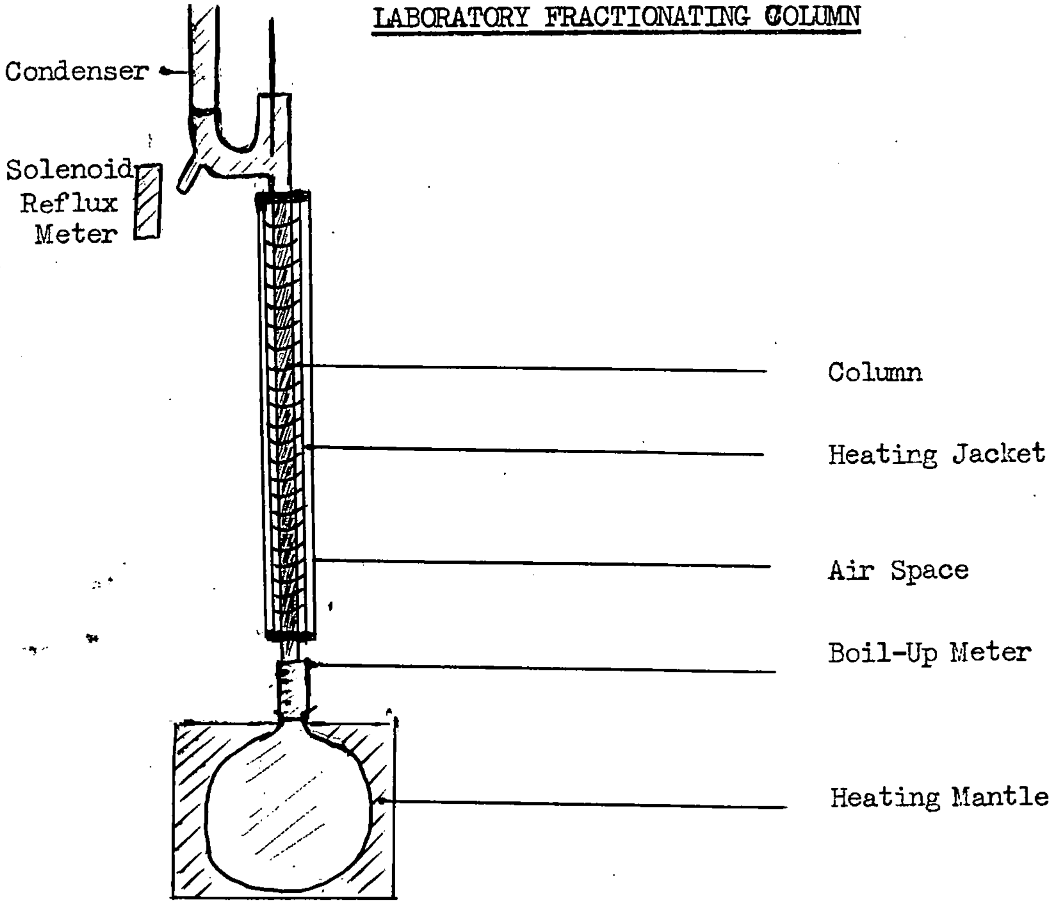
LABORATORY SCALE

Fractionating Column A

48" length, $\frac{3}{4}$" diameter, packed with 1/16" Dixon Gauze. Separating power at total reflux and boil up rate of 1000 mls/hr. - 50 theoretical plates, determined by calibration with n - heptane - methyl cyclo-hexane mixture.

(Separating power determined from refractive index measurements on the overhead and boiler products, after column preflooding and attainment of total reflux, and subsequent reference to a refractive index - separating power calibration chart).

LABORATORY FRACTIONATING COLUMN



EXPERIMENTAL WORK (CONT'D)

LABORATORY SCALE - Fractionating Column A (Cont'd)

Charge contained in a 1500 ml. pyrex boiler, heated by an electric mantle, the power to which was controlled by a Simmerstat unit. A reflux meter was employed to control the reflux ratio under operating conditions. Boil up rate was set by means of a boil up meter. The fractionating column was maintained in an adiabatic state by a concentric tube carrying a heater winding, surrounded by a concentric glass tube. Power to the heater winding was supplied by a variable voltage transformer.

Crystallisation

Cooling rate 5°C/hr. with continuous agitation. Initial temperature of oil - 90°C.

Oil contained in a cylindrical glass tube surrounded by a temperature controlled water bath.

Centrifuging

10.5 ins. M.S.E. bowl centrifuge

Centrifugal force - 1000 x g

Time - 4 mins.

EXPERIMENTAL WORK (CONT'D)

PLANT SCALE

APV - Naphthalene Distillation Unit

(See Flow sheet - Diagram 7)

Description

Twin column continuous unit.

Column I - Forerunnings column

Height 15 ft.

Diameter 3 ft.

APV West fractionating column incorporating 14 APV West type trays.

Fitted with tubular type steam heater.

Column operating pressure - 26"/Hg. produced by a single phase steam ejector.

Column II - Naphthalene column

Height 15 ft.

Diameter 4 ft. 8 ins.

APV West fractionating column incorporating 14 APV West type trays.

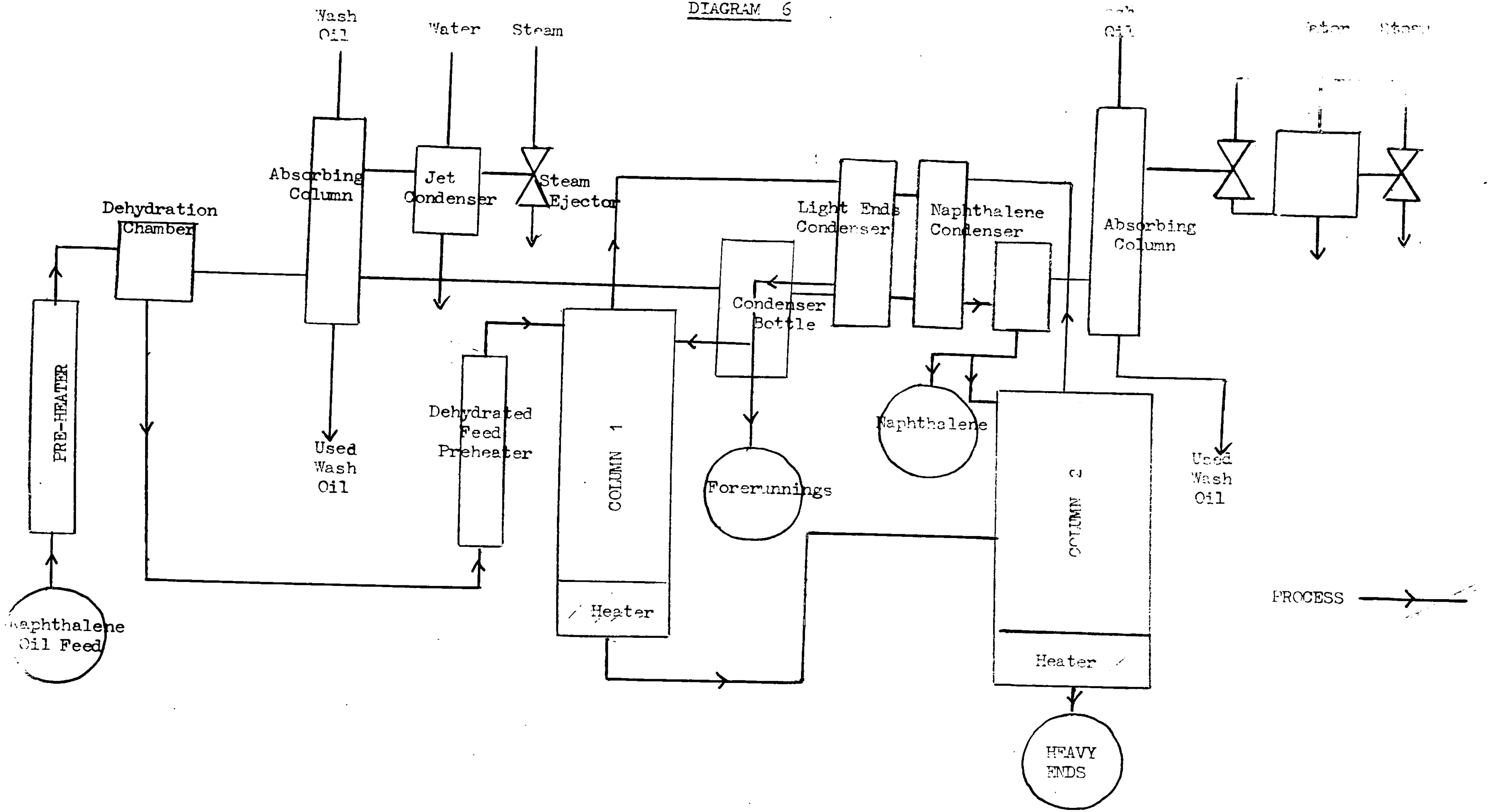
Fitted with tubular steam heater.

Column operating pressure - 28"/Hg. produced by a two phase steam ejector.

Process

Feed liquor at a temperature of 80/85°C is drawn under positive head, through a mesh strainer to the feed pumps. The feed is then pumped through a steam jacketed pre-dehydration heater. Water vapour is separated from the feed in a jacketed dehydration or flash

PROCESS FLOW DIAGR
NAPHTHALENE DISTILLATION UNIT (
DIAGRAM 6



EXPERIMENTAL WORK (CONT'D)

Process (Cont'd)

vessel maintained at a vacuum of 15"/Hg. Vapours from the flash chamber are drawn through an absorbing column (filled with a suitable wash oil) operating under a vacuum of 25"/Hg, so that any entrained naphthalene is removed by the wash oil. The remaining vapours are drawn through a jet condenser to remove water vapour, and then through a single phase steam ejector to remove any permanent gases.

The dehydrated feed from the flash chamber then gravitates to a final feed preheater and then into Column I, which is maintained at a vacuum of 26"/Hg. by means of the steam ejector. From the fractionating column, an overhead fraction is recovered via an evaporative condenser. The condenser is vented to the absorbing column to remove any further entrained naphthalene. Part of the condensed overhead fraction is returned to the column as reflux, whilst the remainder flows to a storage vessel.

The residue from Column I is then delivered to the feed plate of the naphthalene column (Column II), this column operating under a vacuum of 28"/Hg, produced by a two phase steam ejector. The overhead fraction from this column (approximately 80% naphthalene) is delivered, after condensation and separation of a reflux stream to a sealed vessel. The heavy residue from the column is discharged to a further sealed vessel.

EXPERIMENTAL WORK (CONT'D)

Crystallisation

Crystalliser:

Dimensions	27 ft. x 7 ft. 6 ins. diameter
Capacity	8000 gallons
Surface Area	635.5 sq.ft.
Stirrer Motor H.P.	7.5

Stirrers of gate type driven on a horizontal axis.

Cooling Rate 1° to 2°C per hour (water cooled).

Centrifuge:

Sharples C-20 De-hydrator (perforated basket)

Basket Diameter	20 ins.
Centrifugal force	980 x g.
H.P.	20
Max. cycle time	300 secs. (on automatic control)

Operating Sequence of Centrifuge

Screen rinse - spin load - spin idle - cake rinse - spin dehydrate - spin unload.

The above terms are defined as follows:-

Screen Rinse

Washing the centrifuge screen with oil to remove surplus naphthalene.

Spin Load

Entry of the feed into the centrifuge.

Spin Idle

Removal of oil.

EXPERIMENTAL WORK (CONT'D)

Operating Sequence of Centrifuge (Cont'd)

Cake Rinse

Washing of the cake with detergent etc.

Spin Dehydrate

Removal of surplus moisture.

Spin Unload

Automatic removal and discharge of cake.

Crude Tar Distillation Unit

(See Flow sheet - Diagram 8).

Description

Continuous pipe still, distillation column and fractionating column.

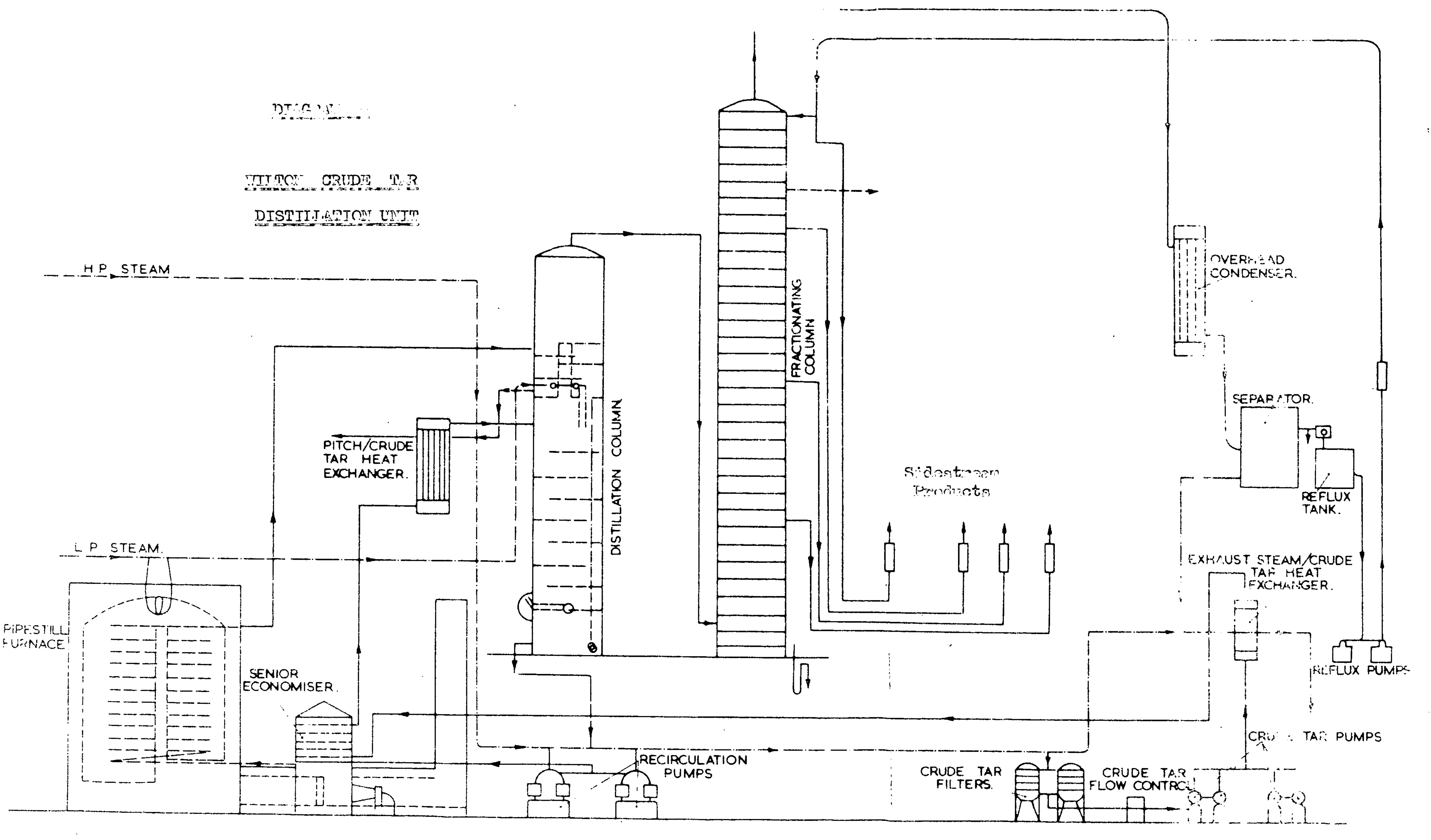
Pipe Still - Oil fired furnace
Distillation Column - Height 35'0"
Diameter 6'0"
Number of plates - 13 (Wilton Patent design)
Fractionating Column - Height 54'0"
Diameter 4'6"
Number of plates - 37 (Wilton Patent design)

Process

Crude tar is pumped through a heat exchange system comprising of an exhaust steam-crude tar heat exchanger, a heat economiser and a pitch-crude tar heat exchanger. From the heat exchange system, the tar enters the distillation column (secondary flash chamber) where light oils are removed. The tar after flowing down over the plates, leaves the base of the column, to be pumped via the recirculation pumps to the pipe

DIAGRAM

WILTON CRUDE TAR DISTILLATION UNIT



EXPERIMENTAL WORK (CONT'D)

Crude Tar Distillation Unit (Cont'd)

Process (Cont'd)

still. On leaving the pipe still, the tar enters the upper part of the distillation column (primary flash chamber) where further light oils are removed. A portion of the residual tar (pitch) is bled off, passing through the pitch-tar heat exchanger, whilst the remainder overflows into the secondary flash chamber and descends to the base of the column along with the incoming crude tar.

From the top of the distillation column, the light oils are fed to the base of the fractionating column. From the fractionating column, four sidestreams are removed and an overhead fraction. Part of the overhead fraction after condensation is returned to the column as reflux.

The bulk of the naphthalene (85%) in the crude tar is concentrated into the third sidestream (from the column base) and is referred to as the naphthalene oil fraction. The remaining 15% naphthalene is lost to the two adjacent sidestreams.

EXPERIMENTAL WORK (CONT'D)

METHODS OF ANALYSIS

The quantitative estimation of the compounds encountered during the investigation was based on the following methods of analysis.

Naphthalene

Naphthalene purity determined from depression of melting point and subsequent reference to a calibration curve.

Phenolic Compounds

Phenolic compounds were determined by extraction from the naphthalene oil with a 10% wt/wt caustic soda solution. Treatment of the caustic extract with hydrochloric acid resulted in the formation of free phenols. The individual phenols were not identified.

Quinoline

Quinoline determined as basic nitrogen utilising Dumas Nitrometer method.

Thionaphthene

Thionaphthene determined by formation of sulphur dioxide and subsequent volumetric determination of sulphuric acid formed by absorption of sulphur dioxide with hydrogen peroxide.

Methyl Naphthalenes

Alpha and beta methyl naphthalenes determined by vapour phase chromatography. (Determined in Laboratories of Coal Tar Research Association - Leeds).

THE LABORATORY FRACTIONATION OF NAPHTHALENE OIL (WASHED)

(Washed with a 10% caustic solution to remove phenols)

Method

A 1000g. charge of naphthalene oil from the Wilton still, was washed with caustic solution and fractionated through laboratory column A. The distillate was collected into fractions and a naphthalene purity determination done on each fraction (naphthalene purity estimated from crystallising point determination).

Fractionation results and details are shown in Tables 8a and 8b.

TABLE 8a

FRACTIONATION OF NAPHTHALENE OIL (WASHED)

Distillate Fraction in gms.	Temperature Range °C	Crystallising Point °C	Naphthalene Purity %
42.4	177 - 202	Oil	
17.0	202 - 205	Oil	
24.2	205 - 208.7	Oil	
18.0	208.7 - 214	32.00	34.00
17.5	214 - 216	50.00	51.00
20.0	216 - 217.2	63.70	70.10
17.1	217.2 - 218.0	66.80	75.20
23.3	218.0 - 219	70.00	80.30
32.0	219 - 219.4	74.40	88.60
71.0	219.4 - 219.7	76.35	92.10
52.0	219.7 - 219.7	76.55	93.00
45.2	219.7 - 219.7	76.60	93.10
37.0	219.7 - 219.7	76.30	92.20
32.0	219.7 - 219.7	76.40	92.21
47.9	219.7 - 219.8	76.36	92.20
45.9	219.8 - 219.8	76.35	92.20
37.0	219.8 - 219.8	76.32	92.19
48.0	219.8 - 228	76.08	92.00
47.1	228 - 230	75.82	91.30
55.0	-	72.40	84.90
	Residual heavy oil discarded		

TABLE 8b

The light oil fractions boiling below 216°C are referred to as Forerunnings, and the solid naphthalene fractions are referred to as Product.

DETAILS OF FRACTIONATION

	Crystallising Point °C	Reflux Ratio	Boil Up Rate mls/hr	Available Naphthalene %	Maximum Crystallising Point
Charge	57.8	-	-	-	-
Forerunnings	-	25/1	600	-	-
Product	75.60	5/1	600	84.7	76.60

Discussion of Results

Fractionation of the washed naphthalene oil through 50 theoretical plate laboratory column did not give the desired 90% recovery of 96% purity naphthalene (corresponding to a crystallising point of 78.0°C). The highese purity attained was 93% and the recovery of available naphthalene was 84.7%. From Table 8a, it can be seen, that the overall naphthalene purity is well below 93%. Consequently to attain a purity approaching the desired 96%, with a recovery figure of 90%, would require a fractionating column of formidable proportions.

It was then decided to compare the above results with those obtained by fractionation of an unwashed naphthalene oil through the same column.

THE LABORATORY FRACTIONATION OF NAPHTHALENE OIL (UNWASHED)

A 700g. charge of unwashed naphthalene oil to which had been added a quantity of phenolic oil, to increase the total phenolic content, was fractionated through Column A. The conditions of fractionation were similar to the former case. As before, the distillate was collected into fractions, and a naphthalene purity determination done on each fraction.

Fractionation results are shown in Table 9.

TABLE 9

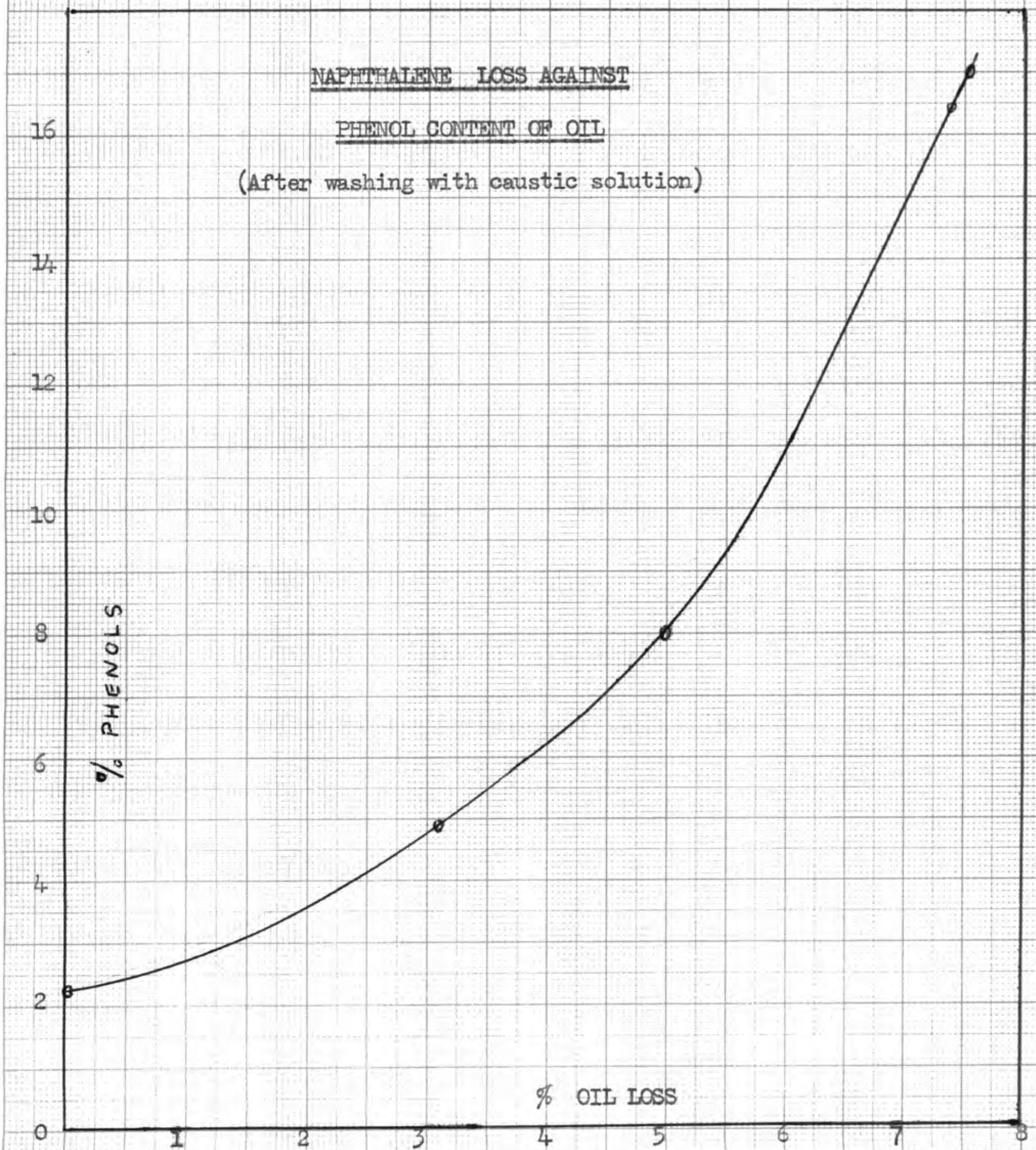
FRACTIONATION OF UNWASHED NAPHTHALENE OIL

Distillate Fraction in gms.	Temperature Range °C	Crystallising Point °C	Naphthalene Purity %
30.0	150-201	43.50	43.40
51.3	201-205	43.50	45.50
48.5	205-207	59.00	49.60
50.2	207-210	50.20	51.30
40.0	210-212	58.0	61.50
46.0	212-224	66.50	75.00
51.8	224-237	61.00	66.00
48.0	237-243	54.00	56.00
52.0	243-250	52.50	54.00
42.0	250-257	46.00	46.00
46.0	257-260	43.00	43.00
32.0	260-269	-	-
30.5	269-280	-	-
	Oils above 280°C discarded		

The distillation fractions collected from the last experiment were each washed with a hot 10% solution of caustic soda. Separation of the aqueous layer and subsequent treatment with dilute hydrochloric acid, liberated the free phenols. The weight of the phenols produced from each fraction was measured and also the weight of the washed oil measured. From the weights of the washed oil and liberated phenols, the loss of oil, if any, occurring during washing can be calculated.

The results of this experiment are shown in Table 10 and Figure 3.

FIGURE 3



NAPHTHALENE LOSS AGAINST

PHENOL CONTENT OF OIL

(After washing with caustic solution)

TABLE 10.

NAPHTHALENE LOSS AFTER CAUSTIC WASHING OF OIL.

Weight of Fraction Before Washing (g)	Weight of Fraction After Washing (g)	Total Weight Loss (g)	Weight of Phenols	Weight of non-phenolic Oil (g)	% Phenols	% Oil Loss (wt).
-	-	-	-	-	-	-
51.3	37.3	14.0	10.0	4.0	19.3	7.8
48.5	36.9	11.6	8.0	3.6	16.5	7.4
50.2	40.6	9.6	6.6	3.0	13.7	6.0
40.0	34.8	5.2	3.2	2.0	8.0	5.0
46.0	42.4	3.6	2.2	1.4	4.8	3.1
51.8	50.6	1.2	1.2	0	-	0

DISCUSSION OF RESULTS.

From Table 9, it can be seen that very poor fractionation is achieved when distilling an unwashed naphthalene oil. The maximum purity attained in this case was only 75% compared with 93% in the case of the washed oil.

Furthermore the spread of naphthalene through the distillation range is considerable, and is mainly due to the formation of low boiling azeotropes between naphthalene and certain of the phenolic compounds.

The results shown in Table 10 and Figure 3, show that with increasing phenol content, there is an increasing weight loss of oil. During the washing treatment, it is inevitable that a quantity of non-phenolic oil will be removed along with the caustic extract, but there is no reason to assume an increasing loss of non-phenolic oil with increasing phenol content. The increasing weight loss could however, be accounted for, on the basis of a theory suggested by Swietoslawski, namely that in a naphthalene-oil system, the presence of phenolic compounds increases the solubility of naphthalene in the non-phenolic oil. Thus with increasing phenol content, the solubility of naphthalene in the non-phenolic oil increases and although the volume of non-phenolic oil lost mechanically, may remain constant, the total weight would increase, due to the presence of naphthalene in solution.

THE LABORATORY CRYSTALLISATION AND CENTRIFUGING OF WASHED NAPHTHALENE OIL

METHOD

Samples of washed naphthalene oil were crystallised at a cooling rate of 5°C/hour, with agitation from 90°C down to 20°C, 0°C, and - 5°C. The samples were then centrifuged at 1000 x g for 4 minutes. After centrifuging, the purity of each sample was determined.

Results are shown in Table 11.

TABLE 11.

LABORATORY CENTRIFUGING OF WASHED NAPHTHALENE OIL

Batch No.	Temperature of Centrifuging	Yield of Solid % wt/wt	C.Pt. of Solid °C	Purity of Solid %	% Recovery Available Naphthalene
1	20	58.0	75.10	90.00	91.50
2	20	55.0	75.25	90.30	87.00
3	20	52.8	76.00	92.00	85.00
4	20	50.0	76.27	92.40	79.20
5	20	55.0	75.50	91.00	87.50
6	20	53.0	75.60	91.10	84.40
7	20	52.9	76.25	92.40	85.30
8	20	53.0	76.18	92.20	85.50
9	20	51.7	76.80	93.70	84.80
10	0	59.5	74.60	89.10	93.00
11	0	58.7	74.40	88.80	92.70
12	-5	59.7	74.50	89.00	92.60
13	-5	59.0	74.45	88.90	93.00

DISCUSSION OF RESULTS

From Table 11, the maximum naphthalene purity obtained when centrifuging at 20°C was 93.7% for a recovery figure of 84.8%, again below the desired limits. Centrifuging at lower temperatures gave higher recoveries but lower purities. The lowered purity was considered to be due to the deposition of eutectic and mixed crystal impurities when crystallising to the lower temperatures.

Consideration of the results obtained by laboratory fractionation and centrifuging of washed naphthalene oils (both processes employed as single operations) shows that the degree of separation achieved by either method is not adequate to attain the desired recovery and purity of naphthalene. The possibility of partial separation or upgrading of the naphthalene oil by fractionation, followed by further upgrading by centrifuging was next studied.

THE PLANT SCALE FRACTIONATION OF WASHED NAPHTHALENE OIL

The operation of the A.P.V. distillation unit results in three product streams namely:-

Forerunnings Product - from Column I consisting of light oils plus a small percentage of naphthalene.

Naphthalene Product - from Column II consisting of naphthelene plus excess oil.

Heavy Ends Product - from Column II - consisting of heavy oils plus a small percentage of naphthalene.

The condenser system of the two columns is equipped with a circulating wash oil system designed to absorb any naphthalene which would otherwise be lost to atmosphere as uncondensed vapour. Consequently from the point of view of yield of naphthalene product, any naphthalene absorbed by the wash oil is lost.

METHOD

Six distillation runs were carried out through the above unit, using washed naphthalene oil as feed material. Variations in Reflux ratio were made on both columns to achieve the highest purity and highest possible recovery of naphthalene product.

The results of these runs are shown in Table 12 and the method of calculating naphthalene product recovery is shown in Appendix 2.

TABLE 12.

DISTILLATION RUNS THROUGH PLANT DISTILLATION UNIT.

Run No.	FEED					NAPHTHALENE PRODUCT.				% Recovery As Naphthalene Product.	Distillation Rate Tons/day.
	% Phenols.	% Oils Bpt.		CPt. °C	% Purity	% Oils Bpt.		Cpt. °C	% Purity		
		< 218°C	> 218°C			<218°C	>218°C				
1	Nil	32.28	10.9	54.0	56.8	18.6	Nil	70.2	81.4	91.70	21.20
2	3.2	27.80	14.4	55.0	57.2	23.8	Nil	68.5	78.0	88.00	21.65
3	Nil	22.30	20.1	55.5	58.0	20.1	1.3	68.3	77.5	91.20	21.65
4	Nil	15.00	23.8	57.50	61.0	10.7	5.3	71.5	83.2	96.70	27.06
5	Nil	19.80	19.6	57.00	60.0	9.9	7.7	70.5	81.5	97.20	27.16
6	UNWASHED NAPHTHALENE OIL						UNABLE TO FRACTIONATE.				

DISCUSSION OF PLANT DISTILLATION RUNS

It was realised that owing to the lower separating power of the Plant distillation unit as compared to the laboratory fractionating column, the overall naphthalene purity would be considerably less. Nevertheless, increasing the reflux ratio on Column I, enabled the light oils to be removed, containing as little as possible naphthalene. Similarly, the heavy ends could be removed from Column II, relatively free from naphthalene. In this way, the maximum recovery of naphthalene was obtained, but at the expense of naphthalene purity. The maximum purity obtained was 83.2%, but with one exception, the recovery figures were all greater than 90%.

Run 2 was the exception and in this case, the recovery figure was 88%. It will be noticed that the feed material for this run, contained a small percentage of phenolic compounds, due to inadequate washing, and analysis of the cractionation products showed that the light oils removed from Column I were nearly saturated with naphthalene, thus suggesting a 'spread' of naphthalene due to azeotrope formation, (resulting from the presence of phenols).

THE LABORATORY CENTRIFUGING OF PLANT DISTILLED NAPHTHALENE OIL

Partially upgraded naphthalene product of crystallising point 70.2°C (purity 81% naphthalene) obtained from Run No. 1 through the Plant distillation unit, was allowed to crystallise at varying cooling rates, and the crystallised material fed to the laboratory centrifuge. Varying times of centrifuging were employed, and after each, the purity of the centrifuged product was determined.

Crystallisation

Oil cooled with agitation from 90°C to 20°C at cooling rates of:-

1. 3.5 °C/hour
2. 10 °C/hour
3. Shock cooled (no agitation)

VARIATION OF NAPHTHALENE PURITY WITH OIL COOLING RATE

Samples of material crystallised at the cooling rates mentioned above, were centrifuged for a period of 5 minutes at a centrifugal force of 1500 x g (3000 r.p.m.). The purity of the centrifugal material was obtained from crystallising point determinations. Results are shown in Table 13.

TABLE 13.

VARIATION OF NAPHTHALENE PURITY WITH OIL COOLING RATE.

Centrifugal force - 1500 x g.

Time - 5 minutes.

Rate of Cooling °C per hour.	Crystallising Point °C	Naphthalene Purity %
3.5	78.40	96.50
3.5	78.36	96.40
3.5	78.30	96.30
10.0	78.29	96.30
10.0	78.25	96.00
10.0	78.30	96.10
Shock Cooled	76.39	92.80
Shock Cooled	76.30	92.50

The above results show that the desired naphthalene purity of 96% can be obtained by centrifuging, when the feed material has a purity of approximately 80% naphthalene, provided crystallisation takes place at a controlled rate of cooling.

There is a slight increase in naphthalene purity when the oil cooling rate is lowered from 10°C/hour to 3.5°C/hour, but a marked decrease in purity when the oil is shock cooled. It has previously been mentioned that shock cooling encourages the formation of intra-crystalline impurites within the crystal structure, thereby lowering the crystal purity. Verification of this fact can be seen from Table 13.

VARIATION OF NAPHTHALENE PURITY WITH CENTRIFUGAL FORCE.

Samples of the material crystallised at a cooling rate of 10°C/hour, were centrifuged at varying speeds for 5 minute time intervals. Purity determinations were made on each centrifuged product, and the results are shown in Table 15.

TABLE 15.

VARIATION OF NAPHTHALENE PURITY WITH CENTRIFUGAL FORCE.

Material crystallised at 10°C/hour.

Centrifugal Force (x g)	Crystallising Point °C.	Naphthalene Purity %
166 (1000 r.p.m.)	77.10	94.0
166	77.00	93.9
166	77.00	93.9
326 (1400 r.p.m.)	77.75	95.2
326	77.77	95.3
326	77.70	95.0
425 (1600 r.p.m.)	77.93	95.5
425	78.00	95.6
425	78.00	95.6
840 (2150 r.p.m.)	78.10	95.7
840	78.15	95.7
840	78.13	95.7
1500 (3000 r.p.m.)	78.29	96.2
1500	78.31	96.3
1500	78.35	96.3

The results given in Table 14 show the progressive increase in naphthalene purity with increasing centrifugal force. The desired 78°C crystallising point material is obtained when the centrifugal force approaches 800 x g.

It can also be seen that after a naphthalene purity of 95.6% is reached, little further separation is achieved in spite of high increases in centrifugal force. At this point most of the surface oils adhering to the crystals have been removed, the remaining impurities being solid in nature or interstitial oils.

An attempt was then made to achieve further separation of the interstitial oils by slurrying the crystallised material with an aqueous detergent solution prior to centrifuging. The detergent solution consisted of a 0.5% aqueous solution of Teepol, and the slurried material was centrifuged for 4 minutes at a centrifugal force of 1500 x g. Excess detergent solution was removed by incorporating a cold water rinse into the centrifuging sequence.

The effect of detergent addition is shown in Table 15

TABLE 15

EFFECT OF DETERGENT ADDITION PRIOR TO CENTRIFUGING

Crystallising Point °C after centrifuging without detergent	Purity %	Crystallising Point °C after centrifuging with detergent	Purity %
78.30	96.30	78.85	97.5
78.35	96.33	78.90	97.6
78.32	96.30	78.85	97.5

Centrifugal force - 1500 x g. Time 4 minutes.

(See note overleaf).

NOTE

(Crystallising points determined on material centrifuged after detergent addition, were corrected for presence of water).

From Table 15 it can be seen that detergent addition prior to centrifuging, has produced an increase in naphthalene purity, due to the removal of further contaminating oils.

The next stage in the process was to transfer the centrifuging operation, to a semi plant scale centrifuging unit. However, it was realised that it was not possible to pump a 70°C crystallising point feed to the centrifuge without prior dilution, owing to the high solids content. Consequently, a further sample of crystallised material was slurried with drain oil obtained from previous centrifuging experiments. The slurried material now had a crystallising point of around 50°C and was, therefore, similar to the original naphthalene oil, with respect to naphthalene purity, prior to partial upgrading by distillation. The slurried material was centrifuged and as before, a purity determination made on the centrifuged product.

The results are shown in Table 16

TABLE 16

EFFECT OF OIL SLURRYING PRIOR TO CENTRIFUGING

Centrifugal force - 1500 x g. Time 5 minutes

Crystallising Point °C After centrifuging without oil addition.	Purity %	Crystallising Point °C After centrifuging with oil addition.	Purity %
78.30	96.30	78.32	96.30
78.26	96.20	78.25	96.20
78.29	96.20	78.30	96.30

The results given in Table 16 show that the crystallising point and purity of the centrifuged product is unchanged by the addition of oil prior to centrifuging.

Consequently, slurrying of the 70°C crystallising point material with oil, so as to produce a feed capable of handling by pumping equipment, should give results after centrifuging similar to those obtained in the laboratory.

PLANT CENTRIFUGING OF DISTILLED NAPHTHALENE OIL

During the early laboratory work, dilution of the feed centrifuge was achieved by addition of oil after complete crystallisation had taken place.

Owing to difficulties of mechanical handling, it would be very difficult to follow this procedure exactly on a plant scale due to the high solids content of the crystalliser feed. Complete crystallisation with constant agitation would be difficult, and furthermore, effective slurrying of the crystallised material would create further problems.

Consequently, with the knowledge gained so far, it was felt that if partial crystallisation occurred so as to produce a crystal nucleus relatively free from impurities, slurrying oil could be added whilst crystallisation was still proceeding. In this way constant agitation could be maintained and effective slurrying would be ensured without the problem of mechanical mixing later. The impurities would tend to be deposited in the outer crystal layers, leaving the nucleus relatively pure, and consequently centrifuging should remove a high proportion of these impurities.

METHOD

Plant distilled naphthalene oil (80% naphthalene) at a temperature of 90°C, was partially crystallised at a cooling rate of 1-2°C per hour. At a temperature of about 40°C, 93% wt/wt oil was added

Method (Cont'd)

to the crystalliser sufficient to lower the overall crystallising point to 50°C (51% purity). Cooling was then continued with agitation until 25°C was reached, after which the material was pumped to the centrifuge via a ring-main system.

> "Temperature of oil equivalent to temperature within crystalliser"

EFFECT OF CAKE THICKNESS AND TIME OF CENTRIFUGING ON PURITY OF PRODUCT

The thickness of the cake and the time of centrifuging was varied, but no cake rinse was given.

The crystallising point of the discharged material was determined in each case. The results are given in Table 17.

TABLE 17

EFFECT OF CAKE THICKNESS AND TIME OF CENTRIFUGING ON PURITY OF PRODUCT

Spin Idle Time (secs).	THICKNESS OF CAKE (INCHES)					
	$\frac{1}{2}$	$\frac{3}{4}$	1	$1\frac{1}{2}$	$1\frac{3}{4}$	2
400	77.56	-	-	-	-	-
300	77.55	-	-	-	-	-
200	77.50	77.35	77.20	77.13	77.50	77.08
180	77.50	77.23	77.10	77.10	77.40	77.10
160	77.00	77.25	77.05	76.90	-	77.38
140	77.00	77.28	76.90	-	-	77.15
120	76.43	77.18	76.82	76.90	-	77.10
100	76.20	77.05	76.60	-	-	76.80
80	75.48	77.15	76.45	76.60	-	76.70
40	75.80	76.55	73.50	73.75	-	76.70
20	-	76.33	-	-	-	-
10	-	74.83	-	-	-	-

From Table 17 it is evident that the thickness of the centrifuged cake has little if any, effect on the crystallising point and subsequent purity of the discharged product. Increasing time of centrifuging (spin idle) naturally increases the crystallising point of the product. However, the most important feature of this experiment, is that the centrifuged product does not attain the desired 78°C crystallising point, even though the centrifugal force developed is 980 x g. In the laboratory experiment (page 75), a crystallising point of 78°C was attained with a centrifugal force as low as 425 x g (see Table 14). (Maximum crystallising point attained is 77.38°C as compared with a crystallising point of 78°C obtained in the laboratory experiment.)

An attempt was made to increase the product crystallising point with the aid of detergent and caustic soda washes. A cake thickness of 1¾ ins. and spin idle time of 100 seconds were chosen as standard setting. The spin-dehydrate time was also set for 100 seconds.

The first experiment deals with the effect of detergent washing for varying periods of time and at varying temperatures, upon the crystallising point of the discharged product. A repeat of this experiment determines the effect of incorporating an 8% wt/wt caustic soda wash in place of the detergent wash. See Tables 18a and 18b.

TABLE 18a.

EFFECT OF DETERGENT WASHING ON CRYSTALLISING POINT OF PRODUCT.

Spin Idle Time (secs).	Washing Time (secs).	De-hydrate Time (secs).	DETERGENT (0.5%) TEMPERATURE °C			
			16	30	50	74
100	10	100	76.90	77.10	77.30	77.75
100	10	100	76.85	77.13	77.36	77.80
100	20	100	77.00	77.20	77.52	77.90
100	20	100	77.10	77.20	77.55	77.91
100	40	100	77.15	77.31	77.70	78.20
100	40	100	77.17	77.30	77.72	78.30
100	100	100	-	-	77.89	78.45
100	100	100	-	-	77.92	78.49

Yield of Product per charge - 24lbs.

Crystallising points corrected for moisture.

NOTE.

A cold water rinse follows the detergent rinse to remove excess detergent solution.

TABLE 19b.

EFFECT OF CAUSTIC WASHING ON CRYSTALLISING PONT OF PRODUCT.

Spin Idle Time (secs)	Washing Time (secs)	De-hydrate Time (secs)	CAUSTIC SOLUTION (8%) TEMPERATURE °C					
			28	50	55	60	63	74
100	10	100	77.65	77.80	77.55	77.55	77.60	78.30
100	10	100	77.60	77.78	77.61	77.59	77.62	78.35
100	20	100	77.50	78.15	77.95	78.30	77.90	78.25
100	20	100	77.54	77.98	77.92	78.21	77.96	78.30
100	40	100	77.46	77.90	77.95	78.25	77.95	78.10
100	40	100	77.51	77.92	77.95	78.20	77.93	78.20
100	100	100	-	-	-	-	-	-

Crystallising points corrected for moisture.

DISCUSSION OF RESULTS.

It was believed intially that after partial crystallisation and slurrying, contaminant formation would be produced in the outer crystal layers, and that detergent washing incorporated, in the centrifuging sequence would effectively remove these impurities. Table 19a shows that effective removal to produce a 78°C crystallising point product occurs only when the detergent solution is applied at a temperature of 74°C. At this temperature, the exuded oil from the centrifuge was at a temperature of 40°C. Accordingly, any contaminents melting at 40°C or less would automatically be dissolved out with the discharged oil, thus increasing the naphthalene crystallising point and purity. Thus, the increased temperature is the factor responsible for increased purity and not the detergent solution as such.

The incorporation of a caustic soda wash in place of the detergent solution was based on the assumption that certain acidic compounds may still be present and that their removal through caustic washing may achieve the desired 78°C crystallising point product. As before, effective removal did not occur until a temperature of 74°C. was reached, the explanation being the same as in the case of detergent washing.

To proceed any further with the process as such defeats the purpose of the investigation, because although the required crystallising point and purity may be attained, the recovery and yield is considerably reduced. Reduction in yield and recovery occurs because of the increased solubility of naphthalene in oil at 40°C. compared to the solubility at 20°C. (increase in solubility amounting to 15 - 20%).

A comparison of the laboratory work and semi-plant work shows that the only deviation in operating sequence is in the crystallisation technique employed during the semi-plant work. In the latter process, partial crystallisation occurred, after which, slurrying oil was added and crystallisation then allowed to proceed. Thus, the inability of the centrifuging operation, to achieve the required degree of separation of the crystalliser feed, must be due to contaminant formation through the addition of oil to the crystalliser. The original assumption, that contaminants would be deposited in the outer crystal layers and thus be easily removed, may be partially true, but obviously some form of intra-crystalline impurities have also formed.

To overcome this difficulty,,consideration must be given to the chemical nature of the oil added to the crystalliser. An analysis of the slurrying oil used previously revealed the following compounds as being present in the oil.

Basic Nitrogen (as Quinoline)	-	4.09%
Beta-Methyl Naphthalene	-	1.90%
Alpha-Methyl Naphthalene	-	0.40%
Sulphur (Thionaphthene)	-	1.58%
Boiling Range of Oil	-	118°C to 241°C.

Both quinoline and thionaphthene form mixed crystals with naphthalene, whilst beta-methyl naphthalene forms a eutectic with naphthalene, melting at 25°C.

In order to demonstrate more fully the contaminating effect of this oil, a sample of the oil was distilled through an 8-pear bulb laboratory fractionating column. The distillate was collected into three fractions, namely:-

Light Oil.

The fraction distilling between 175°C and 200°C.

Middle Oil.

The fraction distilling between 200°C and 220°C.

Heavy Oil.

The fraction distilling between 220°C and 250°C.

Utilizing the three oil fractions prepared as above, synthetic mixtures were made up by mixing 80% by wt. of pure naphthalene (crystallising point 80.1°C) with 20% by wt. of each of the three oil fractions respectively. The resulting mixtures were heated to 90°C and allowed to crystallise at a cooling rate of 5°C per hour. The crystallised material was then fed into the laboratory centrifuge for a period of four minutes and at a centrifugal force of 1000 x g.

See Table 19.

TABLE 19.

VARIATION OF CENTRIFUGED PRODUCT CRYSTALLISING POINT WITH TYPE OF OIL USED FOR CRYSTALLISATION.

Mixture Number	Type of Oil.	Crystallising Point of Crystallised Product °C	Crystallising Point of Centrifuged Product °C.
1	Light Oil 175° - 200°C.	71.76 72.75 72.95	77.90 78.16 78.06
2		73.41 73.48 73.96	78.40 78.23 78.35
3		72.52 72.82 72.15	78.02 78.32 78.30
4	Middle Oil 200° - 220°C	73.00 73.02 73.98	78.30 78.10 78.40
5		73.08 73.02 73.94	78.40 78.40 78.35
6		73.05 73.02 73.05	78.55 78.50 78.40
7	Heavy Oil 220° - 250°C	73.00 73.23 73.12	77.73 77.98 77.90
8		73.27 73.98 73.00	77.95 77.90 77.99
9		73.97 73.12 73.98	77.98 77.90 77.90

Consideration of the results given in Table 19 show that centrifuging of the crystallised material prepared with heavy oil, does not produce the required 78°C crystallising point product, whereas material prepared from light oil and middle oil can be centrifuged to the required purity.

Thionaphthene, beta-methyl naphthalene and quinoline all have boiling points within the range 220 - 250°C and it is therefore obvious that oil of this boiling range cannot be used for crystallisation purposes.

A further experiment was carried out to determine the relative crystal surface contamination produced by addition of each type of oil to pure naphthalene, to produce a cold crystal slurry. The slurry was then centrifuged under the conditions of the previous experiment, and the crystallising point of the product determined.

Method

Synthetic mixtures prepared by slurrying 80% by wt. pure naphthelene with 20% by wt. of light, middle and heavy oil respectively. Each mixture centrifuged for 4 minutes at 1000 x g in laboratory centrifuge.

Results are given in Table 20.

TABLE 20.

VARIATION OF CRYSTAL SURFACE CONTAMINATION WITH TYPE OF OIL USED FOR SLURRYING.

Type of Oil	Crystallising point of Product After Centrifuging °C.
Light Oil 175° - 200°C	79.55 79.51 79.44
Middle Oil 200° - 220°C	79.45 79.51 79.40
Heavy Oil 220° - 250°C	79.50 79.40 79.52

The above results show that there is no significant differences in product crystallising point irrespective of the type of oil used for slurrying. Thus any oil impurities adhering to the crystal surface, can be effectively removed by centrifuging irrespective of the boiling range of the oil.

Having established the fact that once crystallisation has taken place, slurrying oil can be added regardless of boiling range, without adverse effect on the purity of the centrifuged product, it now remains to determine the maximum percentage of light and middle oils which can be added to pure naphthalene prior to crystallisation, without the crystallising point of the centrifuge product falling below 78°C.

Method.

Samples of pure naphthalene were mixed with varying amounts of a mixture of 15% light oil and 85% medium oil. The resulting mixtures were crystallised at a cooling rate of 5° per hour. The crystallised material was then slurried with a quantity of the mixed oil to produce an overall crystallising point of 50 - 55°C. The slurried material was then centrifuged as before.

The results are shown in Table 21.

TABLE 21.

VARIATION OF PRODUCT CRYSTALLISING POINT WITH PERCENTAGE OIL DILUTION.

Type of Oil	% Oil wt/wt	Crystallising Point After Crystallisation °C.	Crystallising Point After Slurrying °C	Crystallising Point After Centrifuging °C.
15% Light Oil, 85% Middle Oil.	20	72.75	52.00	78.45
	20	73.21	52.60	78.39
	30	70.20	53.15	78.37
	30	70.35	52.65	78.51
	35	69.10	52.40	78.21
	35	68.90	52.10	78.20
	40	67.70	54.10	77.88
	40	67.55	53.50	77.85
	50	65.71	53.30	77.21
	50	65.50	54.00	77.35

The theoretical addition of saturated oil to pure naphthalene, sufficient to produce an overall 51°C crystallising point, is 150% wt/wt.

(See Appendix 4, for details of calculation).

The above experiment was repeated to determine whether further contaminant removal could be achieved by incorporating a detergent wash as part of the centrifuging sequence. A cold water rinse followed the detergent rinse to removal excess detergent. The centrifuging sequence was adjusted so as to maintain a total centrifuging time of 4 minutes.

The results are shown in Table 22.

TABLE 22.

EFFECT OF DETERGENT RINSE.

% Oil wt/wt	Crystallising Point After Crystallisation °C	Crystallising Point After Slurrying °C	Crystallising Point After Detergent Rinse °C.
30	70.30	52.60	78.63
30	70.28	52.38	78.59
35	69.20	53.01	78.65
35	69.15	52.40	78.63
40	67.61	52.61	78.61
40	67.72	53.10	78.58
50	65.70	53.20	78.50
50	65.62	53.35	78.51

Detergent solution 0.5% aqueous Teepol.

Consideration of the results shows that a marked increase in crystallising point has resulted from the use of detergent washing, indicating that the greater part of contaminants originating from light and middle oils, are in the form of surface or interstitial oils, and are thus susceptable to detergent washing.

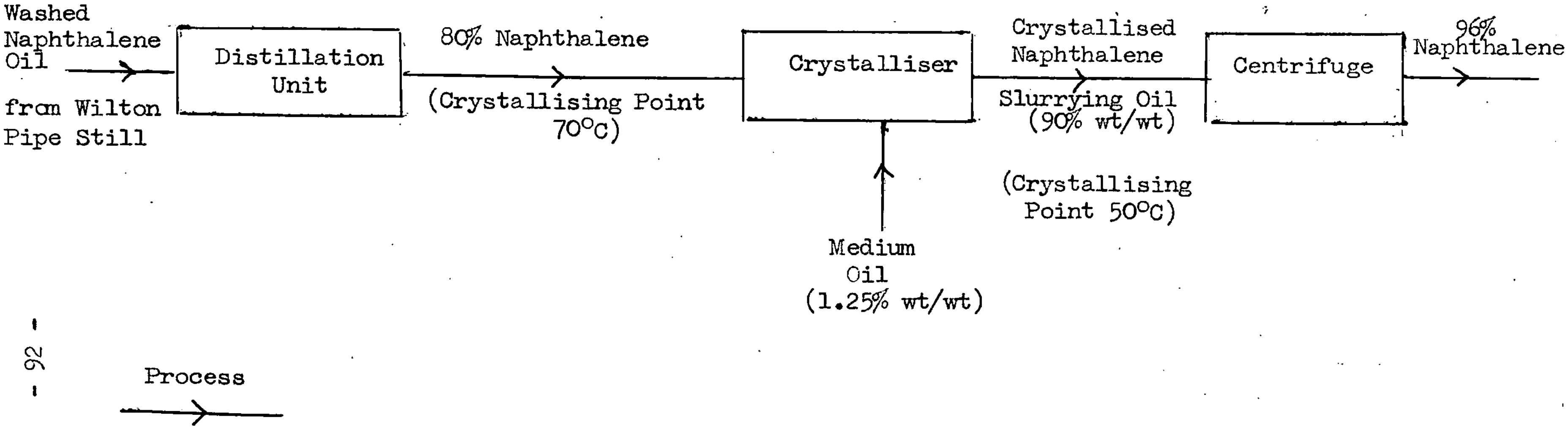
It can now bec understood why failure occurred during the semi-plant scale centrifuging experiments, and the means whereby this difficulty may be overcome is now apparent. Distilled naphthalene (80%) from the distillation unit can be crystallised with a quantity of light or middle oil (boiling range 175 - 220°C), such that the total saturated oil in contact with pure naphthalene remains at a maximum of 35% wt/wt. A proportional calculation shows that to attain this figure a further 1.25% saturated oil must be added to the crystalliser; (the percentage ratio of saturated oil to pure naphthalene for an 80% naphthalene, is initially 33% wt/wt.) The dilution obtained at this stage is sufficient to allow constant agitation to occur whilst crystallisation is in progress. Once crystallisation is complete, or nearly complete, slurrying oil of <u>any</u> boiling range can be introduced directly into the crystalliser, sufficient to produce an overall crystallising point of 50 - 55°C. The slurried material can then be pumped directly into the centrifuge, whereby efficient separation may be ensured. To obtain an even higher degree of separation, a 0.5% aqueous detergent rinse may be incorporated into the centrifuging sequence. (See Diagram 9)

DIAGRAM 9

CRYSTALLISING AND CENTRIFUGING

OF

PLANT DISTILLED NAPHTHALENE OIL



CONCLUSIONS

The significant factors described and discussed during the course of this thesis can be summarised as follows:-

SEPARATION OF THE NAPHTHALENE - OIL SYSTEM

Fractionation

Fractionation is not an efficient method of separating the system due to the relative closeness of boiling points of many of the components. Increased separation can be achieved by the use of very high separating power columns, but the recovery of naphthalene associated with a given degree of purity, decreases with increasing purity.

Phenolic compounds are particularly liable to form low boiling azeotropes with naphthalene, and the resulting spread of naphthalene through azeotrope formation again leads to low recoveries of naphthalene. Providing the system is washed with caustic solution to remove the bulk of phenolic compounds, prior to fractionation, then fractionation is an ideal means of partially separating the system as an intermediate stage for further separation. If the degree of separation aimed at is not too high, then by control of the fractionating conditions, light and heavy oils can be removed comparatively free from naphthalene. A high recovery of naphthalene of intermediate purity is thus obtained.

Crystallisation

Impurities formed during crystallisation are of two types:-

(a) Inter crystalline

(b) Intra-crystalline

Conclusions (Cont'd)

Inter-Crystalline Impurities

Occur as mother liquor on the crystal surface or as oils trapped within the crystal interstices and are found to increase in amount with decreasing crystal size. Thus to reduce as far as possible; impurities of this type, crystallisation conditions should be such as to encourage the formation of large crystals.

Intra-Crystalline Impurities

Occur as mixed crystals or high melting eutectics with naphthalene. Impurities of this type are formed from compounds such as thionaphthene, beta-methyl napthalene and quinoline. The amount of intra-crystalline impurities formed depends primarily on the amount of such material in the oil and on the final crystallisation temperature.

Control of rate of crystallisation, although having no effect on mixed crystal formation, leads to well defined layers of eutectic impurities particularly in the outer crystal layers. Rapid or shock cooling however, leads to supersaturation and subsequent random deposition of eutectics, thus rendering further separation by centrifuging more difficult.

Stirring or agitation dueing crystallisation is beneficial in that it tends to prevent supersaturation from occurring.

Centrifuging

Crystallisation and centrifuging of the original oil will not produce the required degree of separation under any conditions. If however, partial separation of the oil is first obtained by fractionation, particularly the removal of the high boiling oils, then by controlled crystallisation, centrifuging achieves a high degree of separation

Conclusions - Centrifuging (Cont'd)

and with a high recovery.

Increased speed of centrifuging increases the degree of separation up to a given point, beyond which no further separation is achieved. This point corresponds to the maximum removal of outer crystal layer impurities and surface oils. A further increase in oil impurity removal can be achieved by incorporating a detergent rinse during the centrifuging sequence.

A further factor emerges at this stage, with respect to mechanical separation. The presence of phenolic compounds in the oil, increases the solubility of naphthalene in the oil. Thus increased loss of naphthalene to the centrifuge drain oil would occur if these compounds were present, to any extent, in the oil.

On a large scale separation unit, ease of handling of the material from the crystalliser to the centrifuge becomes of great importance. To ensure constant agitation during crystallisation and ease of pumping of the crystallised product to the centrifuge, it is necessary to crystallise the material from the distillation unit with a quantity of oil of maximum boiling point 220°C. such that, the percentage ratio of saturated oil in contact with pure (100%) naphthalene, does not exceed 35% wt/wt.

Once crystallisation is complete, further oil, irrespective of boiling point, can be added to the crystalliser to produce a fluid slurry to the centrifuge.

PROPOSED THREE STAGE SEPARATION SYSTEM.

The proposed system designed to ensure a degree of separation of the napthalene oil, such that a naphthalene purity of 96% (78°C crystallising point) with a minimum recovery of 90% of the available naphthalene in the naphthalene oil, is obtained, is summarised below:-

STAGE I.

Caustic washed naphthalene oil obtained from the Wilton pipe still, is fractionated through the Plant Distillation unit, under conditions such that the light and heavy oils are removed relatively free from naphthalene. A high yield and recovery of naphthalene of intermediate purity (80%) can then be obtained.

STAGE II.

The 80% purity naphthalene is then fed into the crystalliser along with a further 1.25% wt/wt of light and medium boiling oil, (maximum boiling point 220°C). Crystallisation then proceeds with constant agitation at a controlled cooling rate of 2°C per hour. When crystallisation is complete, further oil (approx. 90% wt/wt) irrespective of boiling point, is added to the crystalliser to produce a fluid slurry which can then be easily pumped into the centrifuge.

STAGE III.

A centrifuging sequence consisting of:-

(1) oil discharge spin (time 100 secs.)

(2) aqueous detergent rinse (0.5 teepol) (time 100 secs.)

(3) water rinse (to remove excess detergent) (time 100 secs.)

(4) dehydrating spin (time 100 secs.)

STAGE III (Cont'd).

The centrifuged naphthalene product is now at the required 96% purity, and the calculated overall three stage recovery is 90% (overall recovery from original process is 53%).

A detailed calculation showing the purity and recovery obtained at each separation stage is given in Appendix 1. Diagram 10 gives a flow diagram of the proposed process.

Appendix 1 gives a comparison of the proposed three stage system and the original separation system in operation at the time of this investigation. (See Diagram11).

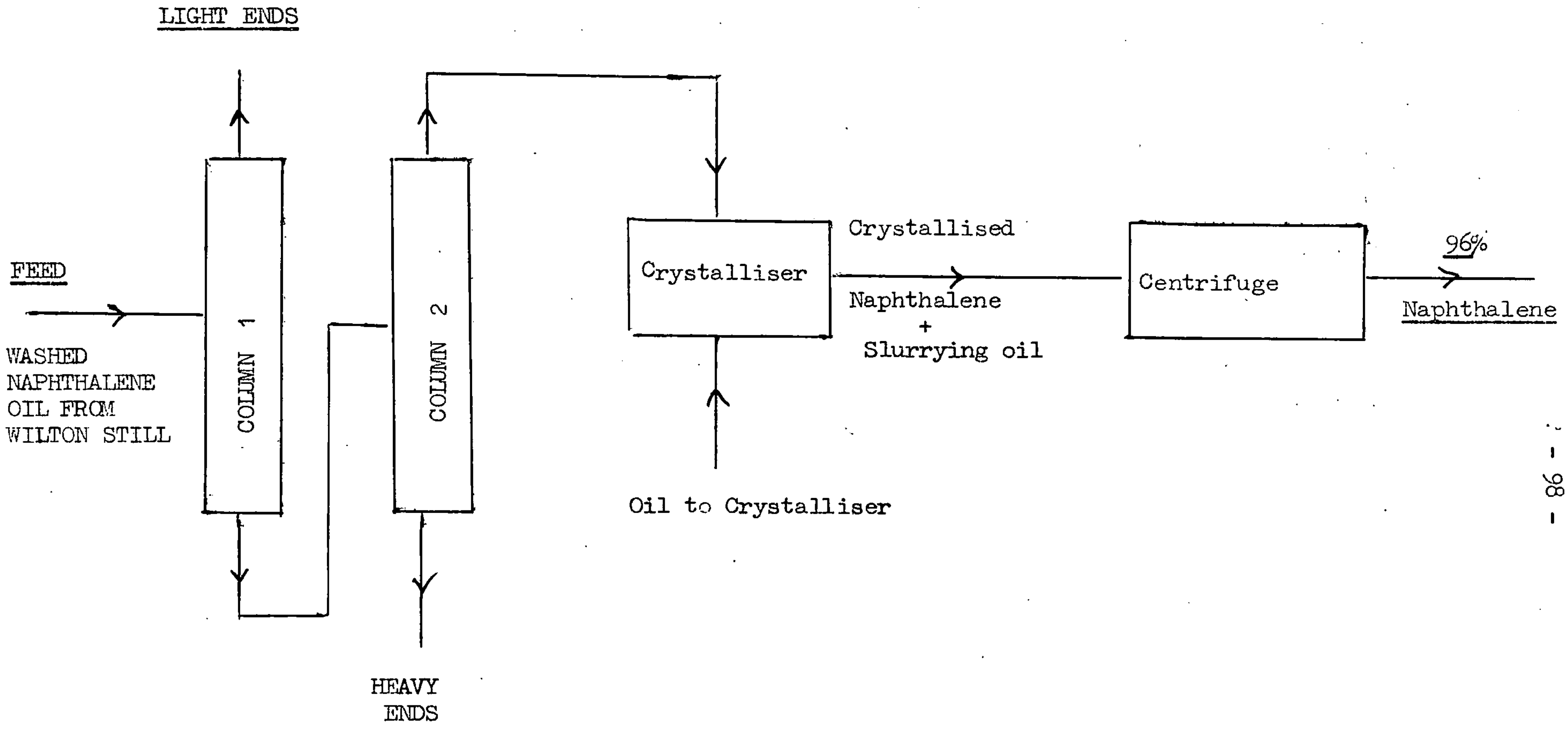
The proposed three stage system described above has been successfully operated at the works of North Eastern Tar Distillers Limited, and has produced a naphthalene of 96% purity with an overall recovery of 90% as specified.

The overall recovery from the original process was 53%.

DIAGRAM 10

FLOW DIAGRAM OF PROPOSED

SEPARATION SYSTEM



APPENDICES.

APPENDIX 1.

CALCULATION OF THE RECOVERY OF AVAILABLE NAPHTHALENE PRESENT IN THE NAPHTHALENE OIL, AFTER PROCESSING OF THE OIL THROUGH THE 3 STAGE SYSTEM DESCRIBED.

Feed. Naphthalene oil of coke oven origin containing approximately 50% naphthalene.

Final Product

96% purity naphthalene.

Data Given.

FEED.

Crystallising Point °C	Naphthalene Purity %	Light Oil %	Heavy Oil %
54.50	56.80	32.28	10.90

1st Stage Separation.

Fractionation of Feed through continuous twin column Distillation Unit.

OPERATING CONDITIONS.

Column	Feed Rate Galls/Hour.	Feed Temp. °C.	Pressure Ins. Hg. Abs,	R/Ratio	Theoretical Plates.
1	200	150	4	15/1	11
2	-	-	2	4/1	11

FRACTIONATION PRODUCTS.

	% Naphthalene	% Light Oils	% Heavy Oils.
Forerunnings Product.	9.0	91.0	Nil
Naphthalene Product.	81.4	18.1	0.5
Heavy Ends Product.	20.0	Nil	80.0

Calculation of 1st Stage Recovery.

To calculate the quantity of naphthalene product obtained from 100 tons feed.

Appendix 2 gives the derivation of an equation enabling the yield of naphthalene product to be calculated. This equation is as follows:-

$$\text{Yield} = 100 \frac{(zh - zY - hX)}{(zh - zy - hx)}$$

where z = % Light oil in Forerunnings Product

h = % Heavy oil in Heavy Ends Product.

Y = % Heavy oil in Feed.

X = % Light oil in Feed.

y = % Heavy oil in Naphthalene Product.

x = % Light oil in Naphthalene Product.

Substitution in this equation gives:-

Yield of Naphthalene Product

$$= 100 \frac{(91 \times 80) - (91 \times 10.9) - (80 \times 32.28)}{(91 \times 80) - (0.5 \times 91) - (80 \times 18.1)}$$

$$= \underline{\underline{64.44 \text{ tons}}}.$$

Since this product contains 81.4% Naphthalene, then

$$\text{Recovery of Naphthalene as Naphthalene Product.} = \frac{64.44 \times 81.4}{56.8} = \underline{\underline{92.35\%}}$$

2nd Stage Separation.

Crystallisation.

Distilled naphthalene product from 1st stage separation introduced into crystalliser at 90°C and mixed with 1.25% wt/wt oil (max. boiling point of oil - 220°C).

Cooling rate - 2°/hour.

3rd Stage Separation.

Crystallised product slurried with oil to give a slurry equivalent to 51% naphthalene and fed into centrifuge.

Centrifugal force = 980 x g.

Cycle time = 5 mins.

Calculation of 3rd stage recovery.

To calculate the recovery of naphthalene when upgrading the centrifuge feed from 51% naphthalene to 96% naphthalene.

Appendix 3 gives the derivation of an equation enabling the recovery to be calculated.

The equation is as follows:-

$$\text{Recovery} = 100\ \frac{(X - 20)}{(Z - 20)} \times \left(\frac{Z}{X}\right)$$

where X = initial % naphthalene

Z = final % naphthalene.

When using this equation it must be remembered, that although the 81.4% naphthalene has been slurried down to 51% naphthalene, the actual uprgrading occurs from 81.4% to 96%. The explanation being, that slurrying oil is in fact, centrifuge drain oil (recycle oil) and as such, is already saturated with naphthalene. Thus on removal of this oil, no loss of naphthalene occurs.

Substitution in the equation gives:-

$$\text{Recovery} = 100\,\frac{(81.4 - 20)}{(96 - 20)} \times \frac{96}{81.4}$$

$$= \underline{95.2\%}$$

Thus overall recovery of naphthalene

$$= \frac{95.2 \times 92.35}{100} = 88\%$$

Recapitulation.

1st Stage. Naphthalene Purity = 81.4%, Recovery = 92.35%

2nd & 3rd Stage. Naphthalene Purity = 96%. Recovery = 95.2%

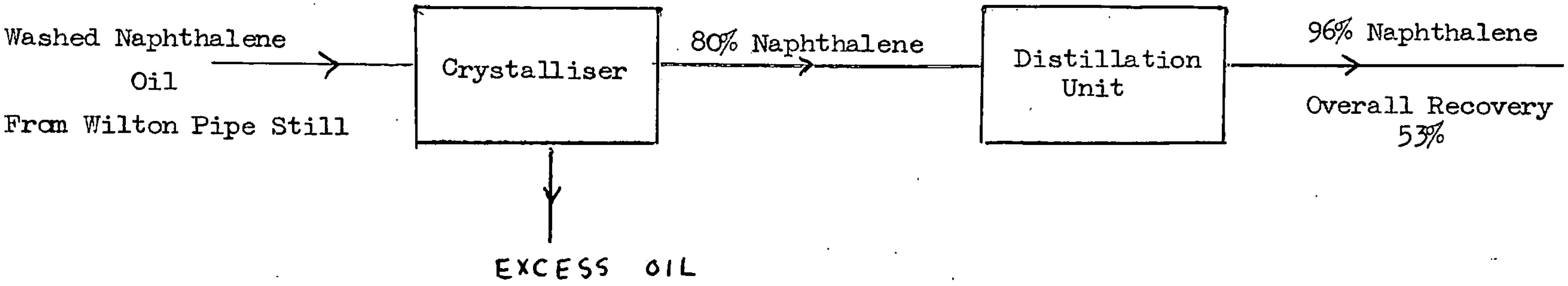
Combined Recovery = 88%

The fact that an overall 88% recovery is obtained rather than the minimum 90%, is due to the low 1st stage recovery. Recoveries at this stage are usually about 95%, and depend to a considerable extent on the feed composition.

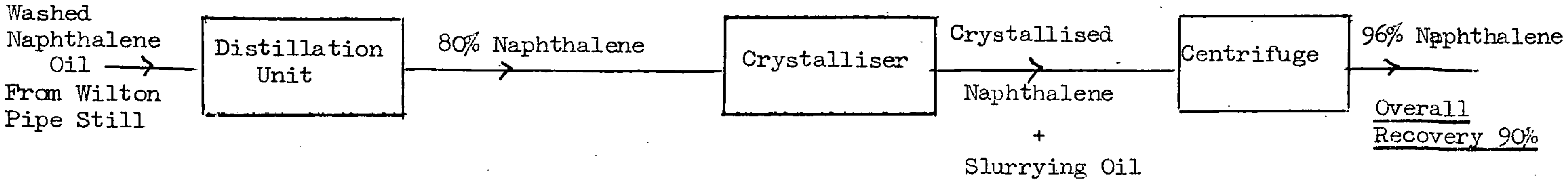
DIAGRAM 11

COMPARISON OF ORIGINAL AND PROPOSED SEPARATION SYSTEMS

ORIGINAL PROCESS



PROPOSED PROCESS



COMPARISON OF PROPOSED AND ORIGINAL SEPARATION SYSTEMS.

(Feed - 50% Naphthalene).

	Proposed System	Original System.
Stage 1.	Fractionate. Purity 81.4% Recovery 92.35%	Gravity draining. Purity 80.0% Recovery 80.85%
Stage 2.	Crystallise. -	Fractionate. Purity 96.0% Recovery 66.5%
Stage 3.	Centrifuge. Purity 96.0% Recovery 95.2% Overall Recovery 88.0%	- - - Overall Recovery 53.8%

APPENDIX 2.

The Calculation of Naphthalene Recovery as Naphthalene Product After Distillation of the Feed Through The Continuous Distillation Unit.

Analysis of the Plant Feed and fractionation products gives the following tabulated data.

	% Light Oil B.Pt.$<$ 218°C	% Heavy Oil B.Pt.$>$ 218°C
Feed	X	Y
Forerunnings Product	z	-
Naphthalene Product	x	y
Heavy Ends Product.	-	h

Calculation.

Given 100 tons Feed.

Let A Tons Naphthalene Product be produced.

B Tons Forerunnings Product be produced.

C Tons Heavy Ends Product be produced.

Let a be quantity of Light Oil in Naphthalene Product.

b be quantity of Light Oil in Forerunnings Product.

c be quantity of Heavy Oil in Naphthalene Product.

d be quantity of Heavy Oil in Forerunnings Product.

Then:- $\frac{z\ B}{100} = b \ldots\ldots\ldots\ldots\ldots\ldots(1)$

$$\frac{x\ A}{100} = a \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

$$\frac{y\ A}{100} = c \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

$$\frac{h\ C}{100} = d \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

$$A + B + C = 100 \ldots\ldots\ldots\ldots\ldots\ldots(5)$$

$$a + b = X \ldots\ldots\ldots\ldots\ldots\ldots(6)$$

$$c + d = Y \ldots\ldots\ldots\ldots\ldots\ldots(7)$$

From (1) (2) and (6):-

$$\frac{z\ B}{100} + \frac{x\ A}{100} = X \ldots\ldots\ldots\ldots\ldots\ldots(8)$$

and from (3) (4) and (7):-

$$\frac{y\ A}{100} + \frac{h\ C}{100} = Y \ldots\ldots\ldots\ldots\ldots\ldots(9)$$

From (9):-

$$C = \frac{100\ Y - y\ A}{h}$$

and from (5)

$$C = 100 - A - B$$

Therefore $A\ (h - y) = 100\ H - 100\ Y - h\ B \ldots(10)$

From (8) and (1)

$$x\ A + z\ B = 100\ X$$

$$(h - y)\ A + h\ B = 100\ (h - Y)$$

Therefore $(h - y)\ z\ A - h\ x\ A = 100\ z\ (h - Y) - 100\ hX$

Therefore $\underline{A} = \frac{100\ (z\ h - z\ Y - h\ X)}{(h\ z - y\ z - h\ x)}$

---

and $\underline{B} = \dfrac{100\,X - x\,A}{z}$

---

and $\underline{C} = 100 - (A + B)$

Consider Distillation Run No.1. Table 13.

Data given.

	% Light Oil	% Heavy Oil	% Naphthalene
Feed	32.28	10.90	56.80
Forerunnings Product	91.00	Nil	9.00
Naphthalene Product	18.60	Nil	81.40
Heavy Ends Product.	Nil	80.00	20.00

$$\text{Therefore } A = 100\ \frac{(91 \times 80) - (91 \times 10.9) - (80 \times 32.28)}{(91 \times 80) - (80 \times 18.6)}$$

$$= \underline{\underline{63.93}}$$

$$B = \frac{(100 \times 32.28) - (18.6 \times 63.93)}{91}$$

$$= \underline{22.4}$$

$$C = 100 - (A+B) = \underline{13.67}$$

Thus from 100 Tons Feed:-

63.93 tons Naphthalene Product

22.40 tons Forerunnings Product

13.67 tons Heavy Ends Product.

Recovery of Naphthalene on 100 Tons Feed (56.8% Naphthalene).

63.93 Tons Naphthalene Product containing 81.4% Naphthalene is equivalent to $\frac{81.4 \times 63.93}{100} = 52.05$ Tons Naphthalene

Therefore Recovery of Naphthalene as Naphthalene Product

$$= \frac{52.05}{56.80} \times 100 \qquad = \underline{\underline{91.7\%}}$$

APPENDIX 3.

The Calculation of the Yield and Recovery of Naphthalene, Obtained By Crystallisation and Mechanical Separation of a Naphthalene - Oil System.

Given:- 100 parts of oil containing X% naphthalene. Crystallisation and oil separation occurs at 20°C, to give Y% crystals containing Z% naphthalene, and (100 - Y) parts of drained oil saturated with naphthalene at 20°C.

On the basis of Potashnikov's data(23) the drained oil will contain 20% wt/wt naphthalene at 20°C.

A naphthalene balance then gives:-

$$X = \frac{Y\,Z}{100} + \frac{1}{5}\quad(100 - Y).$$

$$\text{Therefore } \underline{Y} = 100\ \frac{(X - 20)}{(Z - 20)} = \underline{\%\ \text{Yield of crystals}}.$$

The % recovery of available naphthalene

$$= \frac{Y\,Z}{X} \quad = \frac{(X - 20)}{(Z - 20)}\ 100\ \frac{Z}{X}$$

APPENDIX 4.

Calculation of the Theoretical Quantity of Saturated Oil Required to Produce a 52% Naphthalene (50°C.C.Pt) From 100% Naphthalene (80.3°C. C.Pt).

Given: 100 tons 100% Naphthalene

Let X tons saturated oil be added.

Since saturated oil at 20°C contain 20% naphthalene then:-

$$\text{total naphthalene} = 100 + \frac{X}{5}$$

$$\text{and } \frac{\text{total naphthalene}}{\text{total naphthalene + unsaturated oil}} = \frac{52}{100}$$

$$\text{Therefore } \frac{100 + \frac{X}{5}}{100 + X} = \frac{52}{100}$$

Therefore X = 150 tons.

Thus the theoretical percentage of saturated oil required is 150%.

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