# Extraction of Petroleum Fractions by Ammonia Solvents

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In developing a solvent for the separation of complex hydrocarbon mixtures many factors must be considered, some of the more important of which are listed in Table 1. It is easy to get some of these properties but difficult to get all of them in a single solvent.

TABLE 1.—FACTORS IN SOLVENT SELECTION

1. Selectivity, β
2. Solubility—β relationship
3. Adaptability to various feed stocks
4. Ease of recovery (volatility, etc.)
5. Density
6. Stability
7. Corrosiveness
8. Cost
9. Viscosity
10. Interfacial tension
11. Toxicity
12. Freezing point
13. Latent heat

Consequently the choice has to be based upon a composite evaluation. For example, prime emphasis can be placed on solvent selectivity as defined by β (Table 2), but unless the solvent has a relatively high dissolving power under the conditions for having a good β, the solvent is handicapped because excessive solvent treats may be needed. What is desired (but difficult to obtain) is a high solubility and a high β throughout the concentration range over which the separation is being made. Solubility is the weight percentage of hydrocarbon in solution in the solvent phase.

It is obviously desirable to be able to use the same solvent system for various feed stocks. In this way a plant can be shifted from one feed to another without a new solvent-extraction facility having to be built.

Since some separations will involve circulating large amounts of solvent, the regeneration of the solvent should be easy. Distillation is a convenient method when large amounts of high heat are not needed. However, other methods, such as chilling to separate the solvent or washing with another solvent, can sometimes be used. For a solvent to find its widest use, when distillation is employed for its recovery, the solvent should

TABLE 2.—DEFINITION OF β AND EQUATIONS FOR MINIMUM CONDITIONS

1. Stages $\left(\frac{x_a}{x_b}\right)_e = \beta^N \left(\frac{x_a}{x_b}\right)_r$

2. Reflux ratio $\left(\frac{O_o}{P_e}\right)_{min} = \frac{1}{\beta - 1}\left[\frac{(x_a)_e}{(x_a)_f} - \beta\frac{(x_b)_e}{(x_b)_f}\right]$

3. Solvent: oil ratio $S/O_{min} = \left[\frac{O_o}{P_e} + 1\right]\left[\frac{\text{wt. \% } S}{\text{wt. \% } O}\right]_{sf}\left[\frac{P_e}{O_f}\right]$

**Notation**

$x_a$ = wt.% more soluble component, solvent-free basis
$x_b$ = wt.% less soluble component, solvent-free basis
$N$ = total perfect stages (minimum)
$\beta$ = average β in stage equation (1); β at feed point in reflux ratio equation (2)
$O_o$ = pounds of oil overflow at feed
$P_e$ = pounds of oil removed as extract product
$S/O$ = solvent-to oil ratio, by weight (neglecting solvent removed with final raffinate)
$[\text{Wt.\% } S/\text{Wt.\% } O]_{sf}$ = ratio of wt.% solvent to wt.% oil in solvent phase leaving feed point
$O_f$ = pounds of oil fed to system

**Subscripts**

$e$ refers to final extract
$f$ refers to oil feed point
$r$ refers to final raffinate

boil either below the materials being separated or well above them. A solvent boiling coincident with some of the materials being separated offers many problems.

The other properties, 5 to 13 in Table 1, relate to extractor design, the cost of the operation, and the character of the equipment employed. Density, viscosity, and interfacial tension are important in phase mixing and phase separation. These properties affect the capacity and efficiency of an extractor.

## EXTRACTION VARIABLES

To make a given sharp separation by extraction, it is important to know at least three of the requirements, namely, the number of theoretical stages, the reflux ratio, and the solvent-to-oil ratio. "Oil" is used here to denote generally the material to be separated. Table 2 lists the equations for calculating the minimum values of these three operating variables. These equations are for the usual engineering bases, namely continuous and steady-state operation.

Figure 1 illustrates the use of these relationships for the separation of a binary *A-B* mixture containing 25% *A* to produce 95% *A* in the extract and 5% *A* in the raffinate when the solubility in the solvent is 20% at the feed point (*1*). Many separations can be made by extraction if ten to twenty-five theoretical stages are used, even if $\beta$ is as low as 1.5.

In dealing with a practical extraction case something more than the minimum conditions, shown on Figure 1, is needed.

Figure 2 shows how actual and minimum extraction conditions are related. This is an empirical relationship. The band was calculated using more than 40 points from 4 different hydrocarbon-solvent systems employing reflux. The ranges in values used in these calculations are (*a*) extract to raffinate purity from 90 to 99%, (*b*) solubility of hydrocarbon in the solvent from 5 to 20%, (*c*) $\beta$ from 1.07 to 10, and (*d*) the feed to the extractor from 20 to 50% in extractable component (*1*).

## *SELECTIVITY OF VARIOUS SOLVENTS*

There are so many mixtures that are amenable to extraction and so many liquids potentially useful as solvents that a detailed discussion of all these combinations cannot be given here. A few comparisons, nevertheless, are possible for two hydrocarbon systems, (*a*) methylcyclohexane and *n*-heptane, a naphthene-paraffin pair difficult to separate by distillation, and (*b*) toluene and methylcyclohexane, an aromatic-naphthene pair illustrating the separation of aromatics from hydrocarbon mixtures.

The behavior of different solvents with these two systems is shown in Tables 3 and 4. In Table 3 these $\beta$'s are to be compared with an $\alpha$ of 1.07 for distillation and a $\gamma$ of about 1.3 for vapor-liquid extraction for most solvents.

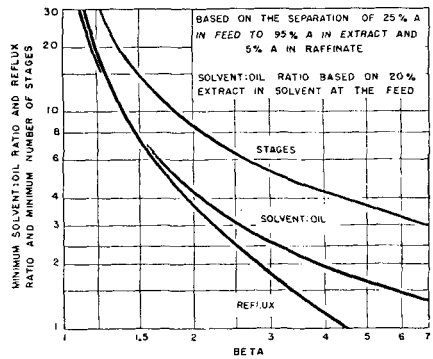


Fig. 1. Variation of minimum solvent: oil ratio, minimum reflux ratio and minimum stages with $\beta$.

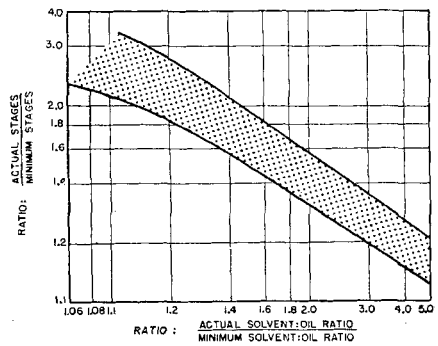


Fig. 2. Estimation of practical operating conditions from minimum values.

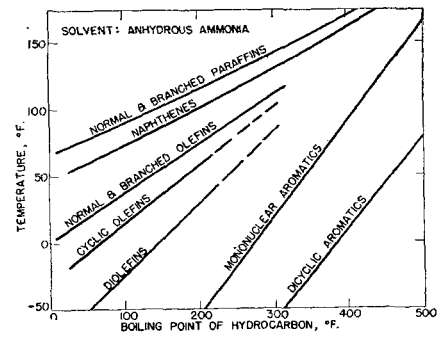


Fig. 3. Temperature for 10 wt. % solubility.

The toluene - methylcyclohexane system (Table 4) differs from the other system in that most of the solvents are completely miscible with toluene. This means that toluene cannot be made pure by liquid extraction unless some way is found to change the solubility behavior as the concentration of toluene increases in the extractor. The limiting purity is listed in the last data column on Table 4. In general there are three ways to open up this type of phase diagram so as to permit the most soluble component (viz. toluene) to be produced in pure form.

1. In one case the temperature can be successively lowered in the extractor as the solvent phase becomes progressively richer in the extractable component. This lower temperature will reduce the solubility, as illustrated in Figure 6. This is an effective procedure when applicable. The limitations are that the solvent or the material being extracted must not solidify or become too viscous to flow readily and that the maintenance of the lowest required temperature must not be too difficult or expensive.

2. A precipitant, or antisolvent, can be injected along the main solvent flow path to reduce gradually the dissolving power of the solvent as it flows toward the extract end of the extractor. For example, the precipitant may be water when the solvent is alcohol, phenol, or liquid ammonia. This is an effective procedure and obviates extensive temperature reductions. It is necessary, however, to separate the precipitant from the solvent because usually it is not needed at the raffinate end of the extractor, or the point of solvent entry.

3. Another solvent incompletely miscible with the main solvent but having good dissolving power for the material being extracted can be introduced at the extract end of the extractor to take the place of the usual reflux phase. Thus there is always a two-phase liquid-liquid system present and the process of extraction can continue to any desired purity if the $\beta$ and the stages are adequate. This second solvent flows countercurrently to the main solvent. The principal disadvantage of this two-solvent system is that two solvents, instead of one, have to be handled and recovered. This double-solvent procedure is particularly valuable when the mixture being separated is very viscous or even solid. Extraction, or the separation of the mixture, can occur as long as there are adequate solubility in the solvents and a suitable $\beta$.

## LIQUID AMMONIA AS A SOLVENT

It has been recognized for some time that liquid ammonia is a use-

TABLE 3.—METHYLCYCLOHEXANE–*n*-HEPTANE-SOLVENT

| Solvent | Temp., °F. | Solubility*, wt. % hydrocarbon in solvent phase | β (average) | Ref. |
|---|---|---|---|---|
| Methanol | −4 | 14 | 1.2 | 3 |
| Sulfur dioxide | 50 | 10 | 1.2 | 6 |
| Ammonia | 110 | 10 | 1.3 | 4 |
| Acetonitrile | 104 | 14 | 1.3 | 3 |
| 2, 4-Dimethylthia-cyclopentane dioxide | 113 | 10 | .. | 7 |
| Methyl cellosolve | 50 | 15 | 1.3 | 3 |
| Acetonylacetone | 86 | 14 | 1.3 | 3 |
| Methyl carbitol | 140 | 13 | 1.3 | 3 |
| Furfural | 140 | 15 | 1.4 | 3 |
| Aniline | 102 | 15 | 1.4 | 3 |
| Phenyl cellosolve | 122 | 15 | 1.4 | 3 |
| Gamma valerolactone | 102 | 14 | .. | 4 |

*Hydrocarbon charge composition is 50 vol.% *n*-heptane and 50 vol.% methylcyclohexane. The solvent:oil-weight ratio is 1:1.

ful solvent, resembling water in some of its characteristics. Being an inorganic compound, it has not been used extensively heretofore for hydrocarbon separations; however, liquid ammonia has good solvency and selectivity for separating several hydrocarbon types. When its solubility becomes too low the use of a low-molecular-weight amine, such as monomethylamine, has been found satisfactory for increasing the solvent power. This is an alternative to raising temperature. When the solubility becomes too high, water is a good antisolvent. Thus this three-component solvent system, comprised of water, liquid ammonia, and monomethylamine, enables a great variety of hydrocarbon mixtures to be separated (*5*).

Figure 3 illustrates the solubility relationships for various hydrocarbon types when liquid ammonia contains 10 wt.% of these in solution. The temperature at which 10 wt.% solubility is obtained is plotted against the boiling point of the various hydrocarbon types. It is evident from this diagram that the use of a prosolvent, such as methylamine, is desired when the higher boiling hydrocarbons and those which are less polar are extracted. Similarly, water is desirable in the solvent when low-molecular-weight hydrocarbons, and particularly those high in polarity such as aromatics, are extracted.

## β-SOLUBILITY RELATIONSHIP

For this solvent system a correlation has been obtained between selectivity, defined as β, and the differences in temperatures in degrees Fahrenheit for 10 wt.% solubility for any pair of hydrocarbons. This is shown in Figure 4. Upon combining it with Figure 3 one can ascertain the feasibility of separating hydrocarbons with liquid ammonia. These relationships are applicable for separating gasolines, kerosenes, gas oils, and lubricating distillates.

β is strongly dependent on the solubility. Thus, to be able to use this ammonia solvent system effectively, it is important to control the solubility throughout the concentration range prevailing in an extractor. This is particularly true for difficult separations and separations involving both high yield and high purity. Figure 5 illustrates the dependency of β on solubility.

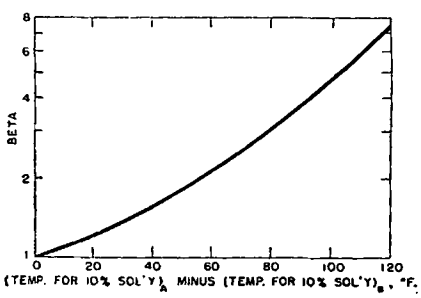


Fig. 4. β for hydrocarbon binary (*A-B*) in liquid ammonia.

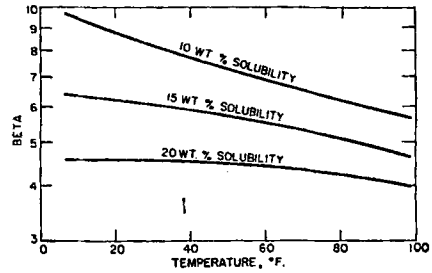


Fig. 5. Variation of β with temperature: toluene-methylcyclohexane-ammonia.

## TOLUENE METHYLCYCLOHEXANE AMMONIA

This system is shown in Figure 6 for anhydrous ammonia. To make a complete separation of both hydrocarbons with anhydrous ammonia, an extractor would have a very pronounced temperature gradient: the raffinate end would be about 100°F. and the extract end below 10°F.

This high gradient can be eliminated by using water as an antisolvent, as shown in Figure 7. To limit the solubility of toluene in anhydrous ammonia to 20 wt.%, the temperature has to be below 0°F. On the other hand, the temperature can be 100°F. if liquid ammonia contains about 13 wt.% water. Figure 8, which shows these relationships as a triangular diagram, illustrates the desirability of having a solubility pattern typified by the line *CJ*.

## OTHER HYDROCARBON SYSTEMS

Table 5 illustrates the selectivity of liquid ammonia for separating various binary hydrocarbon systems at 10 wt.% solubility.

The *C*-7 binary series is of interest. Here one of the components involves the carbon skeleton of methylcyclohexane and one of the components decreases successively in hydrogen content from the other by two hydrogen atoms. Ammonia is selective enough to recognize this difference.

Other naphthene-paraffin separations have been made with these ammonia solvents. Table 6 illustrates the importance of selecting the proper boiling-point relationships for a naphthene-paraffin separation. Since the solvent recognizes differences in molecular weight as well as molecular type, narrow boiling cuts are preferred for naphthene-paraffin separations.

## PILOT PLANT SEPARATIONS

A twenty-stage stacked extractor (*2*) has been used to carry out a variety of separations with this liquid-ammonia system. Both batch and continuous extractions have been made, but this discussion relates only to continuous steady-state operation. These separations do not necessarily represent the optimum. Instead they are intended to illustrate the range of feeds and the versatility of the ammonia type of solvents. Both stripping and enriching stages are employed, for what takes place in the enriching zone determines the purity of the

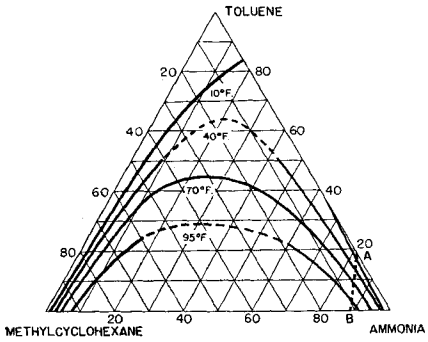


Fig. 6. Toluene-methylcyclohexane-ammonia; for solubilities along $AB$, $\beta = 4.0$ to 5.5.

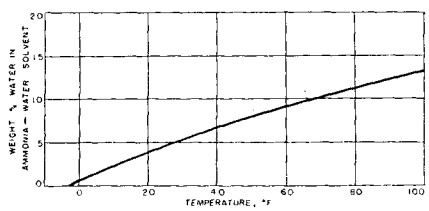


Fig. 7. Relation between temperature and water content to maintain 20 wt. % solubility of toluene in ammonia.

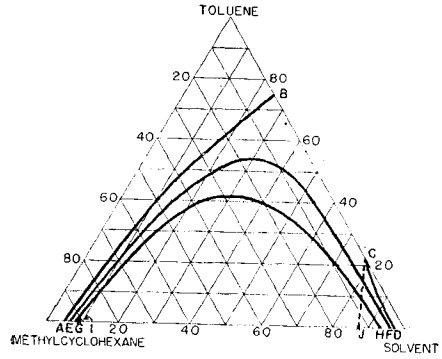


Fig. 8. Toluene-methylcyclohexane-solvent at 110°F.

Solvent composition, wt. %

| Area | $NH_3$ | $H_2O$ |
|---|---|---|
| $AB$-$CD$ | 86 | 14 |
| $EF$ | 90 | 10 |
| $GH$ | 95 | 5 |
| $IJ$ | 100 | 0 |

For solubilities along $CJ$, $\beta = 3.5$ to 5.5.

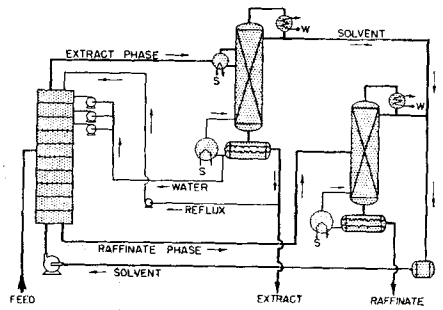


Fig. 9. Liquid-extraction pilot plant.

TABLE 4.—TOLUENE–METHYLCYCLOHEXANE–SOLVENT

| Solvent | Temp., °F. | $\beta$ at 20% hydrocarbon solubility* | At plait point: Wt. % hydrocarbon solubility ($\beta = 1.0$) | At plait point: Wt. % toluene in hydrocarbon | Ref. |
|---|---|---|---|---|---|
| Phenyl cellosolve | 0 | 3.1 | 58 | 38 | 3 |
| Methyl carbitol | 0 | 3.8 | 59 | 51 | 3 |
| Methyl cellosolve | −20 | 4.2 | 65 | 32 | 3 |
| Aniline | −10 | 4.5 | 58 | 42 | 3 |
| Ammonia | 70 | 4.7 | 62 | 73 | .. |
| 2, 4-Dimethylthia-cyclopentane dioxide | 0 | 5.0 | 57 | 45 | 7 |
| Furfural | 10 | 5.0 | 63 | 48 | 3 |
| Gamma valerolactone | 0 | 6.0 | .. | .. | 4 |
| Acetonitrile | 10 | 6.3 | 78 | 48 | 3 |
| Acetonylacetone | −10 | 6.6 | 65 | 43 | 3 |
| Sulfur dioxide | −40 | 17.7 | 59 | 44 | 6 |

*Hydrocarbon charge composition is 50 vol.% toluene and 50 vol.% methylcyclohexane. The solvent:oil weight ratio is 1:1.

TABLE 5.—SEPARATION OF HYDROCARBONS WITH LIQUID AMMONIA

| Hydrocarbon system | $\beta$ at 10 wt. % solubility | Min. theo. stages to make 95% pure extract and 95% pure raffinate |
|---|---|---|
| Isobutylene:isobutane | 2.2 | 8 |
| Butadiene:isobutylene | 2.0 | 9 |
| Trimethylethylene:n-pentane | 1.9 | 10 |
| Isoprene:pentene–1 | 2.0 | 9 |
| Methylcyclohexane:$n$–heptane | 1.3 | 20 |
| 4–Methylcyclohexene–1:methylcyclohexane | 1.5 | 15 |
| 1–Methyl–1,3–cyclohexadiene:methylcyclohexene | 1.6 | 13 |
| Methylcyclohexadiene:toluene | 1.6 | 13 |
| Styrene:ethylbenzene | 1.8 | 10 |
| Octene–1:isopropylbenzene | 2.8 | 6 |

most soluble component. What happens in the stripping zone determines its yield.

TABLE 6.—SELECTIVITY OF NAPHTHENE-PARAFFIN SYSTEMS

| B.P. naphthene − B.P. paraffin, °F. | $\beta$ at 15 wt.% solubility |
|---|---|
| −30 | 1.45 |
| −10 | 1.32 |
| 0 | 1.25 |
| 20 | 1.15 |
| 50 | 1.10 |

$$\beta = \left(\frac{\text{wt.\% naphthene}}{\text{wt.\% paraffin}}\right)_{ext.} \times \left(\frac{\text{wt.\% paraffin}}{\text{wt.\% naphthene}}\right)_{raff.}$$

Figure 9 is a diagram of the pilot plant. Because ammonia and monomethylamine are low boiling, pressure distillation is used to separate and regenerate the solvent. Open steam stripping is used to separate the solvent from the extract and raffinate portions. Part of the water is recycled, as shown, to get solubility control in the extractor.

This pilot plant is operated at a pressure sufficient to maintain the solvent within the extractor in a liquid phase. The pressure required is in the range of 150 to 200 lb./sq.in.abs.

## SOLVING EXTRACTION PROBLEMS

This solvent and the twenty-stage extractor comprise a calculating machine to study and solve a variety of extraction problems. Because of the ease of sampling the phases in the extractor and the ease of removing solvent from these samples, extensive operating-line–equilibrium-curve analyses can readily be made. Figure 10 illustrates the type of data obtainable on a simple system. In this case the distribution of stages and the choice of reflux and of solvent treat was such that most of the stages were used effectively. In a separation of this type where the solubility changes through the extractor can be very large, constant solvent composition and temperature being used, it is important to have the solubility on the stages properly controlled either by temperature reduction or water injection or both. Because of these solubility changes, which affect $\beta$, the equilibrium curve is not really a smooth continuous line as shown. Instead, it is actually saw-toothed

TABLE 7.—LIQUID EXTRACTION OF PETROLEUM FRACTIONS

| Petroleum fraction | A | | | B | | | C | | D | E | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Boiling range, °F. | Catalytic naphtha 200–330 | | | Catalytic naphtha 236–458 | | | Thermal naphtha 100–400 | | Catalytic naphtha 140–195 | Dearomatized catalytic naphtha 195–250 | 250–320 |
| Solvent composition, wt.% | | | | | | | | | | | |
| Ammonia | 80 | 80 | 80 | 85 | 85 | 85 | 85 | 85 | 100 | 68 | 68 |
| Monomethylamine | 20 | 20 | 20 | 15 | 15 | 15 | 15 | 15 | 0 | 32 | 32 |
| Run | 1 | 2 | 3 | 4 | 5 | 6 | 9 | 10 | 11 | 12 | 13 |
| Operating conditions | | | | | | | | | | | |
| Stage distribution, *E/F/S* | 12/*F*/7 | 12/*F*/7 | 12/*F*/7 | 8/*F*/11 | 8/*F*/11 | 8/*F*/11 | 8/*F*/11 | 8/*F*/11 | 12/*F*/7 | 7/*F*/12 | 12/*F*/7 |
| *S*:*O* wt. ratio | 4.5 | 4.5 | 3.0 | 5 | 5 | 3 | 2 | 3 | 1.6 | 20 | 22 |
| Reflux ratio (top of extractor) | 5.7 | 4.0 | 4.3 | 2.2 | 3.7 | 0.7 | 5.5 | 0.8 | 3.0 | 6.0 | 4.2 |
| Temperature, °F. (top-bottom stage) | 72–95 | 63–72 | 72–104 | 71–73 | 68–75 | 68–81 | 61–73 | 63–70 | 79–100 | 68–86 | 43–66 | 72–78 | 63–72 |
| $H_2O$ injection, wt.% of solvent | 12 | 0 | 12 | 0 | 3 | 2.5 | 6 | 0 | 0 | 0 | 17.5 | 0 | 0 |
| Feed | | | | | | | | | | | |
| Vol. % olefins | 43 | 43 | 43 | 16 | 16 | 16 | 16 | 16 | 24 | 24 | 8 | 53 | 45 |
| Vol. % *P+N* | 31 | 31 | 31 | 33 | 33 | 33 | 33 | 33 | 51 | 51 | 73 | 46 | 54 |
| Vol. % aromatics | 26 | 26 | 26 | 51 | 51 | 51 | 51 | 51 | 25 | 25 | 19* | 1 | 1 |
| Raffinate | | | | | | | | | | | |
| Vol. % of feed | 80 | 62 | 80 | 40 | 55 | 30 | 75 | 45 | 50 | 75 | 85 | 50 | 48 |
| Vol. % olefins | 48 | 43 | 46 | 23 | 24 | 12 | 20 | 18 | 18 | 26 | 10 | 21 | 19 |
| Vol. % *P+N* | 43 | 55 | 45 | 77 | 61 | 88 | 40 | 50 | 78 | 60 | 85 | 79 | 81 |
| Vol. % aromatics | 9 | 2 | 9 | 0 | 15 | 0 | 40 | 32 | 4 | 14 | 5* | 0 | 0 |
| Extract | | | | | | | | | | | |
| Vol. % of feed | 20 | 38 | 20 | 60 | 45 | 70 | 25 | 55 | 50 | 25 | 15 | 50 | 52 |
| Vol. % olefins | 5 | 32 | 10 | 6 | 7 | 16 | 5 | 12 | 21 | 15 | 0 | 86 | 73 |
| Vol. % *P+N* | 0 | 2 | 0 | 3 | 1 | 10 | 0 | 10 | 19 | 11 | 0 | 12 | 25.5 |
| Vol. % aromatics | 95 | 66 | 90 | 91 | 92 | 74 | 95 | 78 | 60 | 74 | 99.5+* | 2 | 1.5 |
| Yield | | | | | | | | | | | |
| % of feed aromatics in extract | 72 | 94 | 71 | 100 | 85 | 100 | 45 | 70 | 95 | 65 | 78 | 100 | 100 |
| % of feed olefins in extract | 3 | 31 | 5 | 80 | 20 | 80 | 5 | 40 | 55 | 11 | 0 | 80 | 80 |
| Research octane No. | | | | | | | | | | | |
| Feed | | | | | | 87 | | | 71 | | | | |
| Raffinate | | | | | | 10 | | | 46 | | | | |
| Extract | | | | | | 101 | | | 97 | | | | |

*P+N* = Paraffins+Naphthenes. *E/F/S* = Enriching/Feed/Stripping Stages. * Aromatic is benzene.

and the jogs occur at abrupt solubility changes.

By means of a unit such as this twenty-stage extractor, complex separational problems can be attacked profitably from an experimental rather than a wholly theoretical basis. The problem becomes one of being able to analyze the various stage samples, especially when multicomponent mixtures are used.

## CRACKED NAPHTHAS

Ammonia solvents have been used to separate catalytic naphthas, as shown in Table 7-*A*. The symbol *E/F/S* denotes the proportion among the enriching stages, the feed stage, and the stripping stages in the stacked extractor. The data are believed self-explanatory.

Figure 11 shows an operating diagram for the aromatic:nonaromatic separation in this catalytic naphtha. This plot illustrates how the stages in the extractor have been utilized and demonstrates solubility control. Whenever the solubility dropped, water injection was used to produce this change on the stages indicated.

Since this ammonia system is inert to hydrocarbons, it is effective in extracting stocks containing olefins and diolefins. Table 7-*C* illustrates the separation of a relatively wide-cut thermally reformed naphtha. This type of separation is useful for octane improvement as well as for making aromatic solvents and petrochemicals.

Table 7-*B* and Figure 12 present data on the separation of a heavy catalytic naphtha boiling in the range of 236° to 458°F. The separations between aromatics and olefins, or between olefins and saturates, were relatively good. The research octane numbers again show the usefulness of this process in naphtha refining.

Figure 12 illustrates the compositions of the feed, extract, and raffinate for one of these separations. Since this is a wide boiling feed, the most difficult separation is between the lowest boiling olefins and the highest boiling aromatics. The composition diagram for the extract shows that low-boiling olefins were present in the extract; the diagram for the raffinate illustrates the extent to which the high-boiling aromatics were not removed.

TABLE 8.—LIQUID EXTRACTION OF A CATALYTIC CYCLE OIL (600° TO 1,000°F.)

Solvent composition, Wt. % = 33$NH_3$, 67MMA
Feed composition = 47 vol. % aromatics
Stages, $E/F/S = 4/F/4$

| Operating conditions | | | |
|---|---|---|---|
| $S:O$, wt. ratio | 3 | 3.6 | 2.2 |
| Reflux ratio (top of extractor) | 1 | 2.6 | 1.3 |
| Temperature, °F. | 88–102 | 81–100 | 86–104 |
| $H_2O$ injection, wt.% of solvent | 4 | 3 | 4 |
| Raffinate, vol% of feed | 55 | 50 | 50 |
| Vol.% aromatics | 15 | 11 | 18 |
| Extract, vol.% of feed | 45 | 50 | 50 |
| Vol.% aromatics | 88 | 81 | 79 |
| Yield, % of feed aromatics in extract | 83 | 88 | 79 |

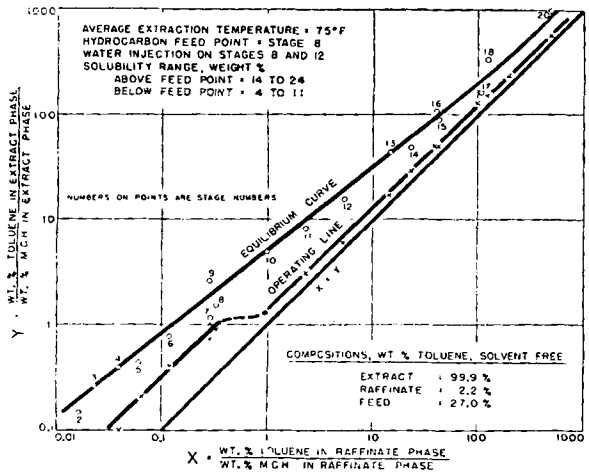


Fig. 10. Operating diagram for the extraction of toluene-methylcyclohexane with ammonia.

## BENZENE SEPARATION

Liquid ammonia can be used to separate benzene from straight-run and cracked naphthas containing olefins. A typical separation of benzene from a cracked-naphtha fraction boiling in the 140° to 195°F. range is shown in Table 7-*D*. Water injection was used to control the solubility in the extractor. In this extraction twelve stages were used in the enriching section and seven in the stripping section.

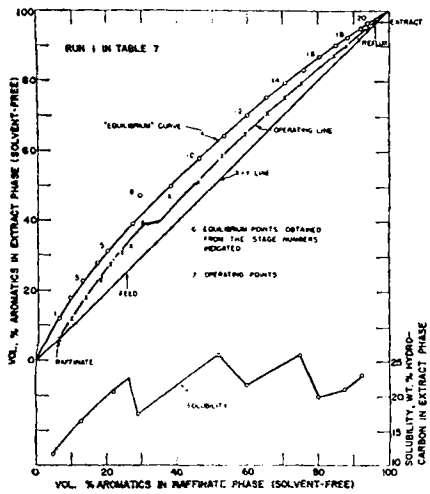


Fig. 11. Volume % aromatics in extract phase (solvent free).

## OLEFIN: SATURATE SEPARATIONS

Olefin:saturate separations are not easy with feed stocks with a wide boiling range. The problem here is one of dissolving the highest boiling olefin without taking into solution the lowest boiling saturate. Accordingly, narrower boiling feeds help materially in getting both high-olefin yields and purities.

Table 7-*E* illustrates this separation for two feeds. The separation would have been much sharper had these feed stocks been of narrower boiling range. These stocks cannot be separated by distillation or extractive distillation to the extent shown by these liquid extractions.

## CYCLE STOCKS AND LUBRICATING OILS

This liquid ammonia system has been used to extract hydrocarbons ranging in boiling point from 0° to about 1,000°F. at atmospheric pressure. In the higher range the separation frequently relates to taking out aromatics. Table 8 typifies separations in a catalytic cycle oil. Olefins and diolefins present in such feeds are not troublesome. Cycle-stock separations are relatively easy, the selectivity is good, phase separation is rapid, and the solvent is easily recovered.

In the Colombian distillate extraction, shown in Table 9, the object was to reduce neutralization number and to remove the highly condensed or cyclic aromatics. Complete dearomatization was not required. In addition to extracting Coastal distillates, this solvent system has been used on paraffinic lubricating distillates to obtain improvements in viscosity index, cleanliness, bearing corrosion, and oxidation stability.

## SUMMARY

Liquid ammonia properly controlled is a versatile solvent for extracting a wide variety of hydrocarbon mixtures. Separations by liquid extraction can be effected between aromatics and olefins, olefins and saturates, and in some cases between naphthenes and paraffins. Solubility varies widely for different types and sizes of hydrocarbons. Because the selectivity of the solvent is dependent upon solubility, it is important that the dissolving power of the ammonia solvent be controlled so that the amount of hydrocarbon in solution in the solvent usually lies between about 10 and 30 wt.%. Thus at all points in a multistage, compound, countercurrent extractor the solvent is incompletely miscible with the hydrocarbons undergoing extraction.

From a practical viewpoint extraction temperatures are usually between 50° and 150°F.

To effect the necessary solubility control of these ammonia solvents in a multistage extractor, water (in concentrations between 0 and 15 wt.%) is used at appropriate extraction stages to reduce the dissolving power of liquid ammonia. To enhance or increase this dissolving power, methylamine has been found very suitable; it is usually in concentrations between 0 and 50 wt.% for many hydrocarbon extractions.

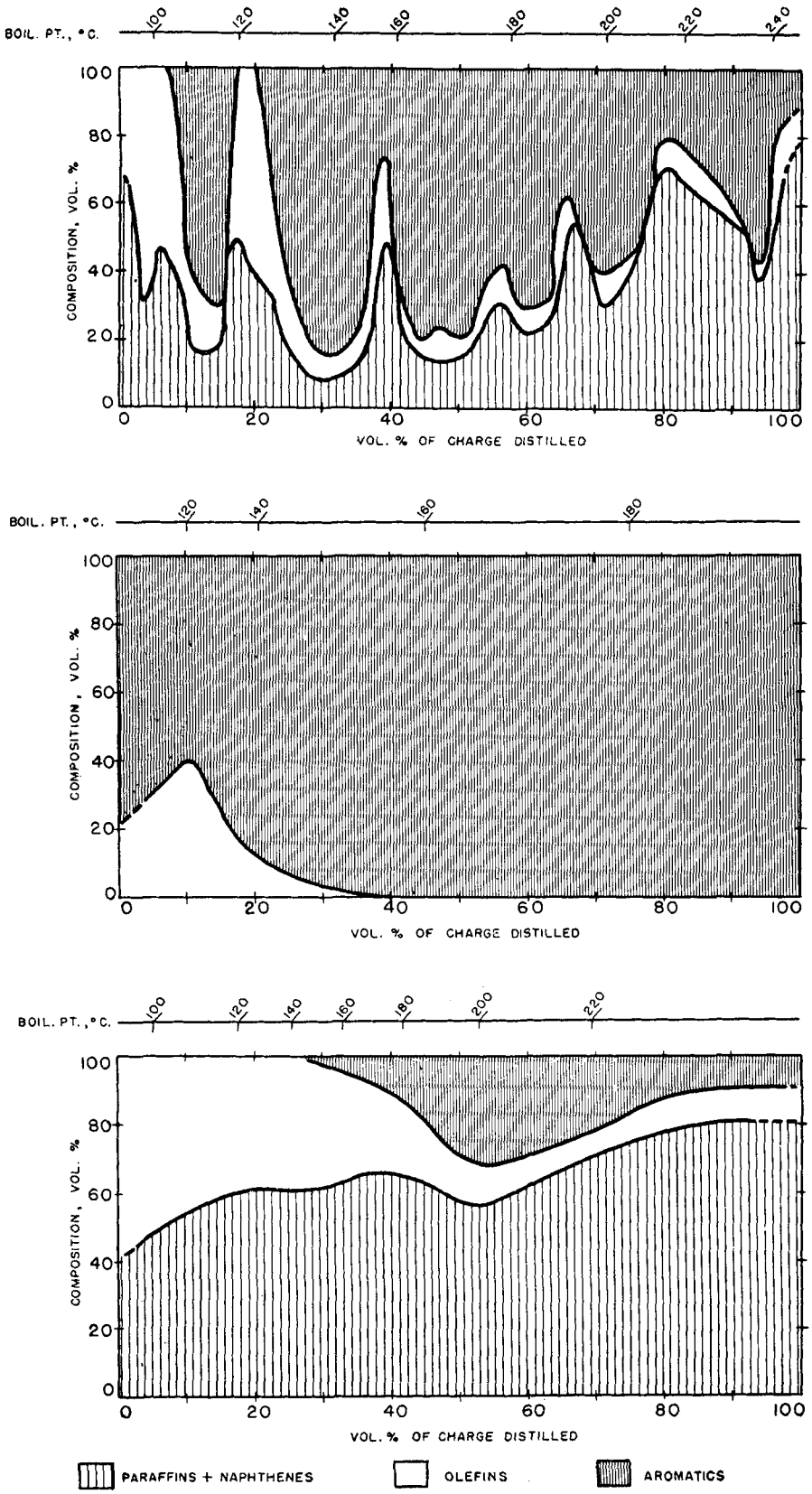


Fig. 12. Fractional distillation of extraction products from catalytic heavy naphtha, 236° to 458°F. (run *B* in Table 9): top, feed; middle, extract (45 vol. % of feed); bottom, raffinate (55 vol. % of feed).

A twenty-stage, countercurrent, stainless steel extractor, with both stripping and enriching zones, has been employed for batch as well as continuous liquid extractions. The hydrocarbon feed rates are usually between 0.5 and 3 gal./hr. and the solvent-to-oil ratios usually range from 1 to 1 to as high as 10 to 1.

Extractions of pure binary mixtures show what goes on in a compound extractor and how the solubility control is realized.

Other data on thermally and catalytically cracked naphthas, catalytic cycle stocks, and Coastal-type lube oils show how this solvent system is applied to petrochemicals, octane improvement, the making of solvents and aviation blending stocks, and the upgrading of lube distillates.

TABLE 9.—LIQUID EXTRACTION OF COLOMBIAN DISTILLATE

Solvent composition, wt.% = 40 $NH_3$, 60 MMA

| | | |
|---|---|---|
| Operating conditions | | |
| Stages, *E/F/S* | 8/F/4 | 8/F/4 |
| *S:O* wt. ratio | 1.0 | 1.7 |
| Temperature, °F. | 112 | 100 |
| Raffinate, vol.% of feed | 88 | 81 |
| S.U.S. at 100°F. | 743 | 716 |
| Viscosity index | 29 | 38 |
| Neut. No. | 0.1 | 0.1 |
| Vol.% aromatics | 23 | 20 |
| Extract, vol.% of feed | 12 | 19 |
| S.U.S. at 100°F. | 1,465 | 1,490 |
| Viscosity index | −107 | −97 |
| Neut. No. | 8.7 | 3.5 |
| Vol.% aromatics | 86 | 80 |
| Feed | | |
| S.U.S. at 100°F. | 880 | |
| Viscosity index | 18 | |
| Neut. No. | 1.7 | |
| Vol.% aromatics | 30 | |


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