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CONTINUOUS SOLVENT EXTRACTION OF A VENEZUELAN REDUCED CRUDE ON A ROTATING DISC CONTACTOR

by

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DEDICATION

I dedicate this thesis to the fulfillment of goals, to my wife Zoila, to my parents Prudencio and Berta and to all my family and friends.

ABSTRACT

The purpose of this research work was to study the effects of changes in operating variables on the extract and raffinate properties and yields obtained in the continuous solvent extraction of the Venezuelan atmospheric residue Zuata 44X.

The solvent used was a tetraethylene glycol-water mixture. The parameters varied were: rotor speed, extraction temperature, solvent-to-oil ratio, and solvent composition. A continuous solvent extraction unit using a rotating disc contactor (RDC) was used to study the effects of the variations in operating parameters. The continuous extractions were performed at solvent-to-oil ratios of 4/1, 5/1, and 6/1; the temperature range was 214 ^{o}F to 230 ^{o}F; the RDC speeds were 100, 300, 500, and 800 RPM, and the solvent compositions were 0%, 5%, and 10% water added. The pressure of the system remained constant throughout all runs.

Increases in extract yield were obtained by increasing the extract temperature, solvent-to-oil ratio, and rotor speed. These increases in extract yield were generally associated with increases of undesirable materials such as

sulphur, vanadium, nickel, asphaltenes, and also increases in the Conradson carbon residue.

The operating variable of main importance seemed to be the extraction temperature, although increases in the rotor speed and solvent-to-oil ratio also produced increased extract yields.

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INTRODUCTION

Today about 50 percent of the world's primary energy demands are supplied from petroleum sources with world consumption totaling over 50 million barrels per day. At present production rates proven crude oil reserves will last only 30 to 40 years. Moreover, most of the future petroleum production will have to come from increasingly marginal deposits in difficult locations, which will result in increasingly higher production costs.

At present, a tremendous imbalance exists between petroleum supply and demand areas because the industrialized countries with high petroleum demand either have minimal oil production or are rapidly depleting their oil reserves.

This production-consumption imbalance has resulted in the formation of a strong producer's cartel --OPEC-- that has the power to set both world oil prices and total production rates. Thus, the oil consuming countries are now faced with economic instability and possible future threats to their national security.

These forces have combined to give increased urgency to the consuming countries efforts to develop alternative sources of liquid fossil fuels that are based on indigenous

resources. Most of the easily developed deposits of higher quality oil have already been developed, so it will be necessary in the future to exploit lower grade oil resources, such as very heavy oil and tar sands.

Recovery of bitumen from tar sands has proven technically difficult and financially costly. The very heavy oil that is recovered from tar sands must be moderately upgraded to reduce the oil's viscosity so that it can be pipelined to the refinery. Moreover, in the refinery, the crude must be severely upgraded to produce the required product slate of specification grade liquid products --also a costly and technically difficult process.

As a result of the aforementioned circumstances, the needs and goals of the petroleum industry have changed. The price spreads between light and heavy crudes are increasing the quantity of heavy crude and residua projected for future refinery runs. Refiners are therefore planning to add facilities to convert heavy crude and their excess residua to marketable light products. At the present, a requirement is to utilize increasingly large quantities of heavy crudes by converting their residuals into distillates and other desirable products, particularly those light and medium types in demand by the fuel market.

Long-term environmental policies favoring burning cleaner, lighter fuels, has also caused the refiner to consider upgrading the residuum to cleaner and/or lighter products, and as a result, different schemes for processing heavy, high sulfur, high metals atmospheric and vacuum bottoms have been developed.

As world reserves of conventional crude oil decrease and the price of oil increases, interest in heavier crudes and in oil obtained from shale oil and tar sands continues to grow. However, while huge deposits of these materials exist in Canada, Venezuela and the United States, these heavy oils have high densities, viscosities, and pitch contents. They also contain impurities such as metals, sulfur and nitrogen, and have high Conradson carbon residues which indicate tendencies to coke.

The upgrading of heavy oil and bottoms is the link between the resource and the market. Its purpose is to provide the necessary and economical means to bring more oil and its derivatives to the market place.

Upgrading increases the hydrogen to carbon ratio in the heavy oil or residuum to the point where the treated material can be sold or used as finished products or processed further via conventional refining techniques. The

upgrading function can be performed either by removing carbon and contaminants from the heavy material, by adding substantial amounts of hydrogen to the oil, or by doing both. Depending on their complexity, upgrading methods can add varying amounts of economic value to the heavy material processed. Table 1 shows several of the carbon removal processes in use in the industry today. Table 2 lists possible dispositions for upgraded products.

One of the many non-catalytic upgrading processes in use today is the solvent extraction process (or solvent deasphalting) which separates and/or removes the asphaltene fraction of the heavy oil or residuum, thereby increasing the hydrogen to carbon ratio of the liquid fraction. The liquids can then be hydrotreated to an even greater H/C ratio. The by-product , or asphaltene fraction, can be used in further processing, either by charging it directly to furnaces as a fuel or by first gasifying to fuel gas or to hydrogen for process use. If markets exist, the residue fraction can be sold as coke or asphalt or used in petrochemical manufacture. Generally the solvent extraction process is less expensive and more commercially proven than hydrogen addition processes. Table 3 lists the primary advantages and disadvantages of solvent extraction for various product dispositions.

Table 1

Carbon Removal Processes (33)

Process Name	Developer	Feedstocks	Key Products
Vacuum Distillation	Many, Non-Propietary	Atm. Residue	Vacuum Residue
Solvent Deasphalting	Many	Vacuum Residue Whole Bitumen	Bright Stocks Cracking Feedstocks
Demex	UOP Process Division	Vacuum Residue	Demetallized Oil
Residuum Oil Supercritical Extraction (Rose)	Kerr McGee	Atm. & Vacuum Residue, Shale Oil & Tar Sands	Asphalt, Lube Oils Resins, Cat Cracking Feed
Asphalt Blowing Bitumen Manufacture	Snamprogetti BP Trading Limited	Vacuum Residue	Bitumen, Asphalt

Table 2

Possible Dispositions of Heavy Oil Upgrading Products (33)

Upgrading Product	Disposition	
	Within Plant	Market
Light Ends (C_1-C_4)	Process Fuel Gas Plant H_2 Production	Petrochemical Manufacture, LPG, Natural Gas.
Light Distillates (C4, Naphtha, Reformate)	Gasoline Blending Petrochemicals Manufacture, Process Fuel	Gasoline, Petrochemicals
Middle Distillates (Kerosene, Diesel,No.2 Oil)	Distillate Blending	Fuel[1]
Heavy Distillates (Gas Oils, Resins)	FCC/Hydrocracker Feed Fuel Oil Blending Lube Plant, Process Fuel	Fuels,Mineral Oil, & Lighter Products, Waxes & Luboils
Heavy Residues (Resins & Asphaltenes)	Fuel Blending, Lube Plant, Asphalt Blending, Gasification, Process Fuel	Fuel Oils, Lube Oils, Petrolatum, Asphalt, Road Oil, Methane
Coke, Tars, Pitch	Petroch. Manufacture Gasification, Process Fuel	Fuels, Electrode Coke, Carbon Black, Methane

(1) Fuel includes Jet Fuels, Kerosene, Diesel, No. 2 Oil.

Table 3

Solvent Deasphalting Relative Advantages and

Disadvantages of Primary Products Disposition Options (1)

Product	Product Disposition	Relative Advantage	Relative Disadvantage
Deasphalted Oil	FCC/Hydrocracking Feed.	High Quality	Low Liquid Yield Conversion of 975+^{o}F Material
Asphaltenes	Asphalt Blending	Simple Cost Effective High Quality	Low Liquid Yield Limited Asphalt Market
	Fuel	Simple	Low Liquid Yield Requires Stack Gas Cleaning
	Coker Feed	Higher Liquid Smaller Coker Required	Coke Formation Low Liquid Yield
	Gasification	Can Provide Needed H_2	Hydrogen or Fuel must be Nedded High Cost

For practical purposes, distillation is always applied first. Initially asphalt is separated as a residue by the refinery distillation process which tends to slice off the lowest boiling fractions while concentrating the highest molecular weight fractions in the residue.

Solvent extraction is then used to cut deeper into the residuum in order to recover higher yields of processable oil and to concentrate asphaltene-containing fractions. Solvents preferentially extract the most saturated hydrocarbons first, then the lower molecular weight fractions of all types. The raffinate or precipitate in this case is found to contain the most aromatic fractions as well as those that are the highest in molecular weight (1).

The quality of the extract may be characterized by the metal and Conradson carbon contents. These two factors are particularly important for evaluating feeds for downstream catalytic conversion processes such as FCC and hydrocracking since they determine catalyst deactivation and consumption rates.

The objective of this research work is to remove the asphaltene fractions, metals (Ni,V), nitrogen, and sulfur from an atmospheric residue by using a solvent extraction continuous unit (RDC column). The solvent used was a

mixture of tetraethylene glycol and water. Effects of changes in extraction temperature, solvent to oil ratio, RDC rotor speed, and addition of polar component to solvent on product oil yield and quality were studied.

THEORY

Constitution Of Heavy Oils

The chemical structure of heavy oils is extremely complex. Besides the major components, carbon and hydrogen, significant quantities of sulphur, nitrogen, oxygen, vanadium and nickel are usually present (1). Other metallic elements such as sodium, copper and iron may also be found, but are usually the result of extraneous contamination (2).

The non-asphaltenic portion of crude oil boils below 1550 ^{o}F while the expected boiling range of the asphaltenes is 1550-2900 ^{o}F, hence, they cannot be distilled using existing techniques (3).

Where sulphur is present in relatively large quantities it is likely that heavy oils consist largely of sulfur-containing molecules. In addition, it is suspected that molecules containing two or more sulphur atoms contribute increasingly to the sulphur compounds of high molecular weight (3). While thiols and aliphatic sulphides are present in the lighter fractions, they form an insignificant part of the heavy oil sulphur compounds which appear to be largely thiophenic in character (4).

Most heavy oil processing difficulties center around

the presence of sulphur, vanadium and nickel and thus the distribution of nitrogen and oxygen is considered of lesser importance. Both basic and non-basic nitrogen compounds are present, normally in a weight ratio of about 1:3 which appears to vary little throughout the heavy oil boiling range (5). Crude oil nitrogen and oxygen contents are always much less than sulphur contents, there being only minor quantities of both these elements present until the heavy oil boiling range is reached. It is likely that most of the nitrogen and oxygen found in heavy oils are in condensed aromatic molecules.

Vanadium and nickel in heavy oils have been fairly extensively studied and are widely known to be present as metalloporphyrins. These porphyrins are volatile with boiling points above 930 ^{o}F and mainly above 1050 ^{o}F; it has been shown that the 1050-1300 ^{o}F distillate usually has the highest metalloporphyrin content (3). However, a proportion of the vanadium and nickel is always present in a "non-porphyrinic" form and is non-volatile, the proportions of porphyrinic to "non-porphyrinic" vanadium and nickel varying widely with crude source. Mass spectrometric data suggest that the lower molecular weight compounds are metal alkylporphyrins (2).

Petroleum Asphaltenes

The asphaltenes are defined as that portion of a heavy oil insoluble in n-heptane. Each asphaltene molecule probably consists of a core of about five stacked sheets of condensed aromatic rings which give a stack height of 16-20 angstroms. The sheets contain nitrogen, sulphur, oxygen and free radical sites which are likely to be the centres at which the "non-porphyrinic" vanadium and nickel are located (6).

The molecular nature of the asphaltene fractions of petroleum and bitumens has been the subject of numerous investigations (7,8). There are indications that asphaltenes consist of condensed aromatic nuclei that carry alkyl and alicyclic systems with heteroelements (i.e., nitrogen, oxygen, and sulphur) scattered throughout in various, including heterocyclic, locations.

Asphaltenes are dark brown to black solids that have no definite melting point, and when heated, usually decompose leaving a carbonaceous residue. Much of the information available on the carbon skeleton of asphaltenes has been derived from spectroscopic studies of asphaltenes isolated from various petroleums and natural asphalts.

Attempts have been made to describe the total structures of asphaltenes in accordance to NMR data and x-rays analyses, but all methods employed for the structural analysis involve assumptions that are of questionable validity when applied to asphaltenes. Figure 1 shows a hypotetical structure of a petroleum asphaltene.

An early hypothesis of the physical structure of petroleum indicated that asphaltenes are the centers of micelles formed by adsorption, or even by absorption of part of the maltenes, that is, resin material, onto the surfaces or into the interiors of the asphaltene particles (9). This has led to the assumption that asphaltenes exist as clusters within the micelle.

The concept of hydrogen-bonding interactions being one of the means of association between the asphaltenes and resins has, however, led to a reconsideration of the assumed cluster as part of the micelle (10). Indeed, it appears that when resins and asphaltenes are present together, hydrogen bonding may be one of the mechanisms by which resin-asphaltene interactions are achieved.

Resin-asphaltene interactions are preferred over asphaltene-asphaltene interactions (10). Thus, if the same intermolecular forces are present in petroleums and

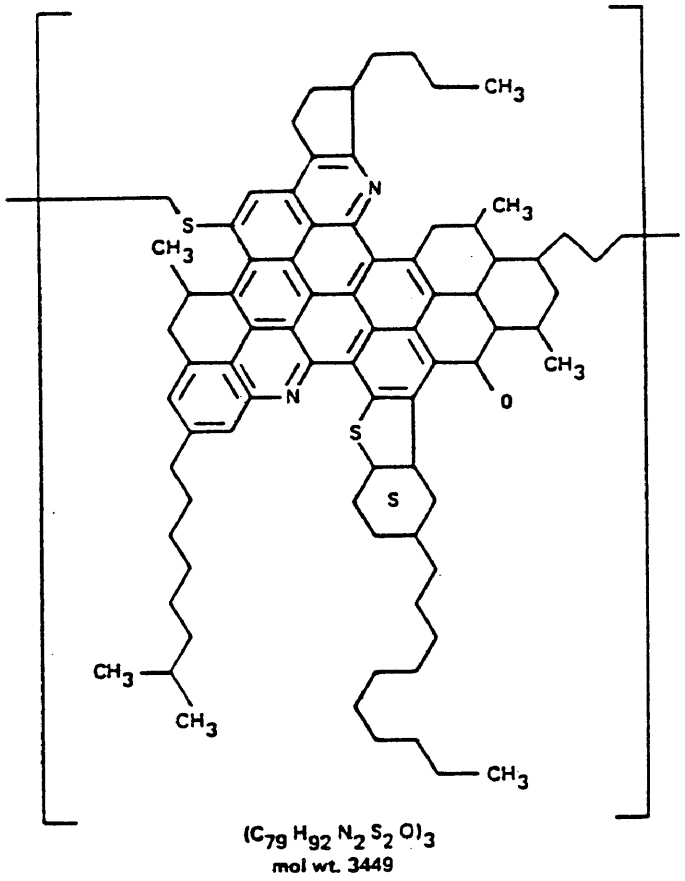


Figure 1

Hypothetical Structure of a Petroleum Asphaltene (35)

bitumens, it would perhaps not be surprising that asphaltenes exist not as the more cumbersome agglomerations but more nearly single entities that are peptized, and effectively dispersed, by the resins.

For the purpose of this research work, an atmospheric residue from a Venezuelan heavy crude oil was utilized. The heavy crude oil which was obtained from the Orinoco Heavy Oil Belt, has all the typical characteristics regarding sulphur and metal contents, low API gravity, and high viscosity mentioned above. Figure 2 shows the average chemical structural model of asphaltenes derived from the analysis of NMR spectra for a Middle East crude (Khafji) and two Venezuelan crudes. Tables 4 and 5 summarize the physicochemical properties and chemical structures of those crudes. From these data we can conclude the following:

1.- Asphaltenes of Venezuelan crudes have extremely high metals content, although their sulphur content is relatively low.
2.- Asphaltenes in Tia Juana, Bachaquero, and Orinoco crudes have average molecular weights that are about half of those in Boscan and Khafji crudes.
3.- The molecular weights of Orinoco and Boscan asphaltenes are slightly higher than that of Khafji asphaltene.

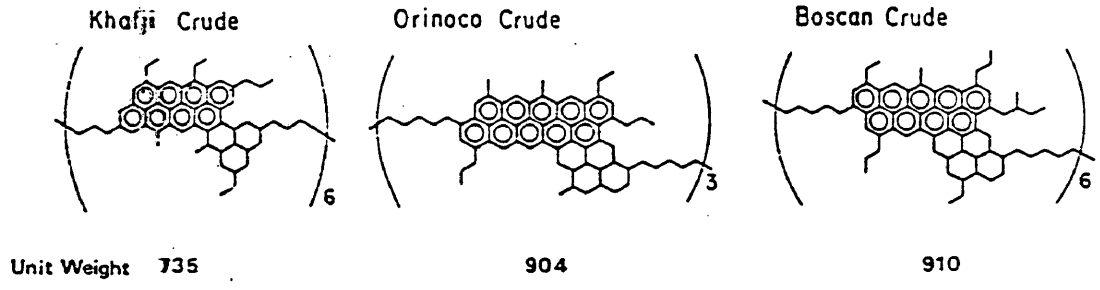


Figure 2

Average Chemical Structural Models of Asphaltenes (1)

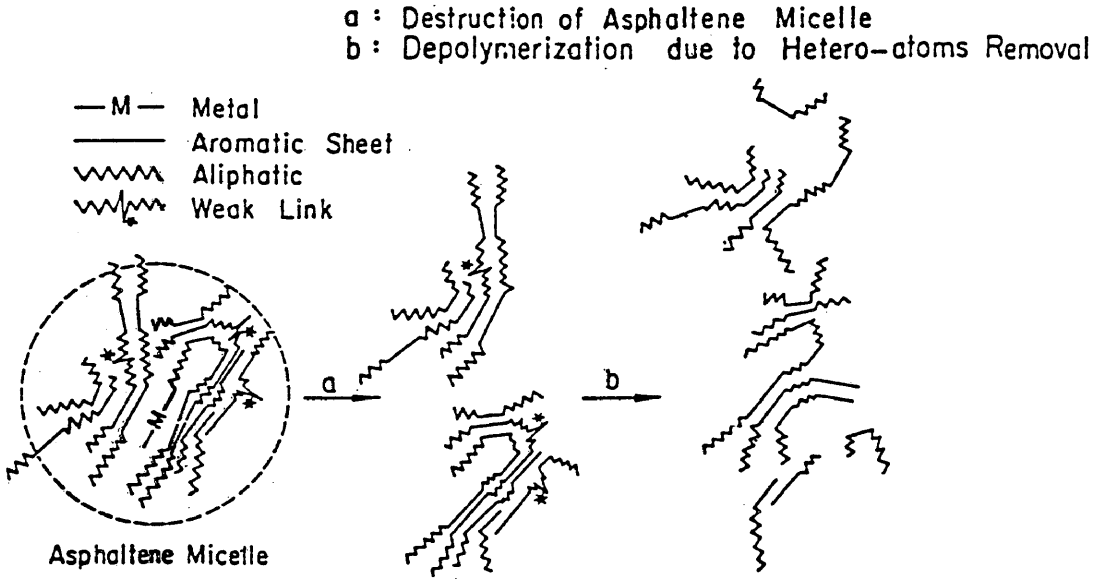


Figure 3

Model of Asphaltene Disintegration (1)

Table 4

Characteristics of Heavy Oils (11)

Property	Khafji VR	Tia Juana VR	Bachaquero VR	Orinoco VR	Boscan Crude
Gravity, ^{o}API	6.8	8.7	6.8	3.0	9.4
Asphaltenes, wt%	11.4	12.5	10.3	16.9	11.9
Carbon Residue, wt%	21.2	21.3	19.3	26.2	16.3
H/C ratio	1.45	1.48	1.45	1.40	1.52
Sulfur, wt%	4.96	2.90	3.34	4.30	5.22
Nitrogen, wt%	0.40	0.60	0.65	0.97	0.69
Vanad./Ni, ppm wt	130/41	669/66	614/82	625/147	1,192/112

VR: Vacuum Residue (950 ^{o}F cut)

Table 5

Characteristics of Various Asphaltenes in Heavy Oils (11)

	Khafji	Tia Juana	Bachaquero	Orinoco	Boscan
H/C Ratio	1.07	1.12	1.11	1.12	1.15
Ave. Molecular Wt.	4,800	2,170	2,670	2,900	5,630
Carbon Residue, wt%	58.7	52.7	54.2	54.8	49.1
Sulfur, wt%	10.57	4.45	4.42	5.50	6.76
Nitrogen, wt%	1.16	1.65	1.72	1.60	1.60
Vanad./Ni, ppm wt	615/201	2,970/201	2,880/388	2,500/530	5,390/466

The mechanism of asphaltene cracking reactions proposed by Takeuchi et al. (11), is shown in Figure 3. The removal of hetero-atoms from the heavy oil by solvent deasphalting has a similar effect in the asphaltene micelle.

Solvent Extraction Process

The main purpose of the solvent extraction process is to separate a general group of offensive materials such as resinuous materials, metals, aromatic compounds, sulphur and nitrogen compounds, or hydrocarbons from the oil.

By using this process, a crude oil or a reduced crude can be separated into low- and high-quality fractions. Improvements in the viscosity index, color, and thermal and chemical stability of the products can be achieved, depending on the operating variables and the type of solvent used (12).

The solution whose components are to be separated is the feed to the process. Liquid added to the feed for purposes of extraction is the solvent. The solvent-lean, residual feed solution, with one or more constituents removed by extraction, is the raffinate. The solvent-rich

solution containing the extracted solute(s) is the extract. The minimum requirement for liquid extraction is the intimate contact of two immiscible liquids for the purpose of mass transfer of constituents from one liquid (or phase) to the other, followed by physical separation of the two immiscible liquids.

Some of the solvents proposed for use in the solvent extraction process are: liquid sulphur dioxide (13), phenol (14), furfural (15), aqueous di-, tri-, and tetra-ethylene glycol (16,17), morpholine (18), N-methyl-2-pyrrolidone (19) and light normal paraffins such as propane. Toxicity, thermal and/or chemical instability, and insufficient solvent power and/or selectivity, have limited the commercial use of extraction solvents to just a few.

Sulphur dioxide is the oldest solvent known in the petroleum industry. Originally it was used for extraction of aromatics from kerosene fractions (13) and it later found application in lube oil base stock extraction. An important disadvantage of sulphur dioxide is its toxicity and air pollution potential. Furfural has been used extensively in lube oil extraction, however, due to its tendency to oxydize and polymerize introduces it requires special recovery equipment, which increases the plant operating cost (15). Phenol has a high solvent power and good selectivity, the

main disadvantage of phenol is its toxicity (14).

Choice Of An Extraction Solvent

Selecting the optimum solvent for a particular application requires a lot of experimental and calculation work, because every change in the properties of a solvent yielding an advantage also involves a disadvantage in another respect (20).

Consideration of the different characteristics is an important factor in the selection of a solvent. The following list describes the properties of an ideal extraction solvent (21).

1.- High selectivity -- for undesirable components, that is a large solubility differential between the undesirable and desirable components.
2.- Good solvent power -- for the undesirable components such that the extraction can be made with a reasonably small amount of solvent.
3.- High extraction temperature -- for good mass transfer.
4.- The vapor pressure at extraction temperature should be low, so that the use of pressure equipment can

be avoided.

5.- Easy recovery -- that is, volatility characteristics should permit easy separation by some form of distillation.

6.- High density -- sufficient difference in density of the solvent or solvent phase and the density of the raffinate phase to allow rapid phase separation.

7.- No emulsification -- Low surface tension in order to permit rapid and complete separation into two liquid phases.

8.- Stability -- no chemical or thermal degradation under any conditions encountered in its use, recovery, or in storage.

9.- Adaptable -- to a wide range of feedstocks.

10.- Available -- at reasonable cost.

11.- Non-corrosive -- to conventional metals of construction.

12.- Non-toxic -- environmentally safe, biodegradable.

13.- Low freezing point -- to allow avoiding complications in cold weather.

Other factors of importance when selecting a solvent are boiling point, polarity, selectivity, capacity, and aromatics range. Apart from the properties of the system to

be extracted the boiling point has been considered as a major characteristic of the solvent. The reason being that solvent recovery from the extracted substance generally is performed by distillation and its cost is of considerable importance in the economics of the process.

For solvents with boiling points higher than the extract, the higher the boiling point of the solvent the lower the reflux ratio for distillation and the higher the energy requirements for heating the solvent to its boiling point. In some cases, the condensation temperatures of the extracted substances also have to be considered.

The term "polarity" is frequently used in extraction technology without a clear definition or measurable criterion. The best criterion is the dielectric constant although alone it does not furnish reliable evidence regarding the behavior of the solvent (23).

The capacity of a solvent is defined by the distribution factor, i.e., the aromatics concentration ratio of solvent phase to raffinate phase. Selectivity is defined by the ratio of the distribution factors of the aromatics to the distribution factors of the non-aromatics. The higher the value of the distribution factor, the higher the capacity of the solvent (23, 34).

$$Ka = [A\text{-raff}]/[A\text{-extr}]$$

$$Kn = [N\text{-raff}]/[N\text{-extr}]$$

$$S = Kn/Ka$$

where Ka = distribution factor of aromatic component

Kn = distribution factor of non-aromatic component

S = selectivity

[A-raff] = raffinate phase aromatics concentration

[A-extr] = extract phase aromatics concentration

[N-raff] = raffinate non-aromatics concentration

[N-extr] = extract non-aromatics concentration.

When choosing a solvent, selectivity is the most important factor, while capacity is given less importance although it plays a heavy role in the decision. Most solvents with high capacity have low selectivity and vice versa. Solvent with very low capacities for aromatics require a much greater solvent treatment rate and hence a higher circulation rate for the solvent. This results in increased operating costs due to the larger solvent inventory and the cost associated with solvent recovery. Muller (19), made an extensive study of selectivity and capacity over a wide range of solvents.

The aromatics concentrations in which two phases still exist in the solvent-aromatics-nonaromatics system is called

the "aromatics range" and it limits the permissible aromatic content in the feed. When the limit of aromatic range is exceeded, the phases in the feed stages of the extractor disappear, and the extraction process breaks down. To reduce the aromatic content in the feed, part of the raffinate may have to be recycled, or the solvent-to-oil ratio may have to be increased. The aromatics range may be increased by the addition of water to the solvent.

Table 6 (Appendix B) shows some of the physical properties of the most used commercial solvents. After analyzing the different physical and chemical properties of the listed solvents, the field can be narrowed to a few solvents suitable for the extraction process.

The solvent chosen for this research work was tetraethylene glycol. This solvent has low toxicity, good thermal and chemical stability, good selectivity and capacity, availability, and is non-corrosive to conventional construction metals. Table 7 (Appendix A) shows the physical properties of the tetraethylene glycol solvent.

TTEG was first used commercially by Sun Oil in their Udex extraction plant at Corpus Christy, Texas. Extensive studies have proven that using TTEG instead of dipropylene glycol, or di- and triethylene glycol increases throughput

and recovery while lowering operating costs (16,17). Pilot studies on BTX Udex process using TTEG at solvent/feed ratios as low as 4/1 give high recovery and high purity aromatics at lower operating costs.

Addition Of A Polar Mixing Component

The advantage of using a polar mixing component such as water is that it increases the selectivity of the solvent for aromatics and decreases its boiling point. On the other hand it has the disadvantage that solvent capacity is reduced and heat consumption in the distillation column rises because water has to be co-evaporated azeotropically during stripping of the aromatics. The greater the proportion of high boiling aromatics to be recovered, the greater the quantity of water to be evaporated.

When the proportion of aromatics in the feedstock is small it is advantageous to increase the capacity of the solvent by reducing the fraction of polar components in the solvent mixture and vice versa.

Catalytic Cracking Feedstocks By Solvent Refining

One product common to almost all petroleum refining is the residuum. For every barrel of distillate produced,

refiners are committed to sell or use a proportionate amount of this residue. The yield of such materials depends upon the crude source. Normally, these residues are blended with lighter oils for sale as low profit liquid fuels. Some residuals have found a ready market as high profit road and building materials, but such outlets can absorb only a small fraction of the potential supply.

In recent years the demand for residual fuels has not kept pace with the increase in crude runs. On the other hand, the lighter oils have been in increasing demand as distillate fuels and for processing into other products. These factors, coupled with the generally low price offered for residual fuels, have made the practice of blending petroleum residues to fuel oil specifications highly unattractive.

Most asphalts and residual fuels are potential sources of additional catalytic cracking feedstock. The amount may be as much as 50 to 75 percent of heavy oil FCC feed. These heavy oils are capable of producing high octane gasoline in yields nearly equal to those from lighter stocks (23). The employment of deep vacuum flashing to recover additional cracking stock can cut the residuum yield by many barrels. Other processes such as visbreaking and coking can likewise

be employed to accomplish the same purpose.

As these processes are applied in an effort to get deeper into the crude, certain components that have an adverse effect on catalytic cracking are included in the recovered oils. The progressively heavier petroleum fractions contain larger amounts of materials deleterious to the cracking operation. The potential cracking stocks of most residua contain relatively large amounts of metal compounds, polynuclear aromatics, resins, and sulfur and nitrogen compounds. Metals, which have received a great deal of attention, differ from most deleterious materials in that they are accumulated in the catalyst. Continued feeding of even trace amounts of metal compounds to a catalytic cracker requires a continuously high catalyst replacement rate. Relatively large amounts of metals may affect the operation entirely.

If high-grade cracking stocks are to be recovered from the low value heavy fuel oils, selective separation processes are mandatory. Solvent extraction with light hydrocarbons or with polar solvents such as glycols meets these requirements.

Operating Variables In Solvent Extraction

Asphaltic bitumen is a colloidal system in which the asphaltenes, because of their adsorption of resins and aromatics, are peptized. Normal liquid paraffins (pentane, hexane, etc.) partially, or completely, dissolve the peptizing agents and the asphaltenes coagulate (26). These solvents have inverse solubility characteristics and as temperature is increased more bitumen is rejected. However, as the the molecular weight of the paraffin series decreases, the solubility of the resins and some of the heavier and more aromatic hydrocarbons in these paraffins decreases. Thus, instead of a dry powdery precipitate of asphaltenes. a tacky material, consisting of asphaltenes, resins, and aromatics, results. As the temperature of these lighter solvents is raised from about 100 ^{o}F to the critical temperature, the solubility of the resins and of the heavier and more aromatic hydrocarbons is further decreased. This will occur with all solvents as the critical solution temperature is approached (22). The critical solution temperature (CST) is the temperature above which all mixtures of two or more components are completely miscible.

Besides producing an oil relatively free of high boiling aromatics, resins, and asphaltenes, the solvent

process also rejects metal (nickel and vanadium), sulfur, and nitrogen compounds. The fact that the metals are rejected indicates that they are associated with the resin or asphaltene fractions produced during the separation process since these fractions contain a very high concentration of those metals.

Countercurrent operation and solvent-to-oil ratio are important in attaining the selectivity required for producing premium cracking stocks. The variables of the process are temperature, pressure and solvent-to-oil ratio.

Either temperature or pressure can be used to control the operation. Except near the critical region, the effect of pressure is minor. Accordingly, pressure is normally maintained at some fixed value above the bubble point of the solvent at the temperatures used in order to keep the solvent in the liquid phase. Therefore, for any given feedstock and solvent, the operating variables can be considered to be temperature and solvent-to-oil ratio.

For light paraffinic solvents, higher temperatures always result in decreased yields of cracking stock. The effect of solvent-to-oil ratio on yield, however, cannot be predicted without equilibrium data. Thus, solvent-to-oil ratio is not an important variable from the yield

standpoint; however, it is important from the standpoint of selectivity. Almost any desired yield can be obtained by adjusting either the solvent type or the temperature.

Effect Of Feed Type

A long reduced crude is produced by atmospheric distillation or a combination of atmospheric and mild vacuum reduction. A short reduced crude is the residual product of deep vacuum flashing.

For a given temperature and solvent-to-oil ratio, it is possible to recover more oil from a long residuum than a short one, but with some sacrifice in selectivity. The use of a long reduced crude as feedstock permits deep extraction of the crude at a selected set of conditions and with a given solvent. However, for a fixed refinery crude charge, the long reduced crude will require a larger unit than a short reduced crude, and, the use of a long reduced crude as a feedstock results in loss of selectivity. On the other hand, the solvent extraction of a short reduced crude using a particular solvent may limit depth of crude reduction. This can be overcome by selection of an appropriate solvent.

The selectivity is very sensitive to solvent-to-oil ratio. At solvent-to-oil ratios below 4:1, the solvent

extraction process is an improvement over vacuum flashing only at deep reductions (23). At solvent-to-oil ratios of 6:1 and higher, the solvent extraction process produces a cleaner oil than does vacuum flashing. This is typical behavior for a long reduced crude.

Effect Of Solvent Type

The solvent power of light hydrocarbons increases with molecular weight. The solvent power of these solvents also depends on the light oil loading of the solvent phase. Thus, as the topped crude is further reduced prior to the solvent extraction step, lower temperatures and/or higher molecular weight solvents must be used in order to recover maximum gas oil. For this reason, the glycol family of solvents have been considered for its use in the solvent extraction process.

Solvent Extraction and Vacuum Flashing Selectivities

The factors affecting selectivity in solvent extraction are solvent-to-oil ratio, solvent type, and the proportion of lighter oils associated with the charge. The effect of the first two factors can be judged from the physical properties of the fractions produced. The effect of the

latter factor is difficult to show, inasmuch as the products to be compared represent different percentages of the crude. This difficulty can be overcome by indirectly comparing the solvent separated fractions with corresponding fractions of the crude prepared by vacuum flashing. Vacuum-flashed and solvent-extracted oils from a short reduced crude have been compared (23) with similarly prepared fractions from a long reduced crude. The results show that changing from a long to a short reduced crude gives a marked improvement in the selectivity of the solvent process.

Rejection Of Metals

One of the criteria used in evaluating a catalytic cracking stock is its metal content. It is well known that iron, nickel, and vanadium are highly deleterious to cracking catalysts. Other metals, such as copper, sodium, and potassium, are also undesirable (2). These metals for the most part find their way to the catalyst via entrainment during vacuum flashing. However, a significant amount of metals may be volatile in nature. Thus, deep vacuum flashing is almost certain to produce metal-contaminated cracking stocks at some stage of reduction, either by entrainment or volatilization, or a combination of the two.

For short reduced crudes the solvent extraction process

is considerably better than flashing in rejecting metals, even at solvent-to-oil ratios as low as 3:1. Thus with short reduced crudes the selectivity of the solvent extraction process is improved and high solvent-to-oil ratios are not required. The solvent extraction process is also effective in removing metals from paraffinic base crudes low in metal content.

Metals-Content Control

Most frequently, the metals content of the overall fresh feed to cracking will govern the depth of extraction. The objective of refiners who have installed (or considered installing) solvent extraction equipment is usually to produce the maximum amount of cracking charge stock containing this specified maximum metals.

In the past, most refiners have limited the metals content of their cracking stock to 1 ppm or less of nickel and other metals. Attempts to run beyond this level resulted in pronounced catalyst poisoning and uneconomical yields of coke at the expense of gasoline. As a result of this restriction, the amount of deasphalted, desulphurized oil produced and the possible reduction in heavy fuel oil in the past were both relatively modest.

With the advent of solvent processes utilizing a wide range of solvents for reducing the effects of metals poisons on cracking catalysts, much deeper extraction may be practiced and more substantial cuts in fuel oil may be accomplished.

Rejection Of Carbon Residue Forming Materials

The carbon residue of a cracking stock appears almost quantitatively as carbon during cracking. Thus, any reduction in carbon residue is economically advantageous. The carbon residue tests (Conradson Carbon, Ramsbottom Carbon, etc.) are strictly empirical but presumably are measures of such materials as resins, high molecular weight aromatics, and asphaltenes. All of these materials are rejected by the extraction solvents.

The Conradson carbon residue test (24) is a means of determining the relative carbon-forming tendencies of oil. Pilot plant data indicate that Conradson carbon residue goes directly to coke in a catalytic cracker; therefore, minimum carbon residue is desirable in a catalytic cracker feedstock. Oden and Granberry (25) report that the Conradson carbon residue of a catalytic charge stock is totally converted to carbon. Carbon residue on average

reduced crude increases with viscosity.

Carbon Formation On The Catalyst Surface

The carbon formation on the catalyst surface is of primary importance for the following reasons:

1.- Carbon burning capacity is the major expense in the design and operation of catalytic cracking equipment and frequently restricts the oil charging rate on commercial units.
2.- Carbon concentrations on the catalyst restricts conversion by reducing the effectiveness of the catalyst.
3.- Increase in carbon deposits lowers the total volume of recoverable liquid and gaseous products.

Solvent extraction greatly reduces the carbon formation on cracking.

Rejection Of Aromatics

Of the various hydrocarbons in petroleum, saturates are the least refractory and produce a small amount of coke. Many aromatic feedstocks with low carbon residues are high carbon-formers in the catalytic cracking process. The aromatic type components in stocks of this nature are

resistant to catalytic cracking and yield principally coke and gas and negligible quantities of gasoline.

Because of the coke-producing tendency of the condensed aromatic nuclei, the most valuable portions of polyaromatics are the saturate appendages (paraffinic side chains). If the side chains are short even they are of little value because the main product is gas (C_2 and lighter). Moreover, certain aromatic or polar type organic compounds are believed to contain the metals found in petroleum. Therefore, the main function of a separation procedure for preparing catalytic cracking feedstock is to recover the more saturated materials and reject the highly aromatic and polar compounds.

Rejection Of Nitrogen And Sulfur Compounds

Sulfur has many deleterious effects on the cracking operation, including modification of catalyst selectivity, reduction in lead response of gasoline stocks, contamination of olefin by-product streams, and corrosion of equipment. Sulfur causes increased coke deposits on the catalyst which requires additional air for combustion. The production of hydrogen sulfide which results when cracking feedstocks contain large amounts of sulfur causes severe corrosion in

product recovery equipment.

Nitrogen is considered a temporary catalyst poison. It is believed to neutralize the acidic centers of the catalyst, thereby reducing the apparent activity. Nitrogen compounds are also highly undesirable in gasolines because of odor and stability considerations.

Production Of High Quality Asphalts

If a profitable asphalt market is available, it is usually desirable to reduce a portion of the crude to the "specification" asphalt stage. This can be done by either vacuum flashing or solvent extraction. The cracking stocks obtained when the solvent process is used are much superior, as have been demonstrated (25). In general, for the same yield, the solvent extraction process produces asphalts of lower penetration and higher softening points that those obtained by using vacuum flashing.

Penetration of asphalt is defined as the consistency of a bituminous material expressed as the distance that a standard needle vertically penetrates a sample of the asphalt under known conditions of loading, time, and temperature. Retention is defined as the percent of the Conradson carbon residue removed from the reduced crude and

retained in the asphalt.

Minimum asphalt is desirable when operating for minimum residual fuel oil production. Minimum asphalt, usually low penetration asphalt, may cause operating problems at times due to difficulties in pumping and blending. Carbon residue on asphalt might be thought of as an indication of the efficiency of the separation process.

Solvent Extraction As A Desulphurizing Process

It has been established that the majority of molecules in high-sulphur residues contain at least one sulphur atom. Any physical separation process such as treatment with superheated water or solvent deasphalting can at most separate high-sulphur residues into fractions of medium and higher sulphur content. However, such physical separation processes could be of value in facilitating residue desulphurization.

Solvent refining methods, such as solvent deasphalting, reduce structural complexity since the most polar molecules, normally the most complex, are least soluble in the solvent (although this is not true for TTEG). Thus, in residue deasphalting, the removal of large, high-molecular-weight molecules such as asphaltenes, polynuclear aromatics and

metallo compounds is achieved (26); these materials contribute greatly to the high cost of residue compared with distillate desulphurization. Everything indicates that solvent extraction has little effect on the sulfur content but significantly reduces the structural complexity of the residue as evidenced by its effects on asphaltene, carbon residue and metals content.

Use Of Rotating Disk Contactors In Solvent Extraction

The rotating disc contactor, RDC, has been applied successfully in a number of liquid-liquid applications. These include lube oil and gas oil extractions, propane deasphalting, sulfur dioxide extraction of kerosene fractions, solutizer treating, recovery of phenol from effluents, extraction of catalytic reformates, and miscellaneous chemicals and specialties applications. The RDC has aroused wide interest in the petroleum industry since it normally provides more extraction stages than the baffle type column normally used for deasphalting or the packed column used for solvent extraction. Extraction efficiency is maintained at all charge rates by varying the rotor speed and temperature, thus generally resulting in a reduction in the quantity of solvent circulated to produce the desired product.

The RDC column (Figure 4) consists of a number of compartments formed by a series of stator rings, with a rotator disk centered in each compartment and supported by a rotating shaft (Figures 5 and 6). The lighter liquid enters the column at the bottom and flows upward countercurrently to the descending heavier liquid which enters at the top. One of the liquids is dispersed by the rotating disks and the size of the droplets formed is controlled in each compartment by rotor speed. The turning of the rotor generates in the liquid in each compartment two toroidal vortices, which rotate in the horizontal plane. In this way a rather uniform degree of turbulence is produced, the intensity of which is governed by the rotor speed for given dimensions and liquid system. Varying the rotor speed provides a simple and effective method of obtaining optimum extraction conditions in each case.

It is believed that by this arrangement an emulsion of relatively uniform drop size is produced since spots with excessive turbulence or very high rates of shear are absent. Low rotor speeds results in large drops which rise rapidly through the contact zone, thereby permitting high throughputs but giving small interfacial areas and low mass transfer rates. A high rotor speed gives very small

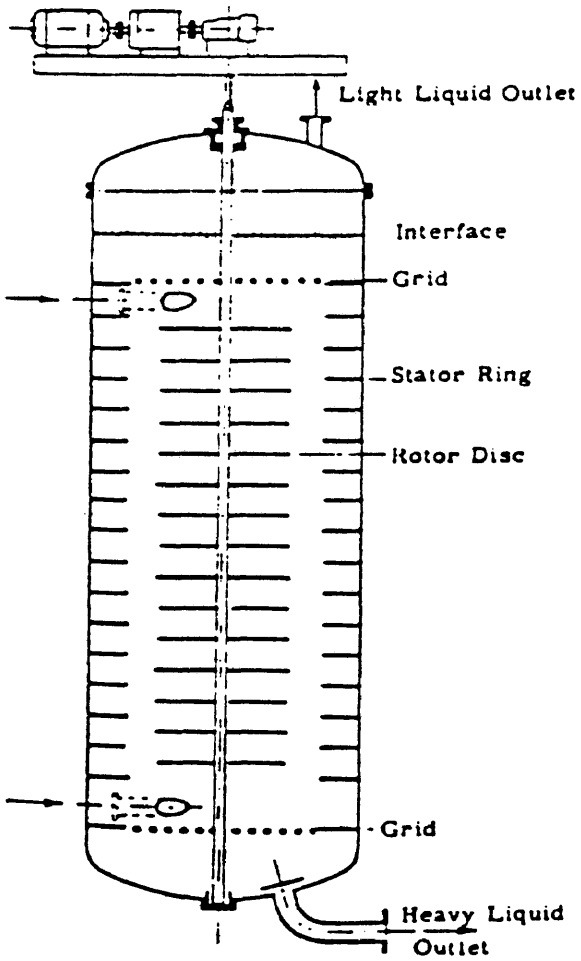


Figure 4

Rotating Disc Contactor (28)

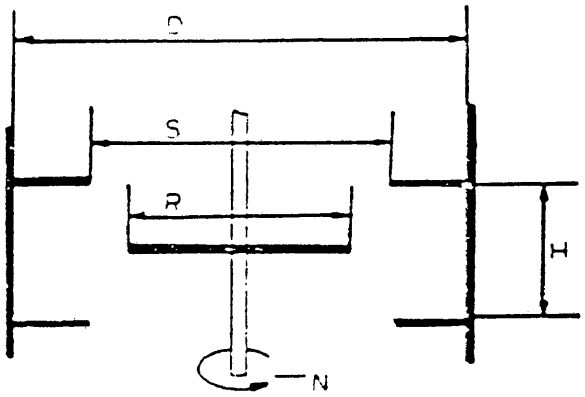


Figure 5

Rotating Disc Contactor Notation

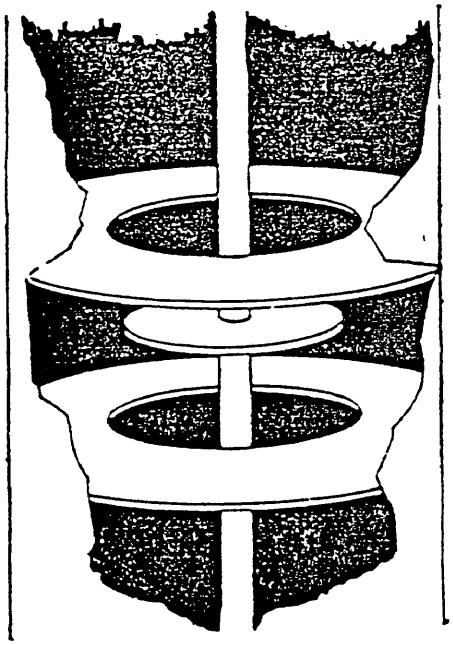


Figure 6

Detail of a Single Compartment of the RDC

approximately spherical drops which revolve many times within a compartment along the toroidal paths. This leads to lower column capacity but gives high mass transfer rates because of the increased interfacial area.

Vermijs and Kramers (27), Reman and van de Vusse (28), and Olney, Strand, and Ackerman (29), have published considerable operational and mass transfer data on specific small and large rotating disk extraction columns. Logsdail, Thornton, and Pratt (30) studied flooding rates for small diameter RDC's in terms of column variables and physical properties. Kung and Beckman (31) observed that during operations of their RDC the size of the dispersed-phase droplet was independent of the phase flow rates and the dispersed-phase holdup.

The principle of contacting the liquid phases as embodied in the RDC stands in sharp contrast to that applied in most conventional types of commercial apparatus. In the latter apparatus an attempt is made to secure a large interfacial area and rapid initial mass transfer by repeating a number of times the process of dispersion under highly turbulent conditions followed by coalescence. However, the uniformity of the dispersion cannot be adequately controlled and interstage coalescence limits capacity.

In the RDC no interstage settling and redispersion is employed. As already mentioned, the size of the droplets formed is controlled and maintained in each compartment with the use of the appropriate rotor speed. Thus, droplet size for a given system depends only on the power dissipated by the rotor discs per unit mass:

$$\text{Power input} = N^3R^5/HD^2 \qquad (1)$$

where N = Rotor speed, revs/sec.
R = Diameter of rotor disc, ft.
H = Height of compartment, ft.
D = Diameter of column, ft.

It has been found that single drop settling velocities can be correlated uniquely by the power input group, independently of phase ratio conditions, degree of contactor loading and RDC dimensions. Interfacial tension turns out to be the most significant property controlling the settling velocity/power input relation when comparing different systems.

With the droplets sizes thus determined by power input, a power input operating range can be defined (Figure 7). The lower limit renders it certain that droplets are small

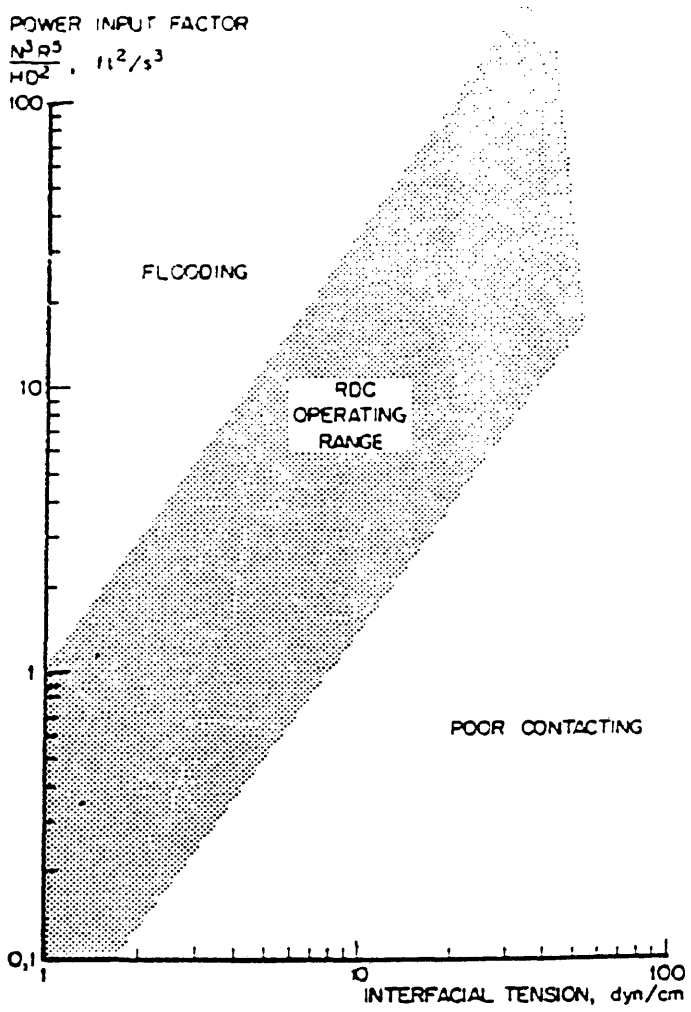


Figure 7

RDC Power Input Group Operating Range (36)

enough to ensure good mass transfer; at the upper limit droplets are becoming too small, so that flooding sets in. The flood-point is characterized by rejection of the solvent phase in the form of a dense layer of small droplets and the formation of a second interface at the bottom of the column.

Flat rotor disks and stator rings without any protrusions create uniform shearing conditions and aid in obtaining a small spread in droplet size (Figure 8). It has been found that protrusions in general give rise to high local shearing stresses and thus to the formation of a considerably amount of fine droplets which under certain circumstances reduce the capacity appreciably.

The flow pattern of the liquid in the compartments is such that the desired countercurrent flow of the dispersed and continuous phase occurs. This flow of liquid consists of a rotation of the whole liquid mass on which there is superimposed a slower movement of the liquid from the shaft towards the wall of the contactor, in the vicinity of the rotor discs, and from the wall back towards the shaft in the vicinity of the stator rings. Thus the resulting flow of the liquid is toroidal. In each compartment two vortices of opposite senses geared together occur and form a complete vortex. Figure 9 shows the dispersed phase flow patterns

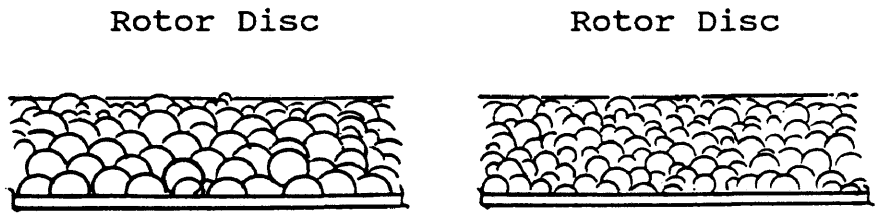


Figure 8

Control of Droplet Size by Variation in Rotor Speed

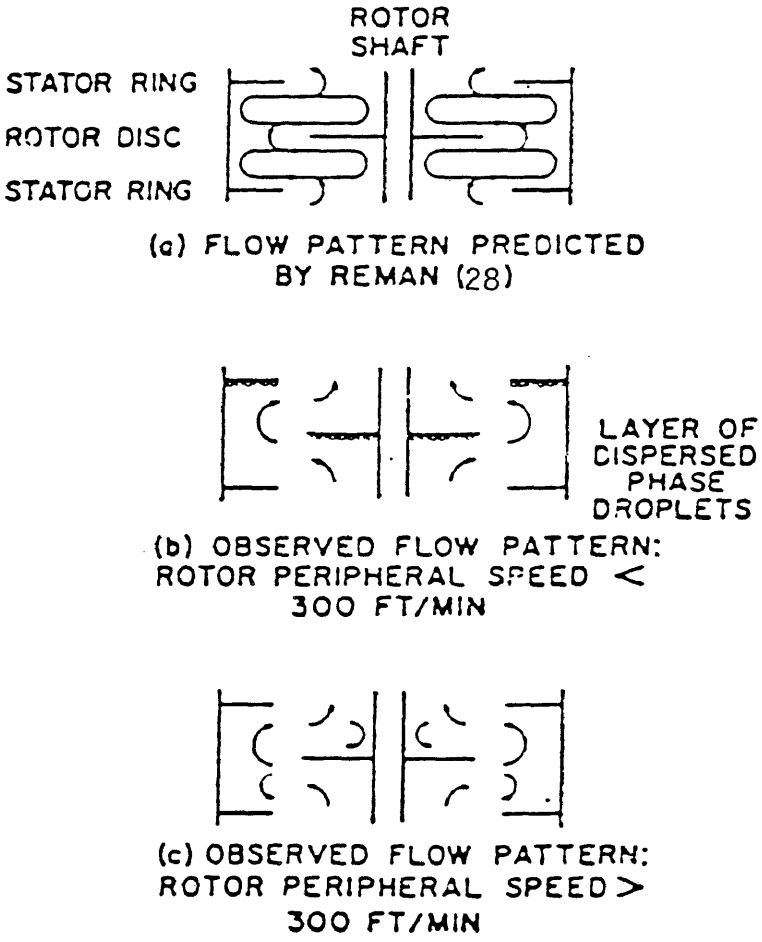


Figure 9

Dispersed Phase Flow Patterns in a RDC (31)

in a rotating disc extraction column.

The energy transferred from the rotor discs to the liquid further creates a rather uniform turbulence in the liquid phase and this appears to be beneficial for obtaining high mass transfer rates, that is, high efficiencies (32).

In addition to increasing the dispersed-phase holdup and the interfacial area, an increase in rotor speed causes an increase in axial mixing of each phase. The two main components of the axial diffusion process are an eddy diffusion or back mixing, most pronounced at highest speeds, and a channeling or Taylor diffusion (radial diffusion) which is specific in the forward direction.

Axial mixing, probably more intense in larger RDC's, reduces the concentration gradient in the solutizer phase and thus decrease the over-all mass transfer efficiency. The above considerations have resulted in a series of studies on axial mixing in RDC's and its effects on mass transfer efficiency. It was found that the axial mixing, expressed as axial diffusivity, could be given for RDC's of 3 in. up to about 7 ft. in diameter by:

$$E_C = 0.5\ HV_C + 0.012\ RNH\ (S/D)^2 \qquad (2)$$

for the continuous phase. Here H, R, N, and D were defined in Equation (1) and also shown in Figure 5, E_c is the axial diffusivity of the continuous phase, S is the diameter of the stator ring opening in feet, and V_c is the superficial velocity of continuous (solvent) phase.

For the dispersed phase the relation has not been so well established. It appears that at the higher rotor speed ranges, dispersed-phase (long residue) diffusivity varies from about one to three times the continuous-phase value.

The effect of axial mixing on extraction efficiency in the most severe case, namely, at an extraction factor of unity, can be approximated by:

$$HTU^*_{ov} = HTU_{ov} + E_d/v_d + E_c/v_c \qquad (3)$$

where HTU^*_{ov} is the apparent overall height of transfer unit, HTU_{ov} is the real overall height of transfer unit, E_d and E_c are the axial diffusivity of the dispersed and continuous phases respectively and v_d and v_c are the real liquid velocity in the dispersed and continuous phases respectively. In this relation, HTU_{ov} characterizes the overall mass transfer efficiency in the absence of axial mixing.

EXPERIMENTAL EQUIPMENT

Figure 10 shows the configuration of the system for the continuous solvent extraction of the long reduced crude. Table 8 gives the legend for the configuration diagram in Figure 10. The system consists of five different sections:

1.- Feed section
2.- Preheat section
3.- Extraction column (RDC)
4.- Sample section
5.- Solvent recovery section

All connections, fittings, tubing, valves, and wetted surfaces are 316 stainless steel, unless otherwise specified.

Feed Section

A positive displacement, reciprocating, metering pump (Bran Lubbe, Model N-P31) of plunger design was used to pump both the solvent and the reduced crude (Figure 11). The solvent pump has an adjustable capacity that ranges from zero to a maximum of 44.4 l/hr. The reduced crude pump also has adjustable capacity and ranges from zero to 2.76 l/hr. The pumps produce pulsating flow resulting in pressure surges of 10 percent. The two pump heads are powered by a

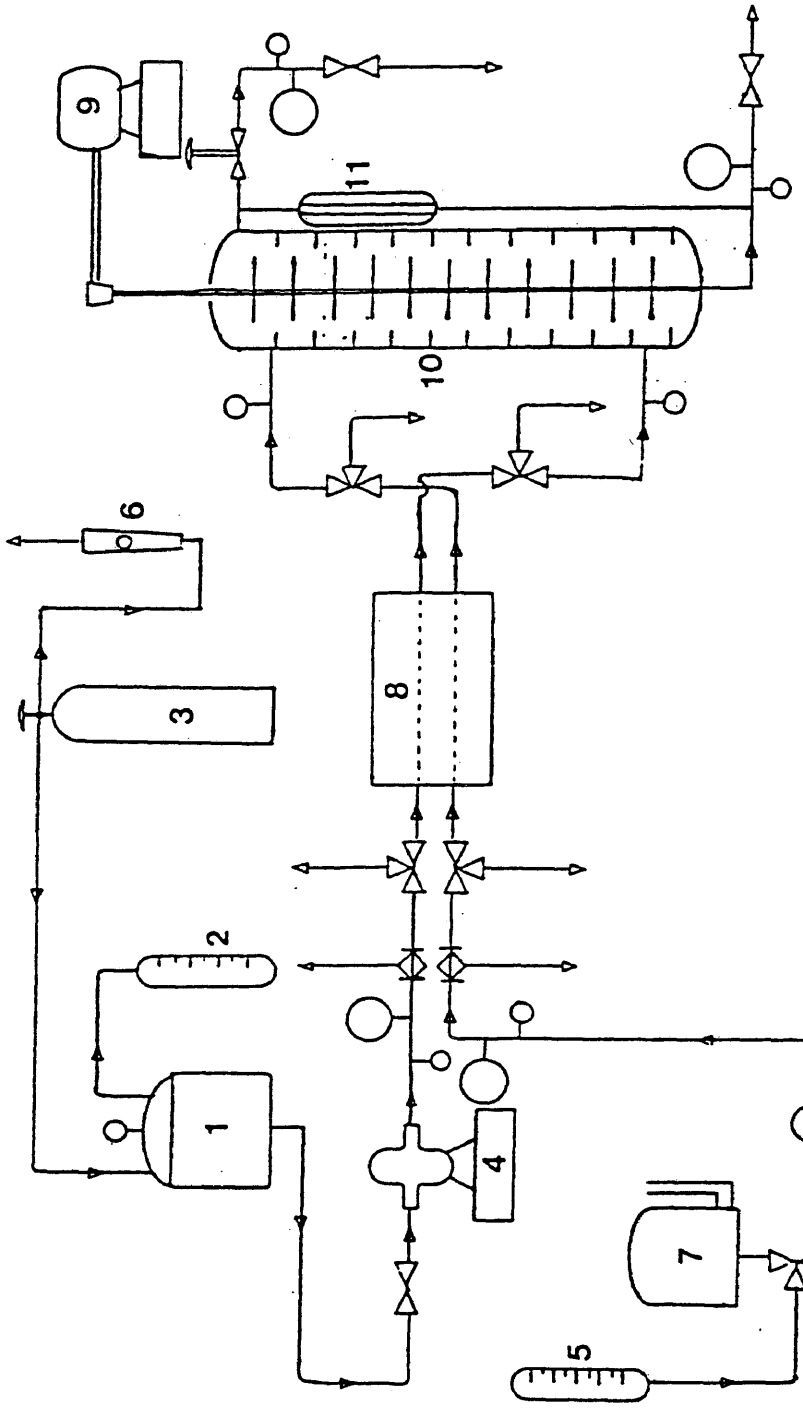


Figure 10

Continuous Solvent Extraction System Configuration

Table 8

Equipment Configuration Diagram Legend

1.- Reduced crude feed tank

2.- Fumes water trap

3.- Nitrogen cylinder

4.- Reduced crude and solvent pump heads

5.- Kerosene/diesel fuel reservoir tank

6.- Nitrogen flowmeter

7.- Solvent feed tank

8.- Tube furnace

9.- RDC Rotor motor

10.- Rotating disc contactor (RDC)

11.- Jerguson liquid level gage

 Needle valve

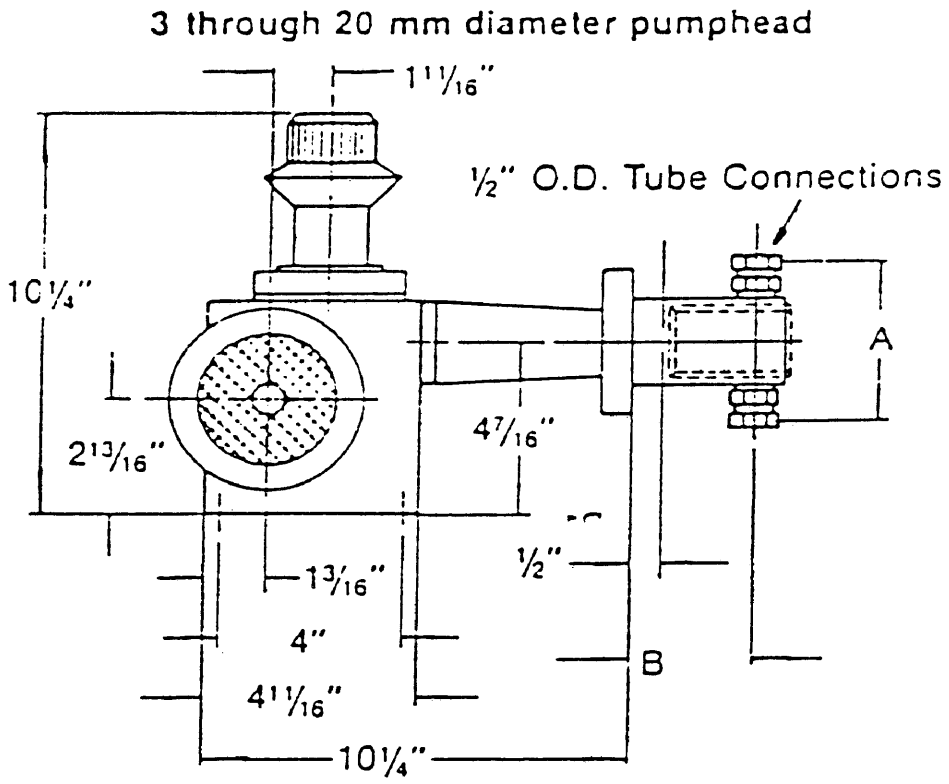
 Relief valve

 Back-pressure regulating valve

 Three-way valve

 Pressure gauge

 Thermocouple



	Dimensions	
Pumphead	A	B
3,5	4 1/4"	2 1/2"
8,12,20	4"	2 3/16"

Figure 11

Plunger Design Type P Metering Pump (37)

common driver allowing for the simultaneous separate pumping of both the solvent and the reduced crude.

The solvent is fed to the pump from a 2 gal. stainless steel tank, its flowrate being controlled by pump stroke. Valves at the pump's suction and discharge lines are kept all open during the pumping operation. The liquid level in the solvent tank can be monitored visually through a open-end Tygon tubing side-level. The reduced crude is fed to the pump from a 3.5 gal. stainless steel tank placed inside a specially designed tank-heater. The tank-heater consists of a metallic frame with Chromalox strip heaters (122V, 250W) attached to its walls. The power input to the tank-heater, which was controlled by a variable autotransformer, allows for a proper temperature setting in the reduced crude tank keeping the residue at a sufficiently high temperature (200-300 ^{o} F) at all times.

The lid of the reduced crude tank was modified to install a nitrogen line, an exhaust line, and a thermocouple. The nitrogen stream was used to provide a nitrogen blanket on the surface of the melted material, to avoid the formation of oxidized compounds. The mixture of fumes and nitrogen leaving the residue tank was passed through a column of water in order to keep the amount of

gases going into the atmosphere at a minimum. A type T thermocouple is installed in the reduced crude tank to monitor the temperature of the residue.

System over-pressure protection is provided by adjustable, spring-loaded relief valves on both the solvent and reduced crude discharge lines. Both relief valves vent into a 1/4 in. stainless steel tube leading to a 30 gal. pressure letdown drum. Heating tape is used to trace the reduced crude pump check valves as well as the suction and discharge lines.

A calibrated rupture disc, designed to rupture at 516 psig provides a secondary over-pressure protection system. The disc is installed on the reduced crude discharge line, venting to the same pressure let-down drum described above.

Preheat Section

The preheat section consists of both the heating tape traces around the solvent and residue tubing, and a Lindberg-Heavy-Duty furnace. This section provides just enough energy to keep the reduced crude melted and to avoid the formation of coke in the lines. The Lindberg furnace is a 1 in. inside diameter by 28 in. long resistance tube furnace.

The heated solvent feed is introduced at the top of the extraction column, while the heated reduced crude feed enters at the bottom of the column. Insulation tape and fiber glass insulation pads are used in order to minimize heat losses. The temperature of both feed streams and exiting streams is monitored by in-line type T thermocouples installed immediately prior to entering the rotating disc contactor (RDC) and at the sample collection lines. A digital temperature readout and manual selector switch allow for the monitoring of the thermocouples.

Extraction Column (RDC)

The RDC shell and internals are built with 316 stainless steel. Stator ring spacing is 2.25 in. resulting in 18 compartments in the mixing zone and 3.5 in. settling zones at each end. The disk diameter is 1.5 in. and the internal diameter of the stators is 2.25 in. A right angle gearbox connected to the top of the shaft allows for shaft speeds of zero to 1000 RPM.

The extraction temperature is controlled in the RDC by a heating tape, powered by a variable transformer, wrapped along the length of the column. The extraction temperature can also be controlled by the temperature of the input

feeds. The column is insulated with a 2 in. layer of foil coated fiberglass.

The interface level in the RDC is monitored with a Series T-12, flat glass Jerguson liquid level gage installed in series with the column. The gage reflects the liquid level changes in the column and its position can be modified to monitor the interface level along the RDC column. The pressure in the column is monitored by pressure gauges located at the extract and raffinate sample lines.

The light phase exiting at the top of the column flows into an adjustable diaphragm back-pressure regulating valve. This valve permits control-operation of the system at the desired pressure without relying only on the exit lines pressure gauges. The interface level is controlled by adjustment of the diaphragm back-pressure regulating valve and/or the needle valve located in the heavy phase draw-off line. The heavy phase exits the bottom of the column in a 1/2 in. line which is also connected to the Jerguson gage.

Sample Section

Samples of extract and raffinate are obtained from the

exiting light and heavy streams; they are collected in 25 ml. glass vials and identified accordingly.

During each run the solvent and the reduced crude are pumped continuously; this produces a continuous flow of extract and raffinate which are collected in 5 gal. cans prior to entering the flash drums and stored for solvent recovery.

Solvent Recovery

The solvent used for the purpose of this research is a mixture of tetraethylene glycol and water (10 and 5 percent by volume). The extract stream is a mixture of extracted material and solvent which is recovered in a Vigreaux distillation column. Due to the closeness of the boiling points of the solvent (314 ^{o}C) and the extracted material (326 ^{o}C), it is necessary to carefully control the distillation temperature. to maximize the purity of the recovered TTEG. The raffinate also contains a small amount of solvent which is recovered by allowing the mixture raffinate-solvent to cool down and then separating the solvent phase by decantation.

EXPERIMENTAL PROCEDURE

Batch Extractions

Prior to operation of the continuous liquid-liquid extraction column, batch extractions were performed in order to determine the solvent-to-oil ratios and percentage of water added that would give a clear phase separation.

These extractions were conducted in a 500 ml separatory funnel. The extraction temperature was reached by wrapping a heating tape around the funnel and controlling its input power with a variable autotransformer; the temperature was monitored with a type T thermocouple.

The volume of solvent used depended on the solvent-to-oil ratio desired. For a reduced crude volume of 50 ml and a desired solvent-to-oil ratio of 3:1, a volume of solvent (90% TTEG - 10% Water) of 150 ml was used. Both, the solvent and the reduced crude were heated until the extraction temperature was reached. The mixture was agitated continuosly for a fixed amount of time and then allowed to settle down and the two phases were separated.

Table 9 shows the solvent-to-oil ratios, temperature of extraction, and number of phases. All of these experiments were carried out at an extraction temperature of 215^{o}F and a

Table 9

Determination of the Minimum Solvent-To-Oil Ratio Required to Give Clear Phase Separation (90% TTEG - 10% Water)

Solvent/Oil	Number of Phases	Temperature (^{o}F)
1:1	One	210.0
1.5:1	One	210.0
2:1	One	210.0
2.5:1	One	210.3
3:1	One	209.9
3.5:1	Two	210.0
4:1	Two	210.0
5:1	Two	210.2
8:1	Two	210.0

water content of 10% in the solvent. These conditions well simulated those planned for the continuous extraction.

The data from Table 9 indicate that solvent-to-oil ratios greater than 3.5:1 were to be used in order to obtain phase separation during the continuous operation. Temperatures lower than 215 ^{o}F were not used because the results would not be of any practical use since this would cause the plugging of the tubing system on the continuous extraction unit.

After determining the range of operational solvent-to-oil ratios, another set of batch extractions was performed in order to determine the percentage of water that would give clear phase separation at a given temperature. The experimental procedure was similar to that performed to determine the solvent-to-oil ratio that gives phase separation. Water was added to a mixture of known volumes of TTEG and reduced crude until the interface was visible. The mixture was kept at a constant temperature of 200 ^{o}F.

Table 10 shows the experimental data obtained for various percentages of water added. These data indicate that for 1% to 5% water added there was no visible interface. However, for 9% to 30% water added, phase separation occurred.

Table 10

Determination of the Minimum Percent Water Required to Give Phase Separation

Water Added (% vol)	Number of phases	Temperature (^{o}F)
1.0	1	210.0
2.0	1	205.7
3.0	1	209.1
4.0	1	211.0
5.0	1	210.1
8.0	1	209.7
9.0	2	209.8
10.0	2	210.2
20.0	2	210.2
30.0	2	210.3

Continuous Extraction

Prior to the continuous operation, the column was heated up to 300 ^{o}F, kerosene was pumped from a third tank connected to the solvent tank through a 3-way valve, and the pressure was allowed to rise to 125 psig. This allowed a check for any leaks in the tubing system and to get rid of undesirable material that might have accumulated in the column. This procedure was repeated before every run was performed.

The following step was to prepare the mixture tetraethylene glycol-water and to preheat the reduced crude feed in a secondary tank-heater. A 5 gal. can containing the hardened reduced crude was placed into the tank-heater and the temperature set to the desired value. When the set temperature was reached, 3 gal. of the melted material were transferred to the continuously heated reduced crude tank which was then connected to the feed pumps through a 1/4 in. stainless steel tubing.

The solvent mixture preparation consisted of the addition of the polar component (water) to the tetraethylene glycol solvent to give a solution containing the percentage of water by volume desired. The solvent reservoir tank was

then charged with 2 gal. of the TTEG-water solution. In order to obtain data for the overall mass balance the bulk collection drums were weighed before and after each run.

Once the reservoir tanks were filled and the pressure test (check for leaks) was performed, the preheat furnace, and RDC and reduced crude heat tapes were turned on until a temperature of about 200 ^{o}F was reached in the system. The pump was turned on with the reduced crude head set at zero and the solvent head set so that the solvent flowrate was about 10 lt/hr. This was done to ensure that the 1/2 in. bottom lines in the RDC would not plug since heat losses were higher at this point; the solvent would also coat the 1/2 in. tubing walls ensuring a clean and fast exit of the heavy material.

After two minutes, the settings in the pumpheads were changed. The solvent head was set to zero and the reduced crude head was set at the maximum stroke. Reduced crude was pumped to the column to about 2/3 of its height and then the pump was turned off; at the same time the temperature of the RDC and the preheat section were set to attain the desired extraction temperature. The temperature in the system was monitored and recorded at all times by the type T thermocouples placed along the preheat section.

Once 2/3 of the column were filled with the reduced crude, the flow rates of solvent and reduced crude were calibrated. This was done by setting either one of the pumpheads to zero and measuring the flow rate of the other one with a graduated cylinder and a stopwatch. Both flow rates were set to attain a solvent-to-oil ratio of 3.5:1. The motor driving the shaft in the RDC was now turned on and set to the desired RPM.

During the start-up process, the material leaving the column was collected in 5 gal. cans for solvent recovery. The back-pressure regulating valve was adjusted to maintain a system pressure of 125 psig.

The interface was visible in the Jerguson gage and it was controlled by the solvent-rich extract phase and raffinate phase flow rates. This required manipulation of the needle valves located at the extract and raffinate exit lines, as well as regulation of the back-pressure diaphragm valve.

When system temperature, exiting flow rates, and interface positions were stable, a digital stopwatch was started. The runs ended after six volumetric throughputs were circulated through the column. The length of the runs varied depending on the flow rates used. For a solvent-to-

oil ratio of 4:1 and a solvent flow rate of 2 lt/hr, the elapsed time for the run was 6.2 hours. For a solvent-to-oil ratio of 4:1 and a solvent flow rate of 6.87 lt/hr, the elapsed time for the run was 2.9 hours.

Solvent and reduced crude flowrates remained unchanged throughout each run. Every 30 minutes a check test for the flowrate was performed. Using side streams installed in the preheat section, it was possible to use graduated cylinders and a stopwatch to measure the flowrates.

Inlet temperatures of both solvent and reduced crude streams and RDC unit were monitored and recorded every 15 minutes. The inlet streams temperatures were controlled by adjustment of the power supplied to the heating tape and preheat furnace. The RDC outlet stream temperatures was controlled by adjustment of the power supplied to the RDC heating tape.

Small temperature changes occurred in the solvent stream when adjustments in flowrate were made, otherwise it remained constant. The temperature in the reduced crude stream varied by a few degrees along the preheat section, but it remained within 5 degrees of the desired temperature. These changes occurred because of heat losses due to poor insulation on some spots in the preheat section.

When interface, temperatures, and product flowrates were stable, composition samples were taken at 15 min. intervals. When the run was completed, the power supplies to the heating tape and preheat furnace in the preheat section were shut off to avoid coke formation on the lines. The rotator shaft motor was also shut off and kerosene was pumped through the solvent pump to flush the system. The collection drums were weighed and their weights recorded. The extract and raffinate samples were analyzed for sulphur and nitrogen content, metals content, Conradson Carbon residue, and asphaltenes content.

TTEG Recovery

The solvent recovery operation was carried out in a packed Vigreaux distillation column. Material from the collection drums containing a mixture of solvent-rich extract and heavy material (raffinate) was poured into a 1.5 liter flask which was connected to a glass-packed distillation column and a glass condenser. The system was kept under vacuum to avoid heating the charge sample above the solvent boiling point (314 ^{o}C) and decomposing the solvent.

Table 11 shows temperature - vapor pressure data for

the tetraethylene glycol solvent. Table 12 shows the distillation data from the solvent recovery operation.

Solvent Stripping of Samples

The solvent contained in the extract and raffinate samples was stripped off prior to the sample analysis. A vial containing the sample was placed on a hot plate and heated until the boiling point temperature of the solvent was reached. A small flow of nitrogen was bubbled through the sample to enhance the stripping process and to minimize the formation of oxidized compounds.

The power input to the hot plate was adjusted by a variable autotransformer and the temperature of the sample was monitored by a type T thermocouple placed inside the sample container. A 3-way valve placed in the nitrogen tank that was used to create the nitrogen atmosphere inside the reduced crude feed-tank, also allowed for the use of the gas for the purpose of stripping the samples. The flow of nitrogen was controlled by the gas-flowmeter described in the Experimental Equipment section.

When there was no visible change in the sample volume the stripping process was considered to be completed. Labeling and storing of the vials followed the stripping

Table 11

Temperature-Vapor Pressure Data for
Tetraethylene Glycol (38)

Pressure (mm Hg)	Temperature (^{o}C)	(^{o}F)
1.00	153.9	309.2
5.00	183.7	362.7
10.00	197.1	386.8
20.00	212.3	414.4
40.00	228.0	442.4
60.00	237.8	460.0
100.00	250.0	482.0
200.00	268.4	515.5
400.00	288.0	550.4
760.00	307.8	586.0

Table 12

Recovery of TTEG From Extract by Distillation

Time (min)	Bottoms Temp. (^{o}F)	Distillate Temp. (^{o}F)	Abs. Pressure mm Hg.	Distillate Vol. (ml)
0.0	115.0	73.0	24.2	0.0
2.0	124.0	76.0	24.0	0.0
6.0	124.0	74.0	23.0	0.0
12.0	124.0	75.0	20.0	0.0
21.0	124.0	75.0	20.0	0.0
29.0	124.0	77.0	20.0	0.0
44.0	140.0	77.0	20.0	0.0
74.0	163.0	77.0	22.0	4.0*
119.0	192.0	76.0	20.0	6.0*
134.0	234.0	76.0	14.0	6.0*
149.0	304.0	76.0	6.0	6.0*
164.0	305.0	77.0	2.0	4.0
179.0	337.0	207.0	1.0	15.0
194.0	349.0	290.0	1.0	56.0
209.0	373.0	311.0	1.0	162.0
224.0	379.0	319.0	1.0	256.0

* Discarded water and light boiling point material.

process.

Emergency Shutdown Procedure

The power input to the reduced crude feed tank, tubing and column heating tape, preheat furnace, shaft motor, pump, and thermocouple digital readout display, is controlled by the main power switch located at the laboratory entrance. The rupture discs installed along the preheat section will burst at a pressure of 516 psig. Plugging of the lines by coke formation or closing of main valves when operating the pump will cause pressure to increase rapidly. In this case, opening of the main valves or shut down of power to the system will prevent the bursting of the rupture discs or any other dangerous event from occurring.

The pressure of the RDC unit was monitored and controlled during the extraction operation. Pressure gauges up to 1000 psig were installed in preheat section and the outlet streams. RDC maximum design pressure is 400 psig.

Telephone numbers of the student, student advisor, and local fire and police departments were placed at the laboratory entrance.

MASS BALANCE CALCULATION PROCEDURE

An overall mass balance was done around the system for several runs to calculate the extract and raffinate yields.

Calculation of Mass Entering the System

The mass of the solvent entering the system was calculated by using the volumetric flowrate, specific gravity of the solvent, and actual elapsed run time. The mass of solvent introduced to the column was then the product of the density of solvent and the volume introduced. The mass of the reduced crude introduced to the extraction unit was calculated by the difference between the initial and final weight of the reduced crude tank determined for each run.

Calculation of Mass Leaving the System

The 5 gal. drums used to collect the extract and raffinate products were weighed prior to and after each run. The volume of the samples collected for analysis was negligible compared to the total mass output. The overall mass balance was then the sum of solvent and reduced crude streams balanced against the sum of the extract and raffinate streams.

Determination of the Extract and Raffinate Yields

After removing the solvent (TTEG-Water) from the composition samples, the recovered solvent and the products were weighed. The weight of the solvent remaining in the samples was determined by washing the samples with distillate water in a separatory funnel. After successive washings the funnel was weighed again and the extract and raffinate products weights were determined by difference. This procedure allowed calculation of the total percent solvent present for each phase in the separatory funnel.

The total solvent recovered from the composition samples is the sum of the solvent recovered by distillation and the solvent recovered by water washings (Tables 13 and 14). Having calculated the solvent content (and hence the oil content) of both phases, these values were applied to the total extract mass and raffinate mass from the overall mass balance for the specific run. This gave the solvent-free masses of each phase. The raffinate oil yield is then, the solvent-free raffinate mass divided by the mass of the inlet reduced crude for the specific run:

$$RY = M\text{-}solv/M\text{-}crud$$

Table 13

Total Amount of Solvent Recovered From Raffinate Samples
(Percent by Weight)

Run	Sample	Wt %	Ave. Wt %
1	R1-R	19.37	19.37
2	R2-R1	19.70	20.011
2	R2-R2	20.32	
3	T1-R	9.92	9.92
4	R3-R1	8.67	9.240
4	R3-R2	9.81	
5	R4-R1	9.33	10.710
5	R4-R2	12.09	
6	R5-R1	21.49	20.120
6	R5-R2	18.75	
7	R6-R1	10.21	8.530
7	R6-R2	6.85	
8	R7-R	9.27	9.270
9	R8-RS	11.20	11.202

Table 14

Total Amount of Solvent Recovered From Extract Samples (Percent by Weight)

Run	Sample	Wt %	Ave. Wt %
1	R1-E	97.06	97.06
2	R2-E1	97.24	97.17
2	R2-E2	97.11	
3	T1-E	97.27	97.27
4	R3-E1	98.21	
4	R3-E2	98.93	98.42
4	R3-E3	98.12	
5	R4-E1	97.15	97.62
5	R4-E2	98.10	
6	R5-E1	97.41	97.04
6	R5-E2	96.67	
7	R6-E1	97.80	98.06
7	R6-E2	98.33	
8	R7-E1	96.97	97.32
8	R7-E2	97.67	
9	R8-E	98.05	98.05

where RY = Raffinate oil yield

M-solv = Solvent-free raffinate mass

M-crud = Inlet reduced crude mass.

Solvent-free extract and raffinate yields for each run are shown in Table 20, page 96.

RESULTS AND DISCUSSION OF RESULTS

Characterization of Zuata 44X Crude Oil

The analyses of the Zuata 44X crude oil used in this research work are shown in Tables 15 through 17. The identification data (sample number, well depth, source, etc.) of the crude are shown in Table 15. The characterization of the crude oil is shown in Table 16. The API gravity was 9.3, the pour point was 70 ^{o}F, the viscosity at 210 ^{o}F was 200.9 centistokes and the asphaltenes content was 11.12% by weight. The sulphur content was 3.68% by weight, vanadium content was 419.63 ppm by weight, and nickel content was 87.85 ppm by weight.

Table 17 gives the yield and properties of Zuata 44X atmospheric residue above 370 ^{o}C. The specific gravity was 1.0254 (API gravity of 6.49), the pour point was 120 ^{o}F, the kinematic viscosity was 906.5 centistokes at 210 ^{o}F, the Conradson carbon residue was 15.40% by weight, and the asphaltenes content was 12.04% by weight. The sulphur content was 4.06% by weight, vanadium content was 430.65 ppm by weight, and nickel content was 99.73 ppm by weight. These analyses were performed by the Venezuelan research institute, Intevep S. A., Process Development Department.

Table 15

Zuata 44X Crude Identification (38)

Sample No.	PDVSA_0195
Crude Oil	SDZ-44X
Field	ZUATA
Area	FAJA ORINOCO
Sample Source	MARAVEN
Depth, ft.	2023 - 2142'
Sampling Date	27/10/81
Report Date	01/06/82

Table 16

Zuata 44X Crude Oil Characterization
Class I Assay (38)

Specific Gravity at 15/4 °C	1.0050	
Gravity API at 60 °F	9.30	
Kinematic Viscosity		
at 100 °F	38505.40	cS
at 122 °F	7245.30	cS
at 140 °F	1785.10	cS
at 180 °F	442.50	cS
at 200 °F	272.60	cS
at 210 °F	200.90	cS
Pour Point	70.00	°F
Flash Point	230.00	°F
Reid Vapor Pressure	NIL	psi
Water and Sediment	1.42	% vol
Salt Content (as Sodium Chloride)	13.40	lbs/1000 BBLS
Sulphur Content	3.68	% wt
Mercaptans (as S)	45.70	ppm wt
Vanadium Content	419.63	ppm wt
Nickel Content	87.85	ppm wt
Existing Hydrogen Sulfide	NIL	ppm wt
Total Acid Number	3.01	mg KOH/g
Asphaltenes	11.12	% wt
UOP K Characterization Factor	11.50	

Table 17

Yield and Properties of Zuata 44X Atmospheric Residue Above 370 °C (38)

Yield on Crude Oil	87.65 % wt
Yield on Crude oil	85.91 % vol
Specific Gravity at 15/4 °C	1.0254
Kinematic Viscosity	
at 180 °F	2571.70 cS
at 210 °F	906.50 cS
Pour Point	120.00 °F
Sulphur Content	4.06 % wt
Vanadium Content	430.65 ppm wt
Nickel Content	99.73 ppm wt
Asphaltenes	12.04 % wt
Conradson Carbon Residue	15.40 % wt

Experimental Data From Batch Extractions

As stated in the previous section, the data obtained from the batch extractions indicate that solvent-to-oil ratios greater or equal to 3.5/1 at 180 ^{o}F must be used in order to obtain phase separation. Somekh and Friedlander (17) have done research work on the use of TTEG for the recovery of BTX. They concluded that it is desirable to operate at a solvent-to-oil ratio of about 4/1 in order to obtain phase separation and a high recovery and high purity aromatics as well as lowering operating costs. This indicates that the results obtained in the batch runs during this research work are in agreement with those obtained by those authors.

Data shown in Table 10 show that an increase in percent water added to the TTEG solvent at a fixed temperature of 210 ^{o}F enhances the separation of phases. At a level of 1% to 5% added water to the solvent there was no visible separation of phases, while at levels of 9% to 30% added water the interface was clearly visible. As the percentage of water in the solvent mixture increased, the interface clarity also increased. The effects of adding a polar component to the solvent were discussed in the previous sections.

Experimental Data From Continuous Extraction

Operating Variables

The RDC pressure was maintained at a constant pressure of 125 psig throughout all runs. Because of the high viscosity of the raffinate phase it was necessary to keep a high pressure in the column at all times to avoid variations in the raffinate flowrates; this was also the lowest pressure recommended by the manufacturer for the operation of the back-pressure regulating valve.

As was mentioned in previous sections, the important operating factors are extraction temperature, solvent-to-oil ratio, and solvent composition. Another variable to be considered is rotor speed, since in the extraction columns with a rotating element such as the RDC the intimacy of the contact between the two liquid phases depends primarily on rotor speed.

The goals of this research work were to study the effects of variation of the operating variables on the extraction performance of the rotating disc contactor (RDC). Other fundamental aspects of the RDC performance such as determination of the relative hold-up of the dispersed phase, estimation of flooding rates, axial mixing and its

effect on extraction efficiency, and calculation of mass transfer data as well as studies of interfacial phenomena, have been widely studied by several authors (29,31,39,40) during the last fives decades.

Table 18 shows the operating conditions of the continuous extractions. The lowest solvent-to-oil ratio used was 4/1 since the batch extractions showed no phase separation below 3.5/1 for a solvent composition of 90% TTEG - 10% Water.

Mass Balances Discussion

The overall mass balances on each run were calculated following the procedure detailed in the previous section. Table 19 shows the total mass balance performed on the solvent extraction unit for run No. 7. The total amount of inlet mass was 47.371 lbs. and the total amount of outlet mass was 47.162 lbs.; this indicates a loss of 0.209 lbs. of material. The losses in each run are thought to be due to sampling errors, transfer losses, and solvent recovery losses. The mass of products calculated as percent of total inlet mass was 99.55% for this run.

The total mass of extract collected was 83.29% while the total mass of raffinate collected was 16.70%. Mass

Table 18

Operating Variables for the Continuous Extraction
(at Constant Pressure of 125 psig)

Run #	% Water content	T(^{o}F)	Rotor (RPM)	S/O	Sample Name
1	10	214	100	4/1	R1-E, R1-R
2	10	214	300	4/1	R2-E1,R2-E2,R1-R1,R2-R2
3	10	214	300	4/1	T1-E, T1-R
4	10	214	800	6/1	R3-E1,R3-E2,R3-E3,R3-R1,R3-R2
5	10	230	800	5/1	R4-E1,R4-E2,R4-R1,R4-R2
6	5	214	800	5/1	R5-E1,R5-E2,R5-R1,R5-R2
7	5	214	800	5/1	R6-E1,R6-E2,R6-R1,R6-R2
8	0	214	800	5/1	R7-E1, R7-E2, R7-R
9	10	214	500	4/1	R8-E, R8-RS

Table 19

Total Mass Balance for the Extraction Operation (Run 7)

Mass In (lbs)		Mass Out (lbs)	
Solvent	39.504	Extract (bulk)	39.100
Reduced Crude	8.367	Raffinate (bulk)	7.812
		Extract Samples (R6-E1, R6-E2)	0.360
		Raffinate Samples (R6-R1, R6-R2)	0.390
Total Mass In	47.871	Total Mass Out	47.662

Mass Out as % of Mass In = 99.56%

* 95% TTEG - 5% Water

balances and hydrocarbon balances for each run are given in Appendix A.

Products Yield Results

The sample analyses were performed by Lagoven S. A., Amuay refinery laboratories in Venezuela. The following methods were used for those analyses (43):

a) Conradson carbon residue, ASTM D-189 Method
b) Vanadium and nickel content, Sulphated ash-Spectrophotometry Method
c) Asphaltenes content, IP 143 Method
d) Sulphur content, ASTM D-2622 and X-rays Fluorescence Methods
e) Kinematic viscosity, ASTM D-2170 Method.

Procedures for the determination of the raffinate and extract yields were discussed in previous sections. The raffinate yield was calculated as the ratio of the solvent-free raffinate mass to the total inlet mass of reduced crude. Similarly, the extract yield was obtained by dividing the solvent-free mass of extract by the total reduced crude inlet mass. Table 20 gives the solvent-free extract and raffinate yields as well as the operating parameters for each run.

Table 20

Solvent-Free Extract and Raffinate Oil Yields
Based on Inlet Reduced Crude Mass

Run #	Temperature (^{o}F)	Raffinate Yield	Extract Yield	S/O	Rotor (RPM)	% Vol Water
1	214	91.78	7.99	4/1	100	10
2	214	90.87	8.98	4/1	300	10
3	214	90.76	9.01	4/1	300	10
4	214	89.79	9.94	6/1	800	10
5	230	87.71	11.30	5/1	800	10
6	214	91.22	8.95	5/1	800	5
7	214	89.43	9.12	5/1	800	5
8	214	89.58	9.07	5/1	800	0
9	214	89.08	9.15	4/1	500	10

Effects of Rotor Speed on Extract and Raffinate Properties and Yields

Changes in rotor speed were performed in order to study its effect on the mass transfer rates, and hence, on the extract and raffinate yield. Rotor speeds of 100, 300, 500, and 800 RPM were used. Rotor speeds greater or equal to 800 RPM (equivalent to a peripheral rotor speed of 314 ft/min) are required in an RDC in order to establish toroidal fluid flow patterns in the compartments, rather than a simple rotation of the whole mass around the rotor shaft of the RDC (31).

In the RDC the drop size distribution depends mainly on the flow conditions in the extractor, which are determined primarily by the rotor speed, so a proportionality between the overall mass transfer coefficient and the volume fraction occuppied by the dispersed phase can be expected for a constant speed of the rotor.

Variations in the rotor speed cause changes in the uniform degree of turbulence of the fluids, the intensity of which is governed by the specific rotor speed used. Hence, relatively uniform droplets size

is produced since spots with excessive turbulence or very high rates of shear are absent (if toroidal flow pattern is present).

Increase of the rotor speed results in the creation of smaller droplets size which increases the total mass transfer area. This results in enhancement of the overall mass transfer coefficient, hence, increasing extract yield. As a result of the reduction in the average drop size of the dispersed (raffinate) phase there is an improvement of the efficiency of the column (the values of the H.E.T.S. or height equivalent to one theoretical stage decrease with rotor speed), and the maximum throughput of the column is limited to a lower value.

The effects of rotor speed on the extract and raffinate yields are given in Table 20 for runs 1, 2, and 9. The rotor speed was changed from 100 RPM (39.25 ft/min) in run 1 to 300 RPM (117.75 ft/min) in run 2, to 500 RPM (196.25) in run 9, all other variables being constant. The extract yield increased from 7.99% in run 1 to 8.98% in run 2, for an increase of 11.02%; the raffinate yield decreased from 91.78% in run 1 to 90.87% in run 2 for a yield reduction of 0.99%. The rotor speed was then increased from 300 to

500 RPM (117.75 to 196.25 ft/min) in runs 2 and 9. The results indicate again an increase of the extract yield with an increase of rotor speed at the same temperature of extraction, solvent composition, and solvent-to-oil ratio. Figures 12 and 13 show the increase and decrease of the extract and raffinate yields respectively when runs 1, 2, and 9 data were compared. These results were expected since, as was discussed previously, an increase in rotor speed reduces the droplet size increasing the mass transfer area hence increasing the flux of species i transfering from the dispersed phase to the continuous phase. Thegze, et al (32) have shown that the rotor speed not only affects the extract and raffinate yields, but also the viscosity of these products.

All runs performed in this study produced small extract yields. The reasons for these low yields are thought to be due to the use of low rotor speeds; since all runs except one were performed at rotor speed below the 800 RPM (314 ft/min) required to create the toroidal fluid flow patterns, there was probably just a simple rotation of the whole mass around the rotor shaft which had a serious effect in the creation of small droplets, therefore, affecting the overall mass

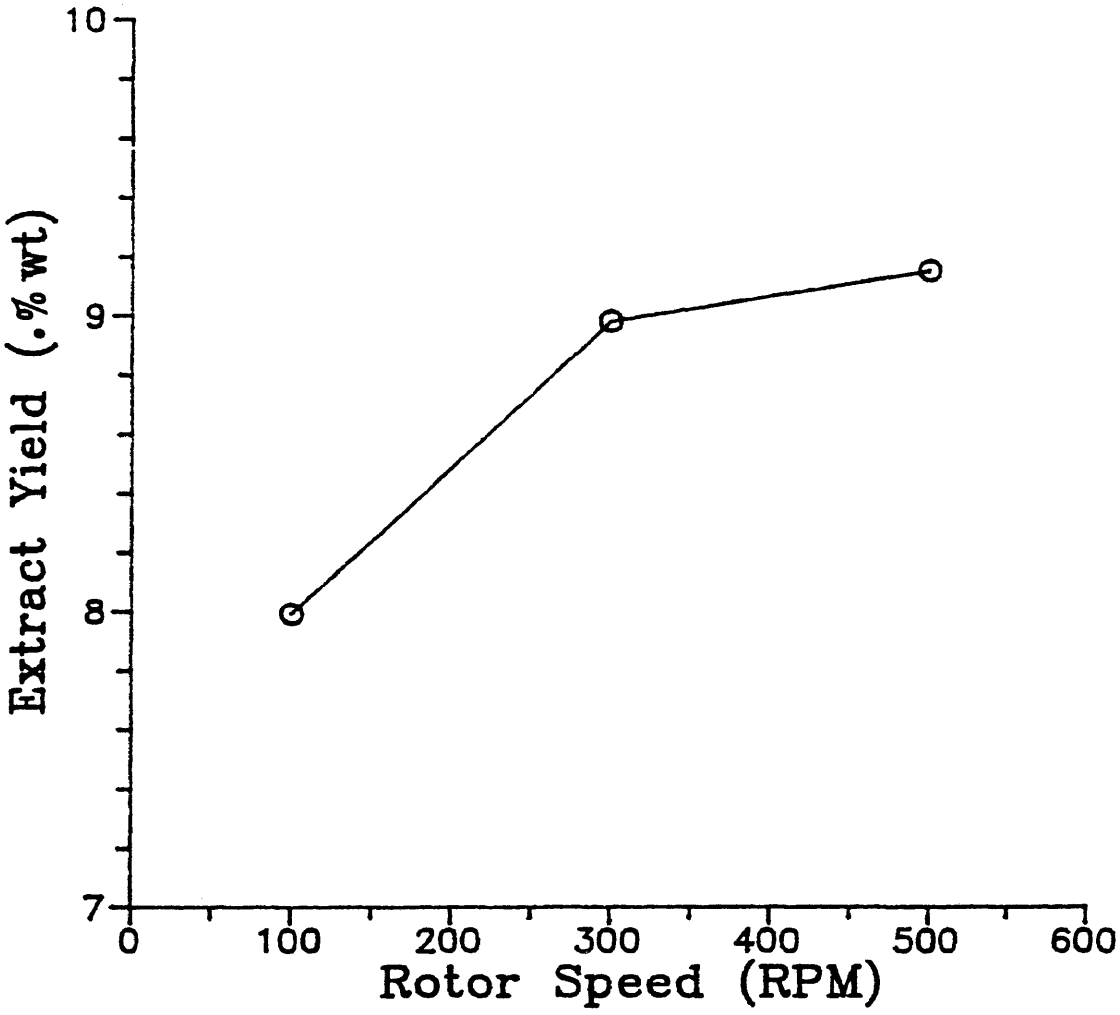


Figure 12

Effects of Rotor Speed on Extract Yield

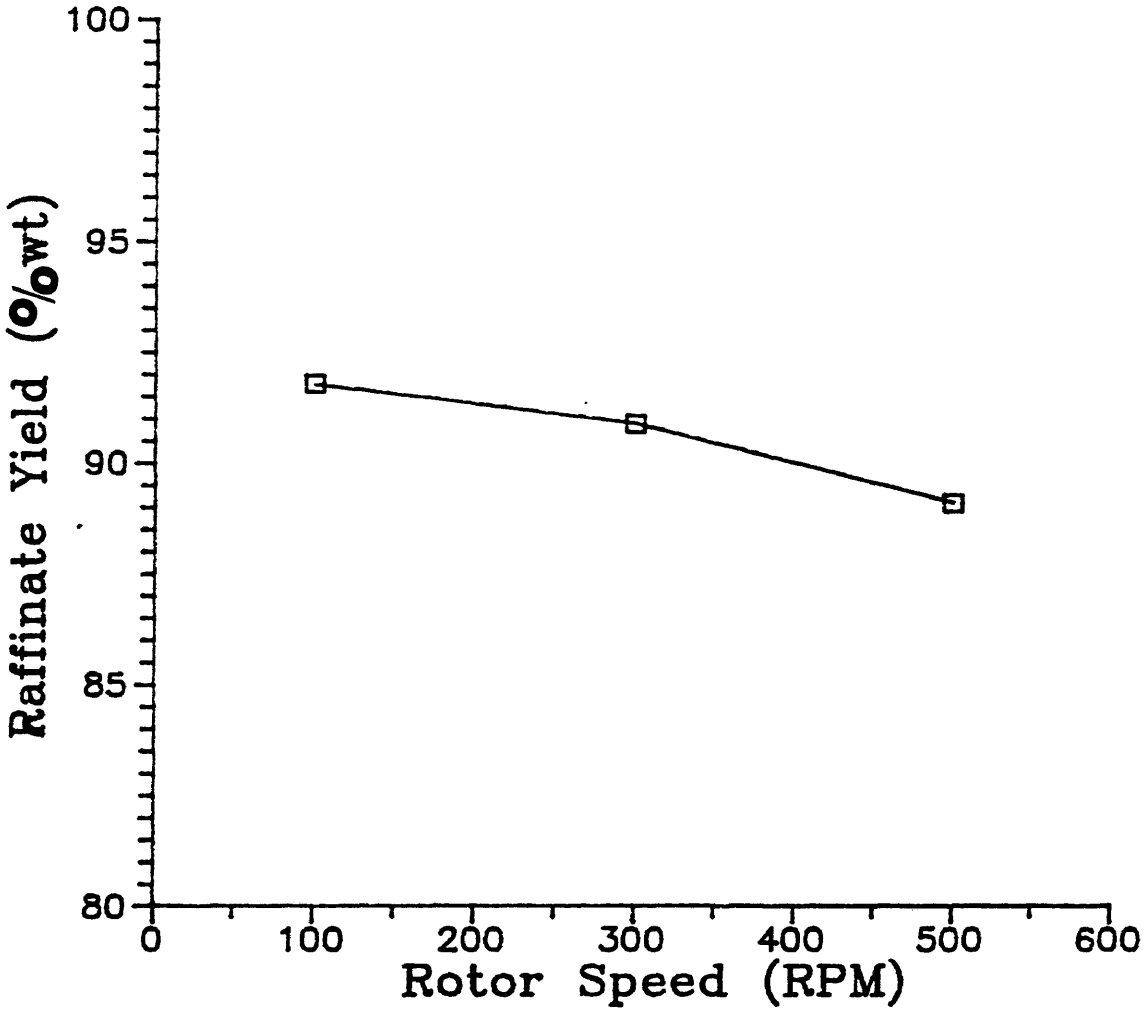


Figure 13

Effects of Rotor Speed on Raffinate Yield

transfer process.

Table 21 shows an increase in the kinematic viscosity of the extract for runs 1, 2, and 9. It changed from 17.98 centistokes (122/120 ^{o}F) in run 1 to 16.50 centistokes (122/120 ^{o}F) in run 2, and to 15.85 centistokes (122/120 ^{o}F) in run 9 for the extract. Table 22 shows an increase in the kinematic viscosity with rotor speed for the raffinate which changed from 3.39 centistokes (210 ^{o}F) in run 1 to 2130 centistokes (210 ^{o}F) in run 2. Data on kinematic viscosity for raffinate in run 9 are not available.

The increase of extract yield shown with the increase in rotor speed has a trade off; that is, for higher yields we get higher amounts of undesirable components such as sulphur, metals, asphaltenes, and higher Conradson carbon residues.

Tables 21 and 22 show increases in sulphur content for the extract in runs 1, 2, and a decrease in run 9. Sulphur content changed from 0.032 wt % (run 1) to 0.206 wt % (run 2), and to 0.072 wt % (run 9) for the extract; it changed from 0.105 wt % (run 1) to 2.568 wt % (run 2), and to 1.198 wt % (run 6) for the raffinate.

Table 21

Analytical Data for Extract Samples

Run #	Sample Name	S (%wt)	CCR (%wt)	Kinem. Visc. (cS @ 122/120 F)	V (ppm)	Ni (ppm)
1	R1-E	0.032	0.35	17.98	3.0	0.4
2	R2-E1	0.206	2.42	19.47	2.9	-
2	R2-E2	0.023	0.15	-	3.7	0.4
3	T1-E	0.012	0.35	15.36	1.0	0.0
4	R3-E1	0.066	0.98	17.96	17.7	0.7
4	R3-E2	0.094	1.44	18.87	2.7	0.1
4	R3-E3	0.023	0.21	13.12	12.1	0.1
5	R4-E1	0.108	1.59	19.31	7.5	0.0
5	R4-E2	0.062	0.74	17.16	7.9	0.0
6	R5-E1	0.038	0.50	15.91	21.4	0.3
6	R5-E2	0.059	0.90	18.13	10.6	0.3
8	R7-E1	0.033	0.25	12.46	0.9	0.7
8	R7-E2	0.076	1.00	19.32	7.7	0.3
9	R8-E	0.072	3.67	15.85	6.6	1.7

Table 22

Analytical Data for Raffinate Samples

Run #	Sample Name	S (%wt)	CCR (%wt)	Kinem. Visc. (cS @ 122/120 F)	V (ppm)	Ni (ppm)
1	R1-R	0.105	0.450	3.39*	3.1	0.9
2	R2-R1	-	8.320	-	235.0	40.0
2	R2-R2	2.568	12.95	2130*	272.0	39.7
3	T1-R	3.071	16.11	-	357.0	52.2
4	R3-R1	2.431	8.0	-	243.0	38.1
4	R3-R2	1.984	10.96	-	280.0	31.0
5	R4-R1	1.462	9.85	5662*	180.0	13.2
5	R4-R2	2.250	14.84	-	299.0	60.1
6	R5-R1	1.141	4.870	-	102.8	16.1
6	R5-R2	1.256	4.420	2508*	44.8	7.0

* Kinematic viscosity calculated at 210 ^{o}F

It must be noted that there are no available data on raffinate properties for run 9, therefore, data from run 6 is being used. The vanadium content of the extract changed from 3.0 ppm by wt (run 1) to 3.3 ppm by wt (run 2), and to 6.6 ppm by wt (run 9). The vanadium content of the raffinate changed from 3.1 ppm by wt (run 1) to 253.5 ppm by wt (run 2), and to 73.8 ppm by wt (run 6). The nickel content in the extract was constant at 0.4 ppm by wt for both runs 1 and 2, and it increased sharply to 1.7 ppm by wt in run 9. The nickel content of the raffinate changed from 0.9 ppm by wt (run 1) to 40.0 ppm by wt (run 2), and to 11.55 ppm by wt (run 6). Table 21 shows that there is a decrease in CCR from 0.35 wt % in run 1 to 0.15 wt % in run 2, and to 0.67 wt % in run 9 for the extract. Table 22 shows an increase in CCR from 0.45 wt % in run 1 to an average value of 10.63 wt % in run 2, and there is a decrease to 4.64 wt % in run 6 for the raffinate.

A comparison between the properties of the feed, and the properties of the extract and raffinate for changes in rotor speed is given in Tables 23 and 24. Figures 14 and 15 are graphical representations of the experimental data in runs 1, 2, and 9.

Table 23

Comparison of Properties of Feed with Properties of Extract for Rotor Speed Changes

Property	Feed	Run 1	Run 2	Run 9
Sulphur Content, % wt	4.06	0.032	0.206	0.072
Vanadium Content, ppm	430.65	3.000	3.300	6.600
Nickel Content, ppm	99.73	0.400	0.400	1.700
CCR, % wt	15.40	0.350	0.150	0.670

Table 24

Comparison of Properties of Feed with Properties of Raffinate for Rotor Speed Changes

Property	Feed	Run 1	Run 2	Run 6
Sulphur Content, % wt	4.06	0.105	2.568	1.198
Vanadium Content, ppm	430.65	3.100	253.5	73.8
Nickel Content, ppm	99.73	0.900	39.85	11.55
CCR, % wt	15.40	0.450	10.63	4.64

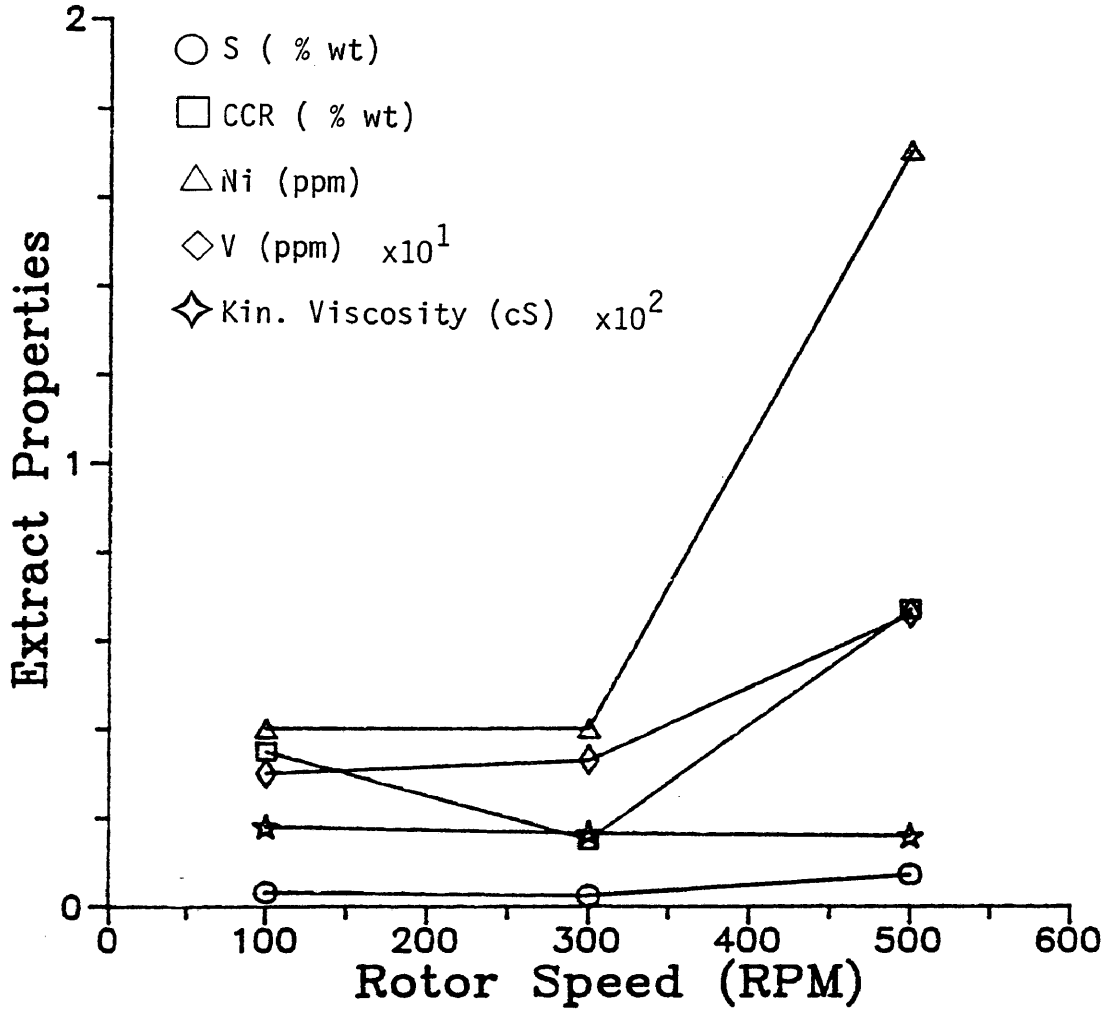


Figure 14

Effects of Rotor Speed on Extract Properties

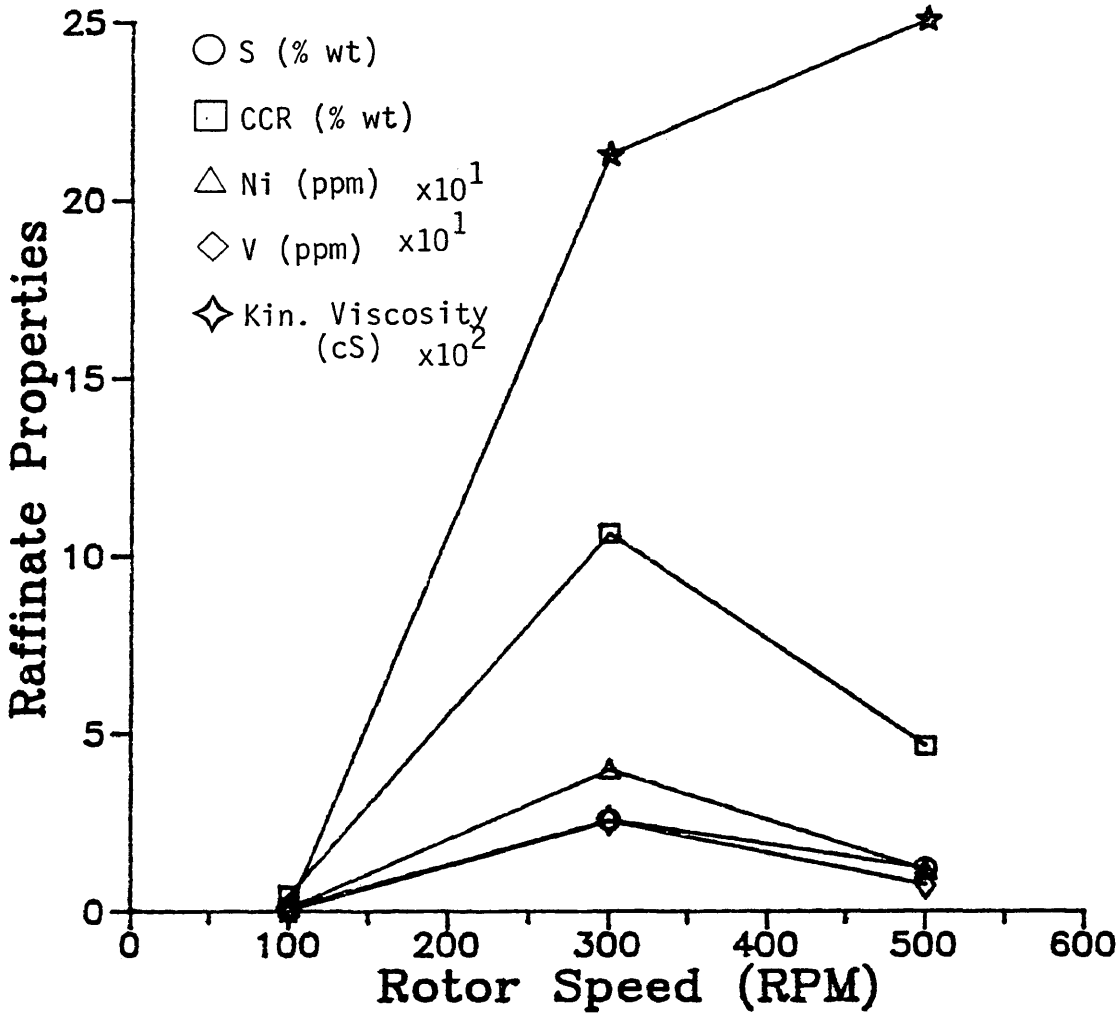


Figure 15

Effects of Rotor Speed on Raffinate Properties

Effects of Temperature and Solvent Composition Changes on Yield and Product Properties

The operating temperature was kept constant for all runs but one, to show the effects of changes in this operating variable in the column performance. Dahm (34) reports enhanced mass transfer (increased extract yield) with increasing temperature. The results obtained in this research work also indicate increase of extract yield with temperature.

Extraction temperature for runs 1, 2, 3, 4, 6, and 7 was 214 ^{o}F. Run 5 was performed at a temperature of 230 ^{o}F.

Increased temperature increases the solubility of the dispersed (reduced crude) phase and above the critical solution temperature they would dissolve completely. At higher temperatures the area of hetereogeneity decreases. Liquid extraction operations such as this one, which depend upon the formation of insoluble liquid phases (extract and raffinate), must be carried on at temperatures below the critical solution temperature.

The addition of polar components to the solvent was discussed in detail in previous sections. Solvent

mixtures with 10 % and 5 % of water added and pure solvent (0%) were used in this extraction operation. The addition of higher amounts of water was avoided for the following reasons: the selectivity of the extraction solvent is improved by the addition of water, however, water drastically reduces the capacity of the solvent for the components to be recovered. Therefore, only small proportions of water can be incorporated into the solvent.

Data from Table 20 indicate that lowering the extraction temperature from 230 ^{o}F in run 5 to 214 ^{o}F in run 6 at a constant pressure of 125 psig, a constant solvent-to-oil ratio of 5/1, and constant rotor speed of 800 RPM, increases the raffinate yield from 87.71 in run 5 to 91.22% in run 6 (and decreases the extract yield from 11.30% to 8.95%). This increase in raffinate yield and conversely a decrease in extract yield, is expected because of the solubility changes discussed previously.

All operating conditions in runs 5 and 6 were kept constant except for the extraction temperature (214 to 230 ^{o}F) and the solvent composition (10% to 5% water). Figure 16 shows both the increase of extract yield and the decrease of raffinate yield for these two runs.

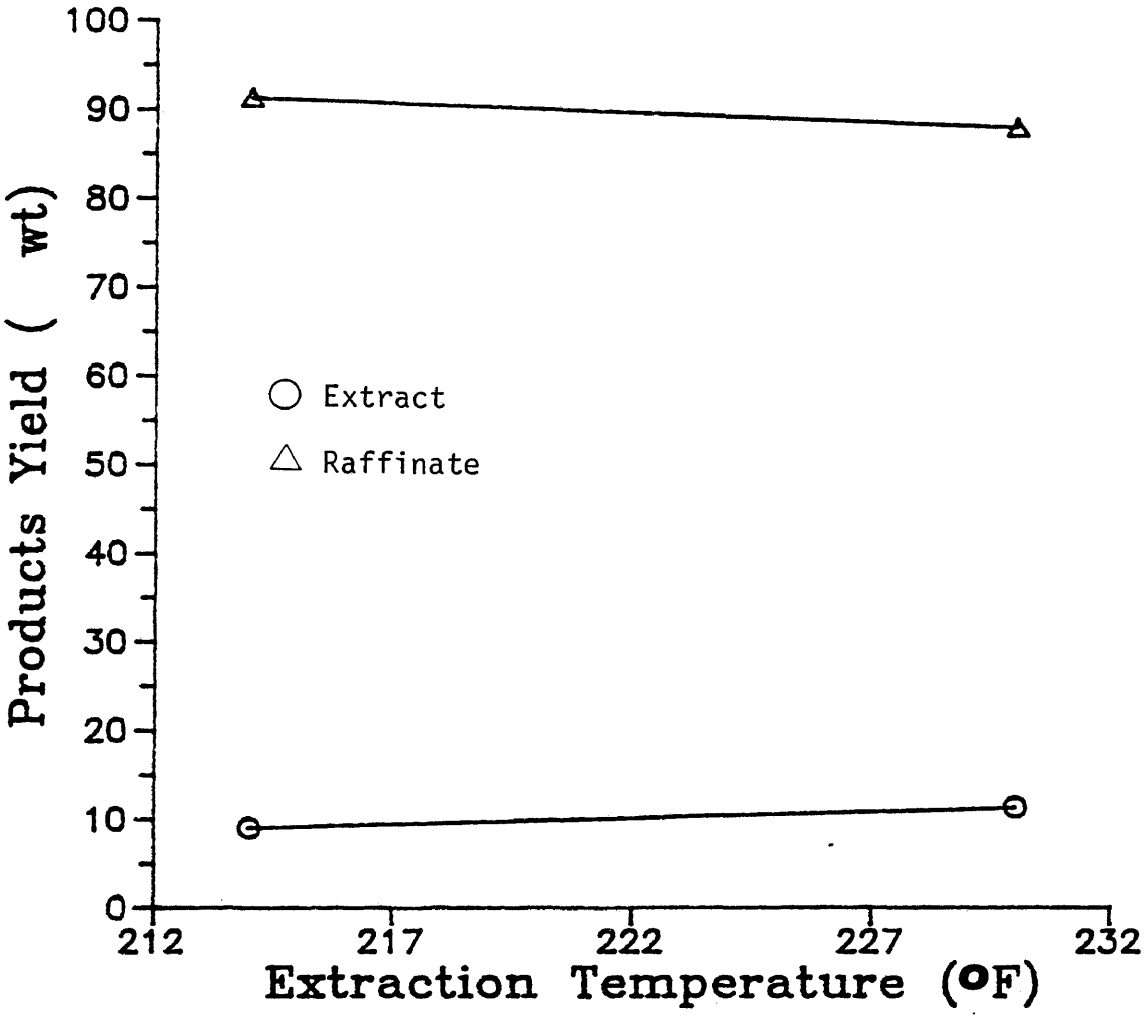


Figure 16

Effects of Extraction Temperature on
Extract and Raffinate Yields

Table 21 and 22 indicate that while the vanadium and nickel contents of the raffinate increase with increasing temperature (or decreasing raffinate yield), the metals content in the extract decrease (see Figure 17, 18, and 19). The vanadium content of the extract changed from an average value of 7.7 ppm by wt (run 5 at 230 ^{o}F) to an average value of 16.0 ppm by wt (run 6 at 214 ^{o}F) and that of the raffinate changed from an average value of 239.5 ppm by wt (run 5 at 230 ^{o}) to an average value of 73.8 ppm by wt (run 6 at 214 ^{o}F). The nickel content of the extract changed from 0.0 (run 5 at 230 ^{o}F) to 0.3 (run 6 at 214 ^{o}F) and that of the raffinate was changed from an average value of 36.6 ppm by wt (run 5 at 230 ^{o}F) to an average value of 11.5 ppm by wt (run 6 at 214 ^{o}F).

In order to show the effects of solvent composition on the yield, runs 7, 8, and 9 were compared. Those runs were performed at the same operating conditions except a change in solvent composition. The extract yield is not greately affected by changing from 10% , 5% and 0% water added. Table 20 show that the extract yield was almost constant for all three runs. Run 8 with 0% water

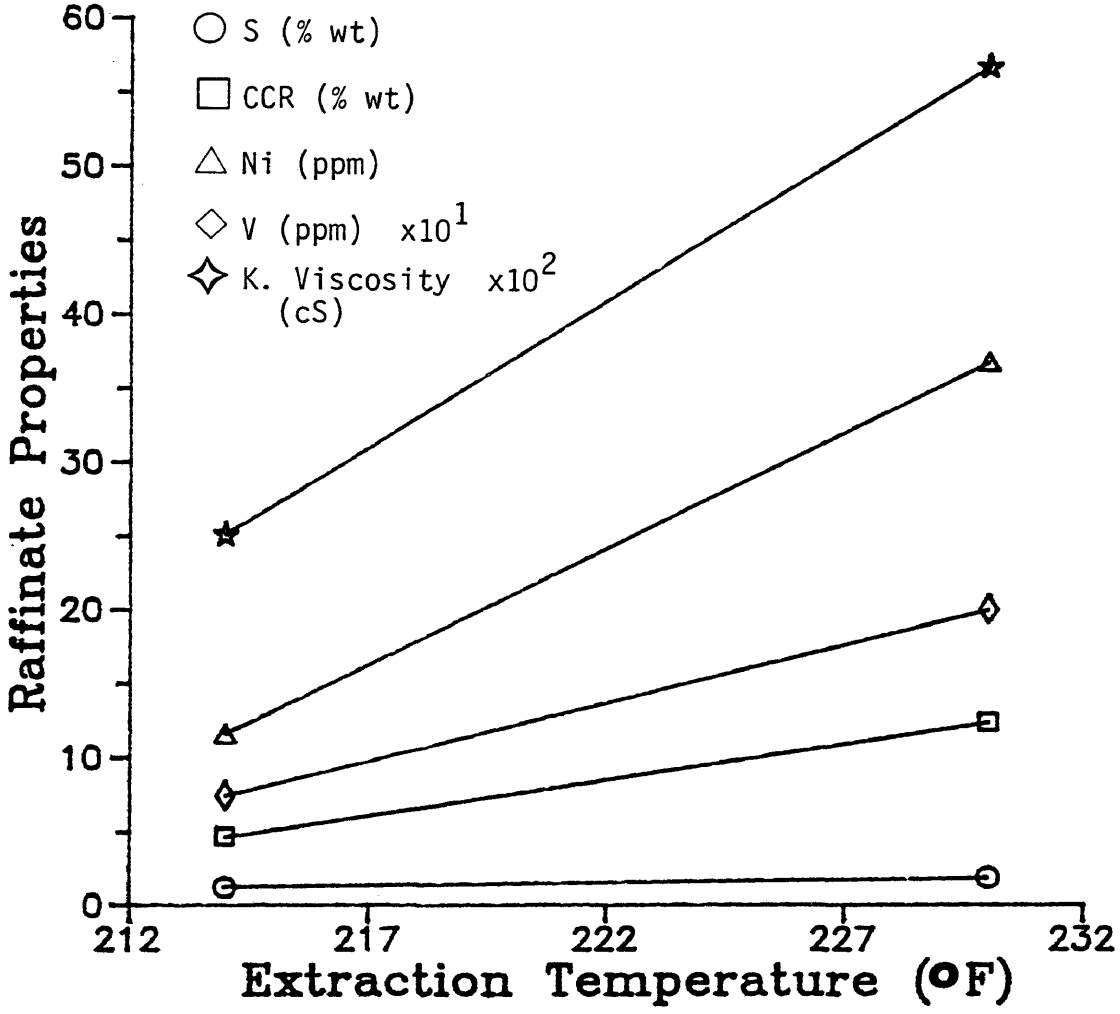


Figure 17

Effects of Extraction Temperature on Raffinate Properties

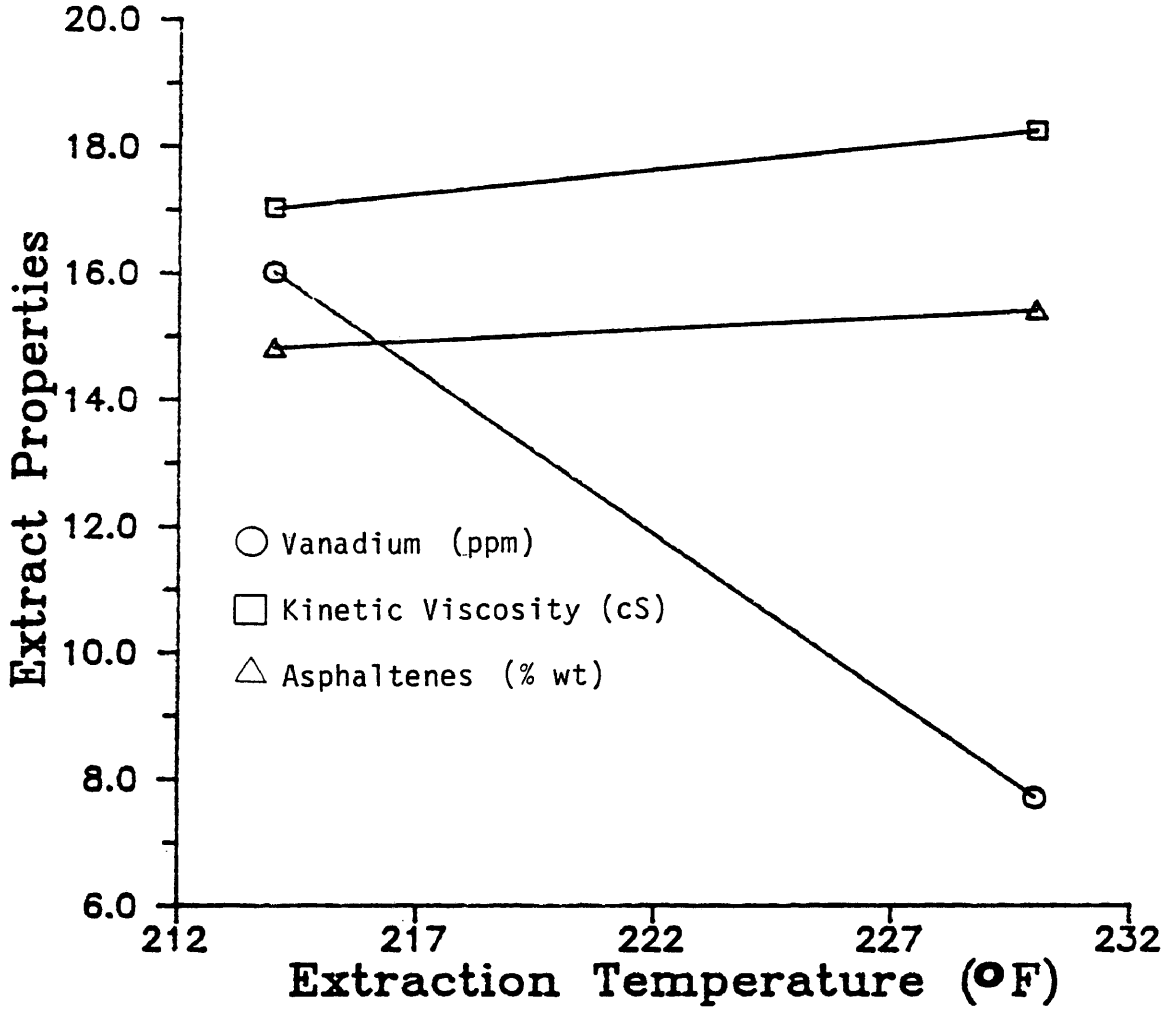


Figure 18

Effects of Extraction Temperature on Extract Properties

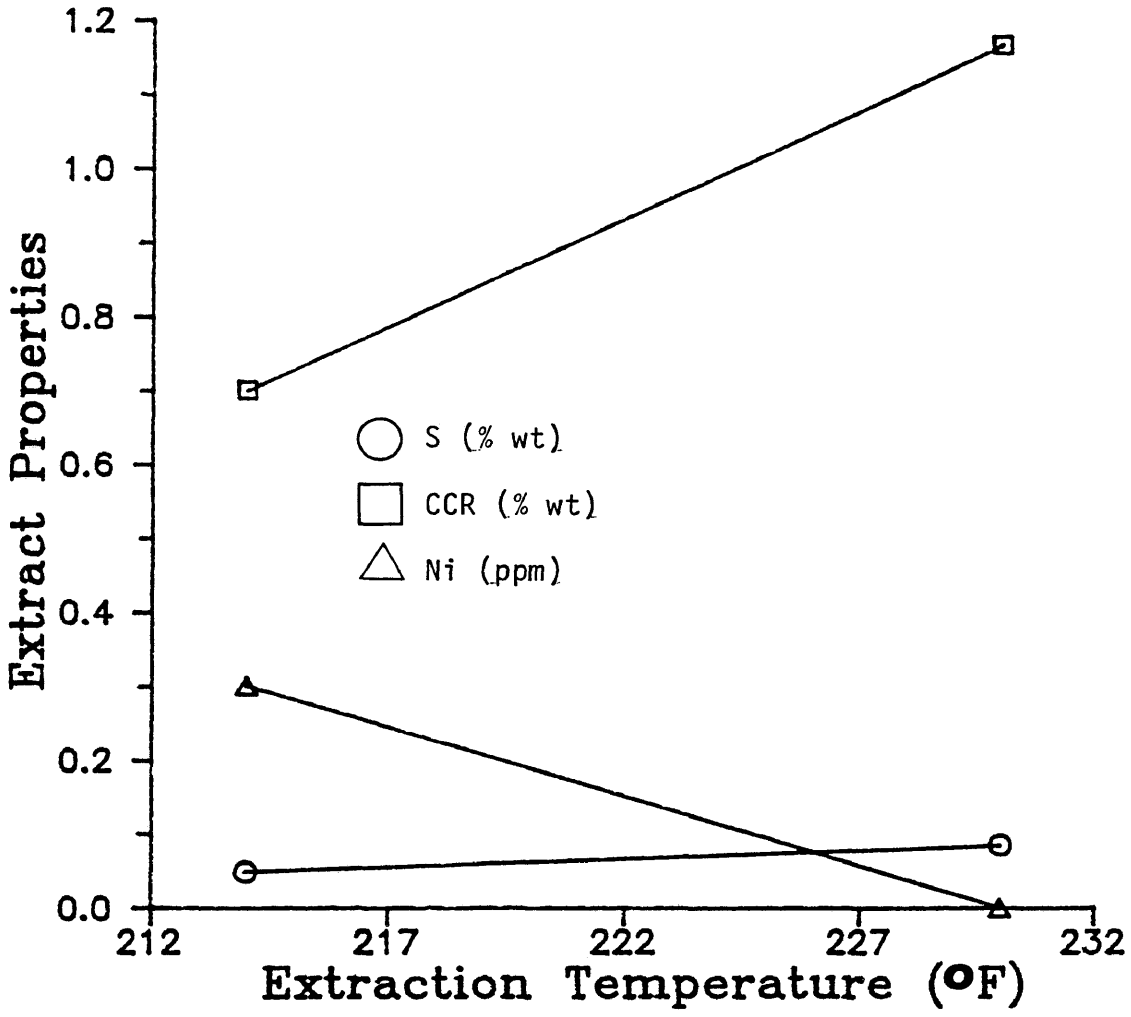


Figure 19

Effects of Extraction Temperature on
Extract Properties

produced an extract yield of 9.07, run 7 with 5% produced 9.12%, and run 9 with 10% produced 9.15%. This indicates that the solvent composition does not greately affect the extract yield, at least for small increments of water added. Figure 20 shows the effects of solvent composition changes on the extract yield. Figure 21 shows the effects os solvent composition on the extract properties. The changes occurred due to variations in solvent composition can then be neglected for this particular operating conditions.

The Conradson carbon residue, sulphur content, kinematic viscosity, and asphaltenes content of the extract are expected to increase with increasing temperature (or increasing yield).

Tables 21 and 22 show, for a decrease in extraction temperature, a decrease of the sulphur content from 0.085 wt % (run 5) to 0.048 wt % (run 6) for the extract and a decrease from 1.856 wt % (run 5) to 1.198 wt % (run 6) for the raffinate; a decrease in Conradson carbon residue from 1.165 wt % (run 5) to 0.7 wt % (run 6) for the extract and a decrease from 12.34 wt % (run 5) to 4.645 wt % (run 6) for the raffinate, and a decrease of the asphaltene content from 15.4 wt % (run 5) to 14.8 wt % (run 6) for the

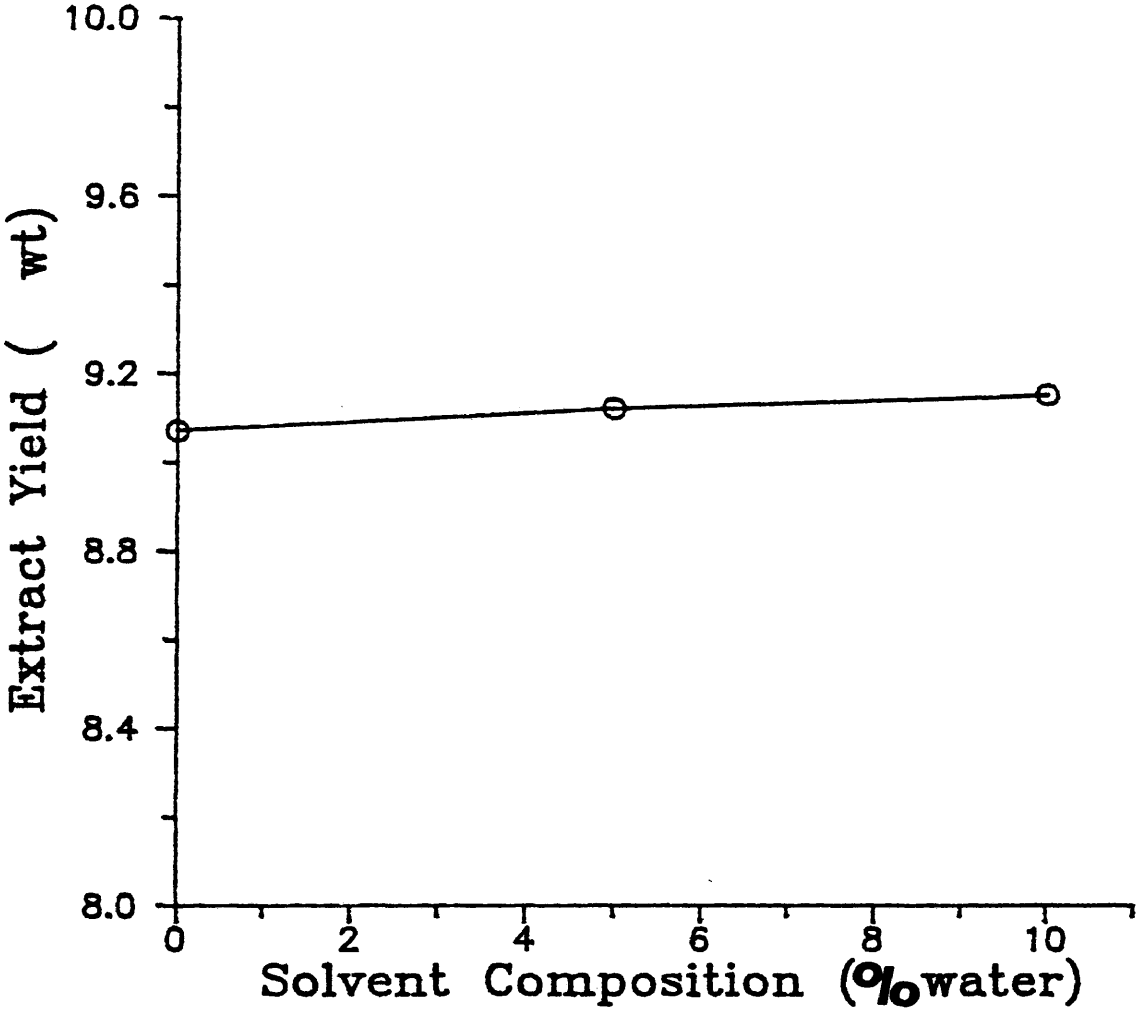


Figure 20

Effects of Solvent Composition on Extract Yield

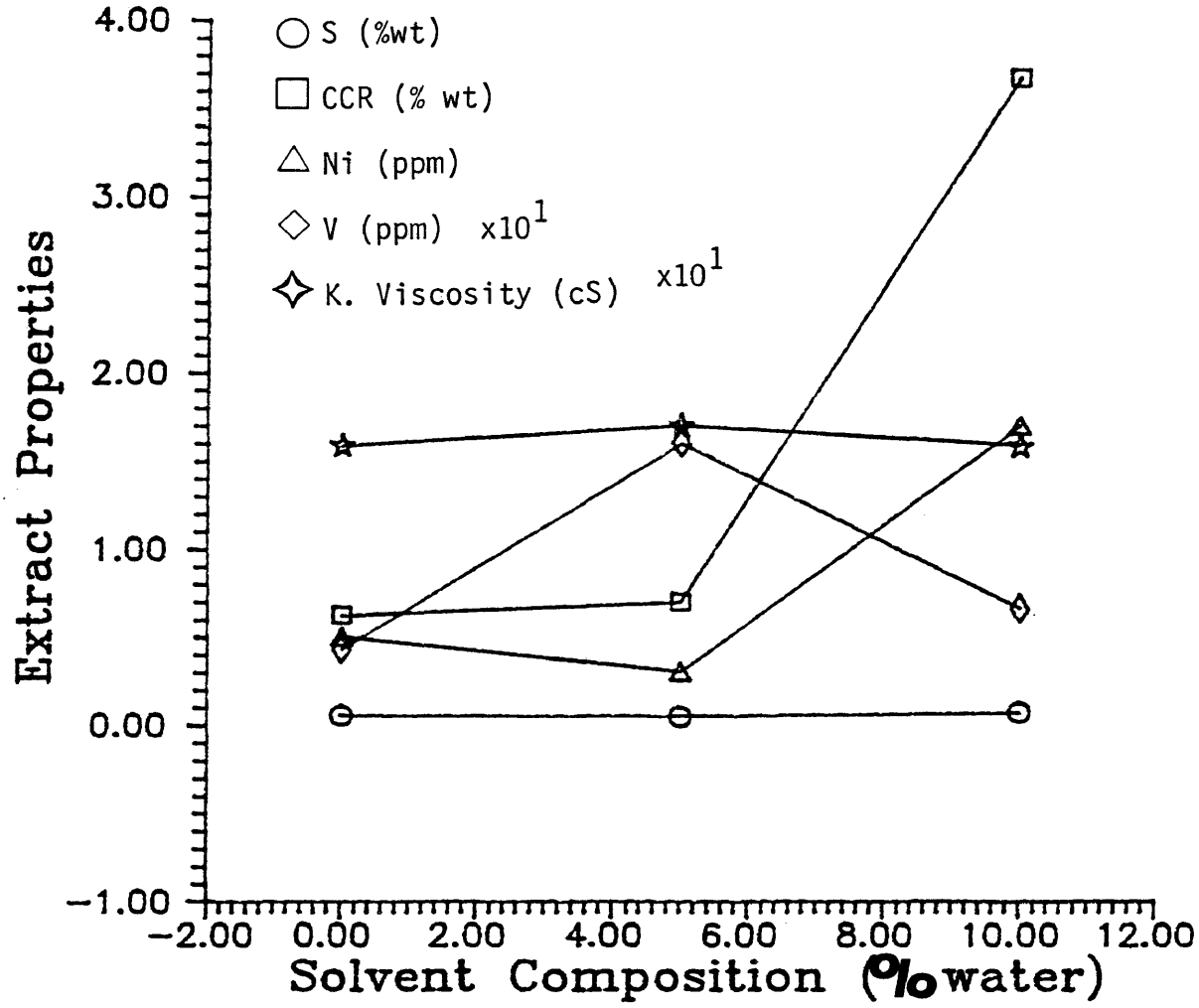


Figure 21

Effects of Solvent Composition on Extract Properties

extract (see Table 25). The kinematic viscosity was also reduced from 18.23 centistokes (122/120 ^{o}F) in run 5 to 17.02 centistokes (122/120 ^{o}F) in run 6 for the extract and it was reduced from 5662 centistokes (210 ^{o}F) in run 5 to 2508 centistokes (210 ^{o}F) in run 6. Tables 26 and 27 show a comparison between the properties of the feed and the properties of the extract and raffinate for changes in extraction temperature.

Effects of Solvent-To-Oil Ratio on extract and Raffinate Properties and Yield

Solvent-to-oil ratios of 4/1, 5/1, and 6/1 were used to study its effects on the extract and raffinate properties and yield.

When the solvent-to-oil ratio is increased while maintaining the total throughput constant, the volume fraction occupied by the dispersed (reduced crude) phase is increased and the value of the overall mass transfer coefficient with reference to the dispersed phase passes through a maximum. The most probable explanation for the maximum is that at high solvent-to-oil ratio values, the continuous phase is entrained by the dispersed phase to a marked extent. This especial

Table 25

Asphaltene Analysis of Solvent-Free Extract Samples

Run #	Sample Name	Asphaltene (%wt)
4	R3-E1	4.1
4	R3-E2	13.3
4	R3-E3	5.3
5	R4-E1	9.3
5	R4-E2	21.5
6	R5-E1	14.8

Table 26

Comparison of Properties of Feed with Properties of Extract for Temperature Changes

Property	Feed	Run 5	Run 6
Sulphur Content, % wt	4.06	0.085	0.048
Vanadium Content, ppm	430.65	7.700	16.00
Nickel Content, ppm	99.73	0.000	0.300
CCR, % wt	15.40	1.165	0.700
Asphaltenes, % wt	12.04	15.40	14.80

Table 27

Comparison of Properties of Feed with Properties of Raffinate for Temperature Changes

Property	Feed	Run 5	Run 6
Sulphur Content, % wt	4.06	1.856	1.198
Vanadium Content, ppm	430.65	239.5	73.80
Nickel Content, ppm	99.73	36.65	11.55
CCR, % wt	15.40	12.34	4.645

kind of "back-mixing" in the continuous phase impairs the efficiency of the extraction operation (efficiency is defined by the number of actual stages per foot of column height).

Data from Table 20 indicate that the extract yield increases with a increase in solvent-to-oil ratio. This can be observed when data from run 4 is compared with data from runs 6 and 9 for the same operating conditions. The extract yield changes from 9.94% at a solvent-to-oil ratio of 6/1 (run 4) to 8.95% at a solvent-to-oil ratio of 5/1 (run 6) and to 9.15% at a solvent-to-oil ratio of 4/1 (run 9). As mentioned previously the selectivity is enhanced by the addition of water, and it is known that large amounts of water added cause the solvent to lose some capacity for the components to be extracted, but in this case the change in composition is very small and the capacity is not affected greatly. Figure 22 shows the changes in extract and raffinate yields with solvent-to-oil ratio for runs 4, 6, and 9. Figure 23 shows the changes in all the extract properties with increase in solvent-to-oil ratio for runs 4, 6, and 9. Figure 24 shows the changes in all raffinate properties with an increase in solvent-to-oil ratio for runs 3, 4, and 6. Tables 28

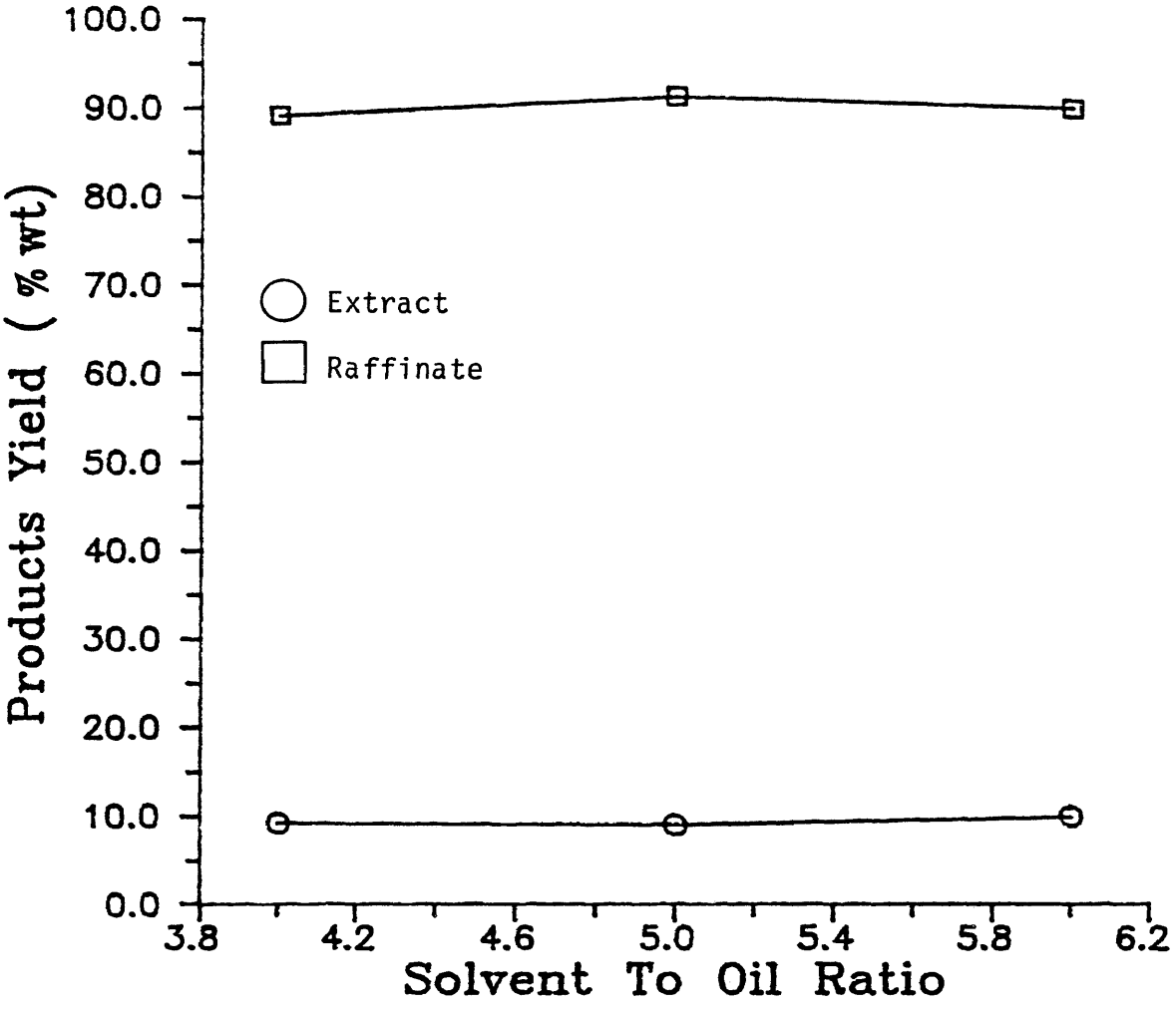


Figure 22

Effects of Solvent-To-Oil Ratio on
Extract and Raffinate Yields

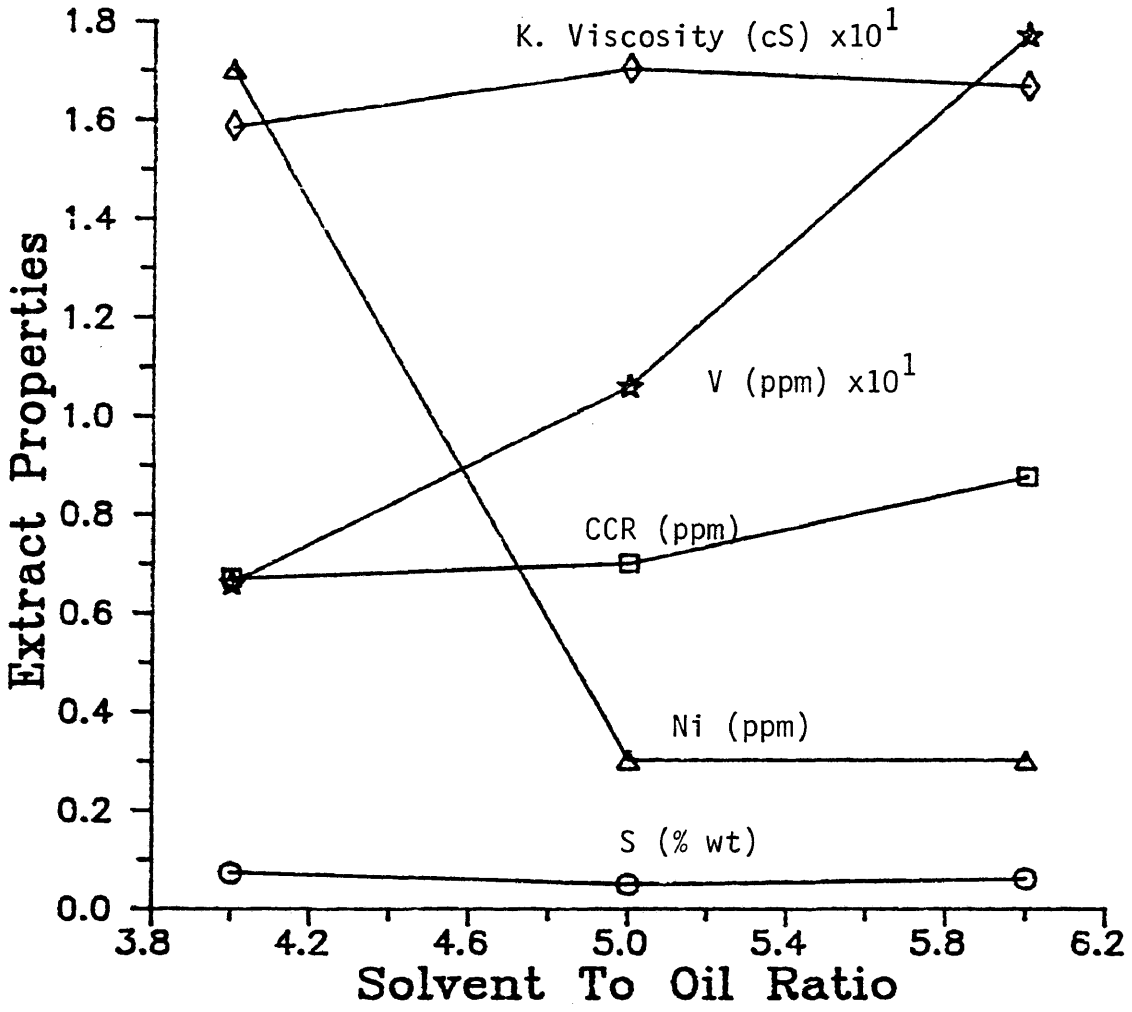


Figure 23

Effects of Solvent-To-Oil Ratio on Extract Properties

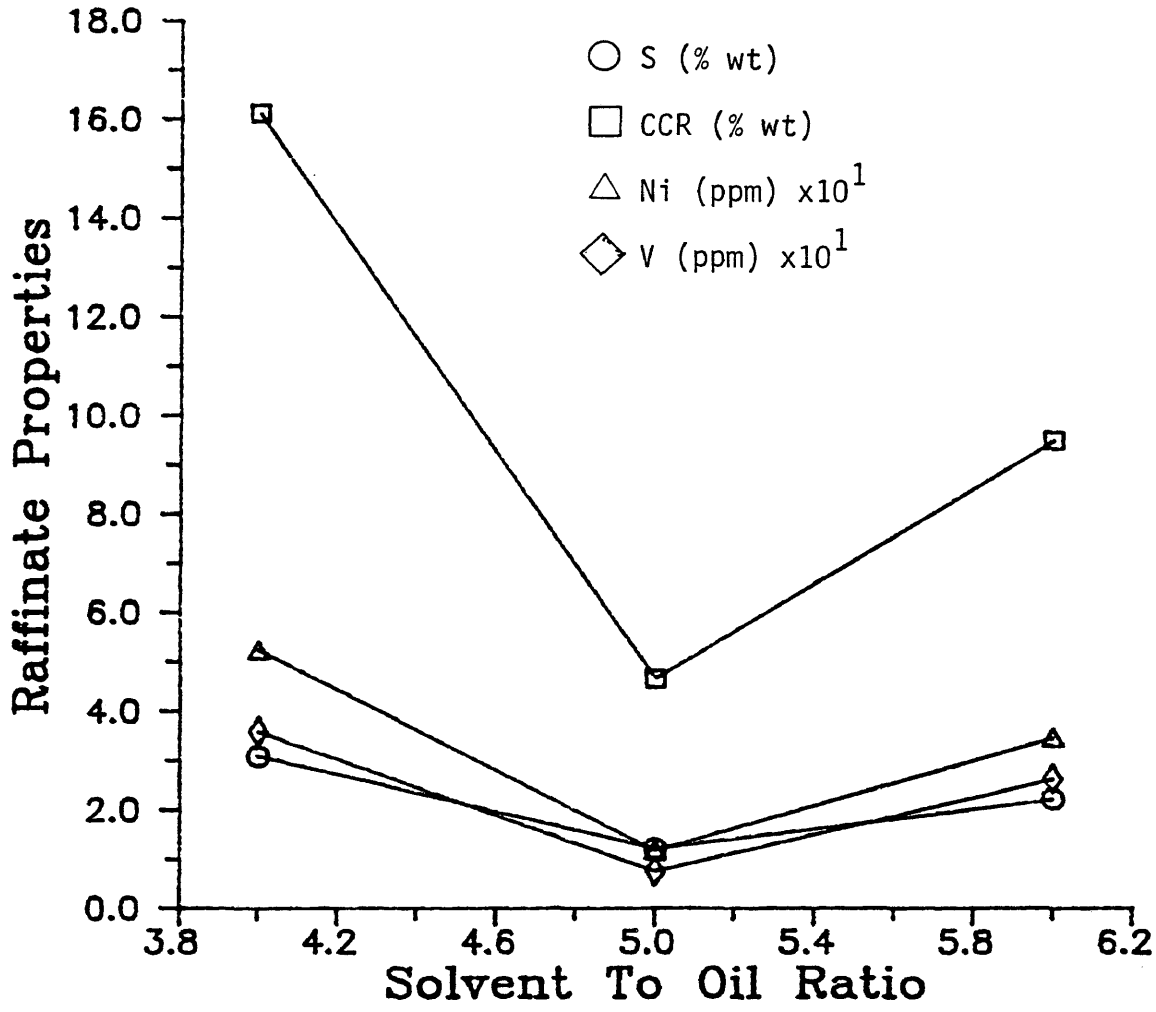


Figure 24

Effects of Solvent-To-Oil Ratio on
Raffinate Properties

and 29 show a comparison between the properties of the feed and the properties of the extract and raffinate for changes in solvent-to-oil ratio.

Reproducibility of Experimental Data

In order to demonstrate good data reproducibility, two runs were performed at the same operating conditions. An extraction temperature of 214 ^{o}F, a system pressure of 125 psig, a solvent-to-oil ratio of 4/1, a solvent composition of 10% water, and a rotor speed of 300 RPM were used for both runs 2 and 3; the extract yields were 8.98% and 9.01% for runs 2 and 3 respectively (see Table 20). These results differ only by 0.03% indicating good reproducibility given the difficulty of controlling all the operating conditions and the sources of error associated with each one of them.

The other two runs used to check data reproducibility are runs 6 and 7. An extraction temperature of 214 ^{o}F, a system pressure of 125 psig, a solvent-to-oil ratio of 5/1, a solvent composition of 5% water, and a rotor speed of 800 RPM were used for both runs 6 and 7; the extract yields were 8.95% and

Table 28

Comparison of Properties of Feed with Properties of Extract for Solvent-To-Oil Ratio Changes

Property	Feed	Run 4	Run 6	Run 9
Sulphur Content, % wt	4.06	0.061	0.048	0.072
Vanadium Content, ppm	430.65	10.83	16.00	6.600
Nickel Content, ppm	99.73	0.300	0.300	1.700
CCR, % wt	15.40	0.876	0.700	0.670

Table 29

Comparison of Properties of Feed with Properties of Raffinate for Solvent-To-Oil Ratio Changes

Property	Feed	Run 3	Run 4	Run 6
Sulphur Content, % wt	4.06	3.071	2.207	1.198
Vanadium Content, ppm	430.65	357.0	261.5	73.80
Nickel Content, ppm	99.73	52.20	34.55	11.55
CCR, % wt	15.40	16.11	9.480	4.645

9.12% for those two runs. The results differ only by 0.17% and can be considered very good again considering the number of sources of error involved.

CONCLUSIONS

A number of batch extractions were performed to determine the solvent-to-oil ratios and solvent compositions adequate to give phase separation for the solvent extraction of the Venezuelan long reduced crude Zuata 44X.

The solvent used for these experiments was tetraethylene glycol (TTEG) which was paired with different proportions of water. Solvent-water pairing percentages of 1% to 30% and solvent-to-oil ratios of 1:1 to 8:1 were utilized.

The batch extractions were carried out at a temperature of 210 ^{o}F and atmospheric pressure. The interface was visible in batch extractions using solvent-to-oil ratios greater than or equal to 3.5:1 (for a solvent composition of 10% water) and batch extractions using solvent-water pairings greater than or equal to 9%.

A continuous solvent extraction unit using a rotating disc contactor (RDC) was used to study the effects of variations in the operating conditions, namely, solvent-to-oil ratio, solvent composition, extraction temperature, and RDC rotor speed, on the extract and raffinate properties and yields.

The continuous unit extractions were carried out at a constant pressure of 125 psig. The extraction temperatures used were 214 and 230 ^{o}F, the solvent-to-oil ratios used were 4/1, 5/1, and 6/1, solvent compositions use were 5% and 10%, and rotor speeds were 100, 300, and 800 RPM (39.25, 117.75, 196.25, and 314 ft/min respectively).

Undesirable materials such as metals (vanadium and nickel), sulphur, and asphaltenes initially present in the crude feed were reduced substantially in the extract product (see Tables 23, 24, 26, 27, 27, and 29), although, analysis of experimental data indicates that in general an increase in extract yield was associated with an increase in the sulphur content, vanadium and nickel content, Conradson carbon residue, and kinematic viscosity of the extract and raffinate products (see Figures 25, 26, and 27).

Increases of the extract yield occurred with increasing extraction temperature, rotor speed, and solvent-to-oil ratio (see Figures 28 and 29). Increments in these parameters then can be associated with an enhanced mass transfer process. Changes in the solvent composition did not affect the yields significantly, although it becomes an important factor as the % water increases.

The most important operating parameter yieldwise was

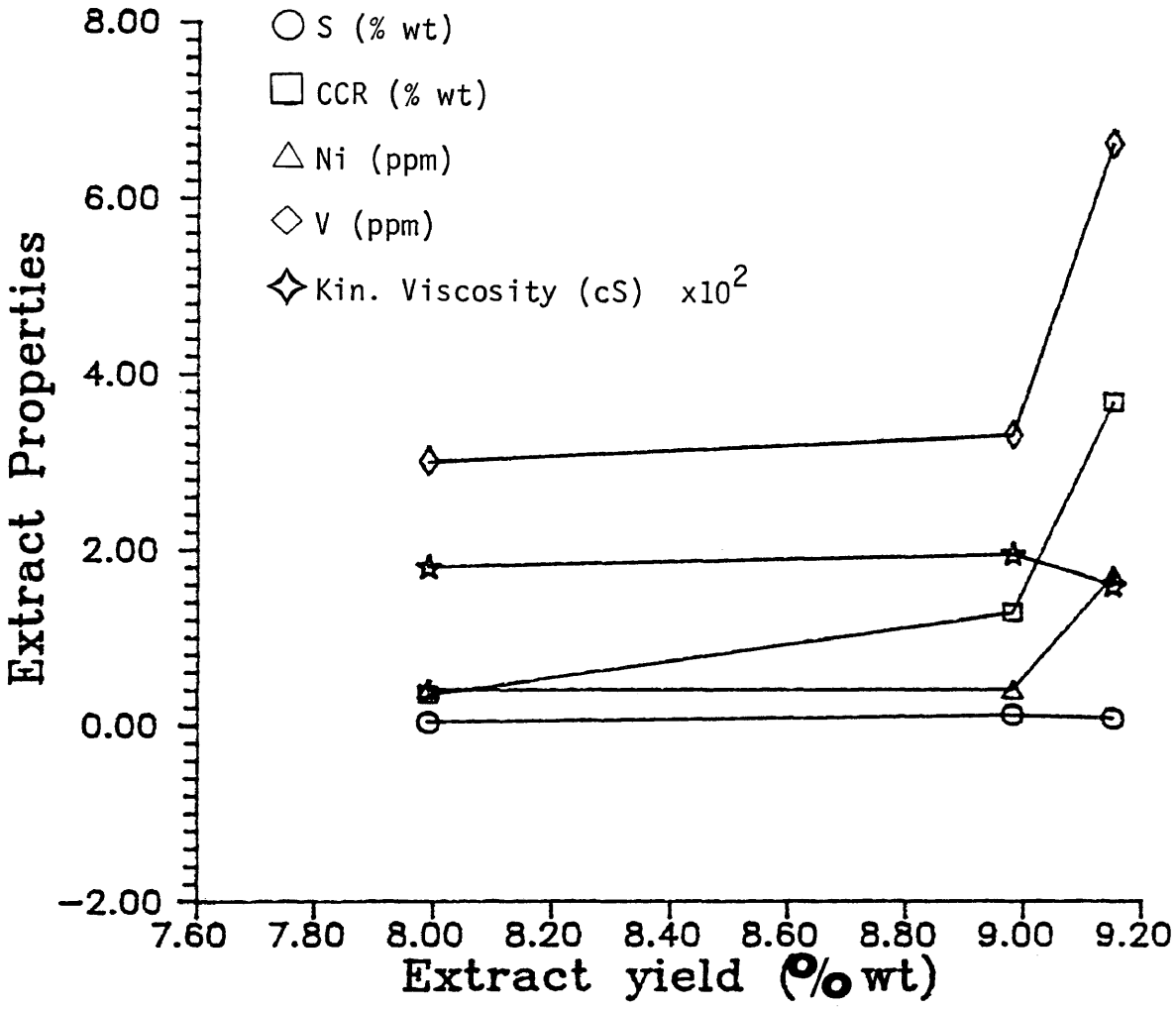


Figure 25

Effects of Increasing Extract Yield on Extract Properties for Rotor Speed Changes

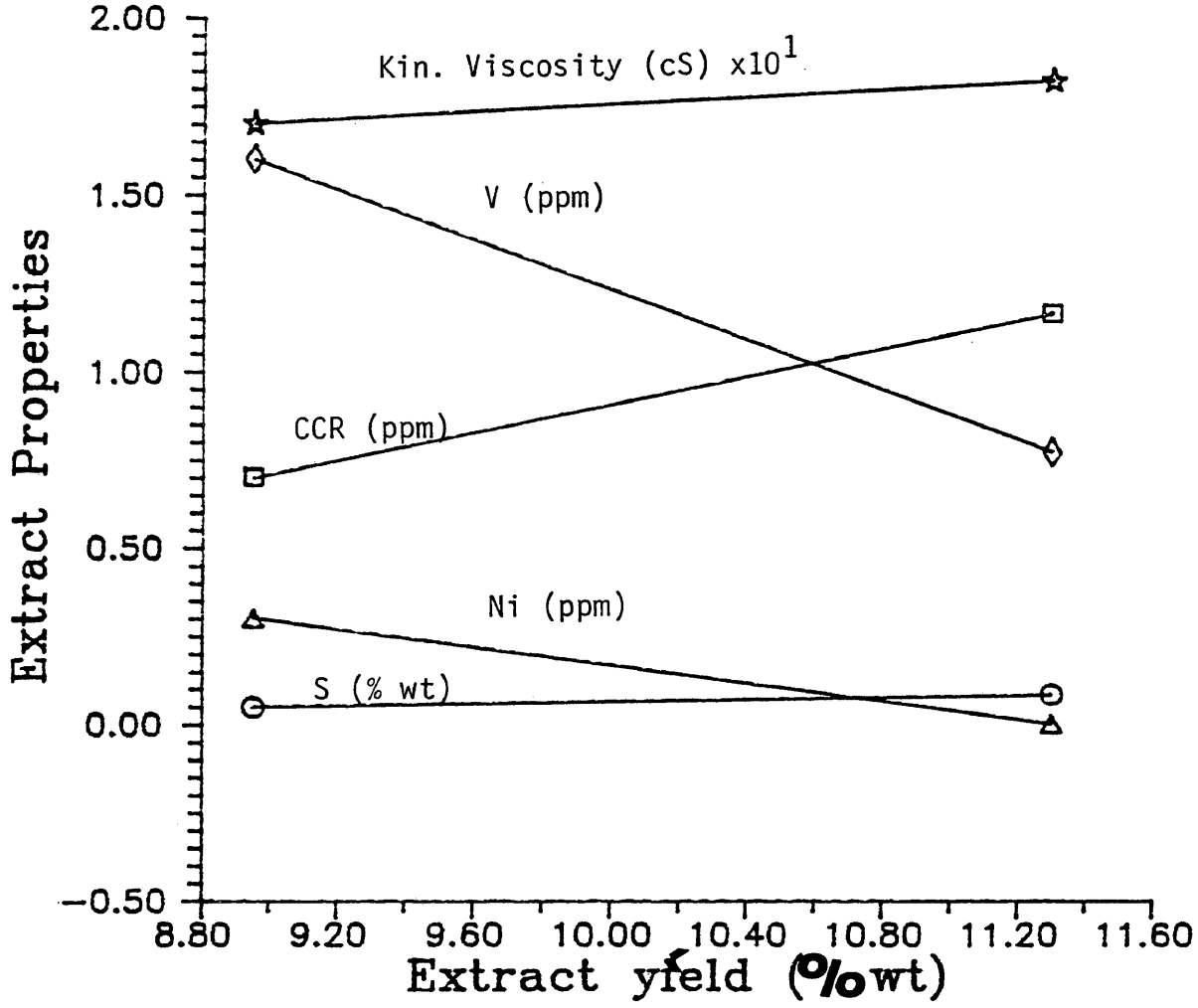


Figure 26

Effects of Increasing Extract Yield on Extract Properties for Extraction Temperature Changes

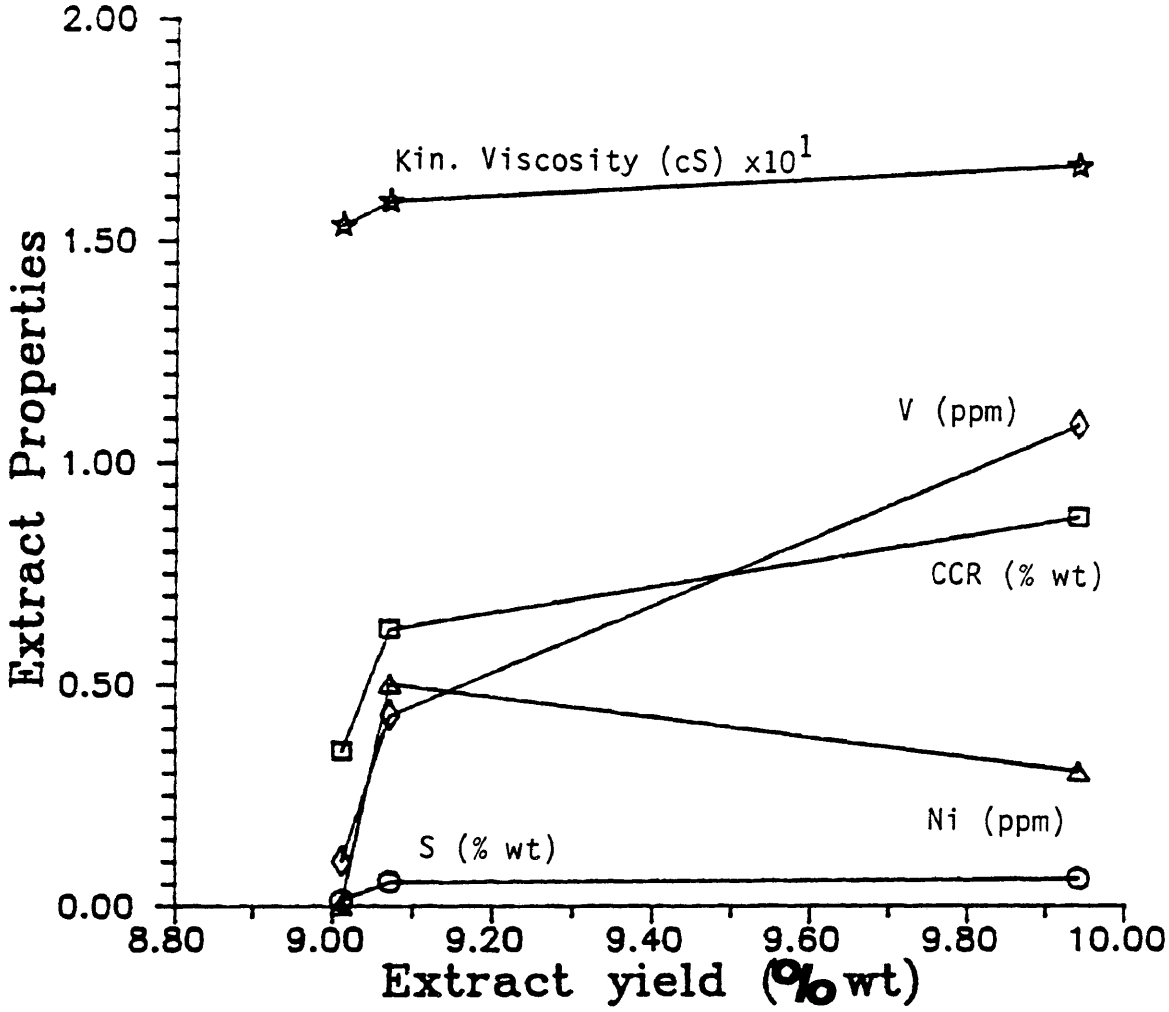


Figure 27

Effects of Increasing Extract Yield on Extract Properties for Solvent-To-Oil Ratio Changes

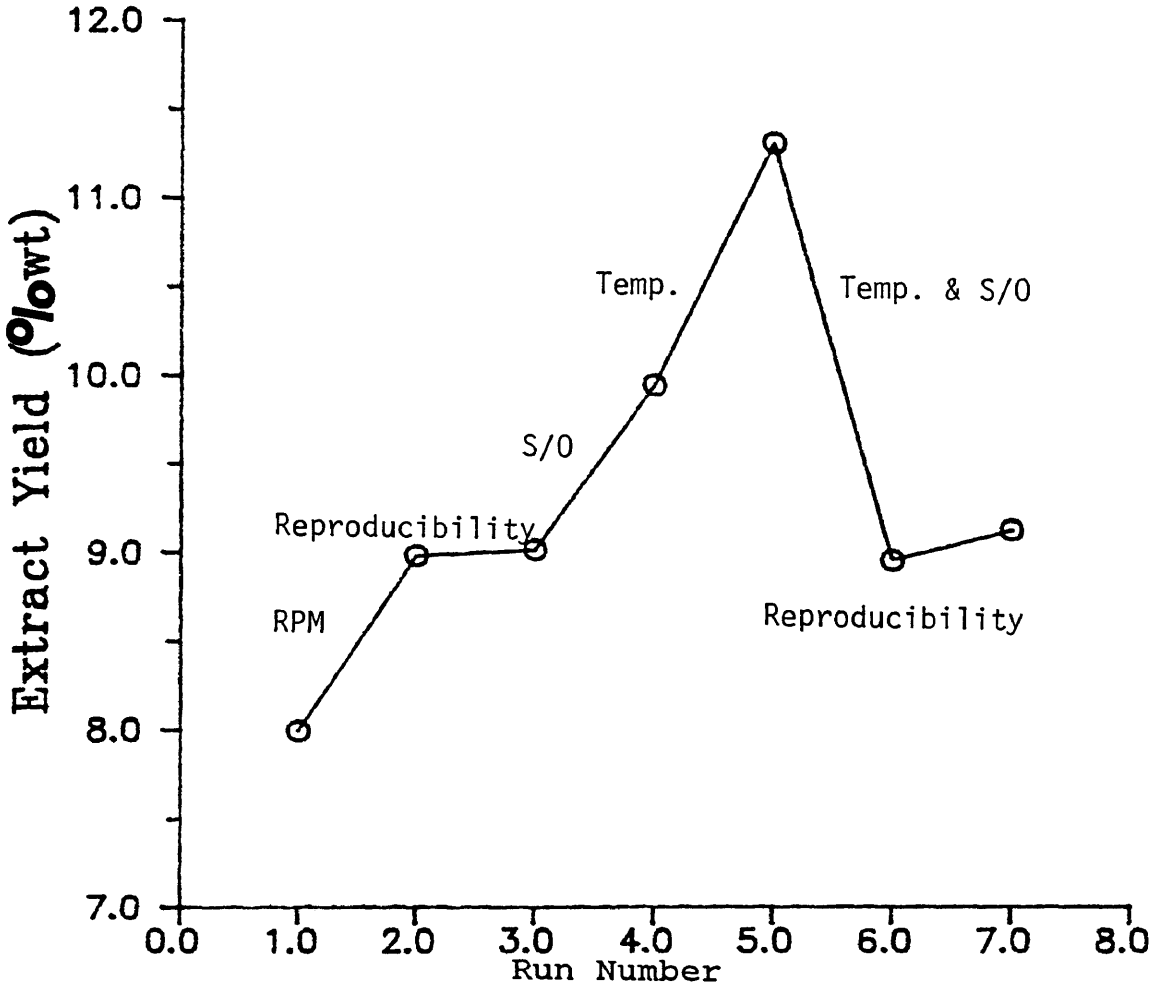


Figure 28

Run Number vs. Extract Yield

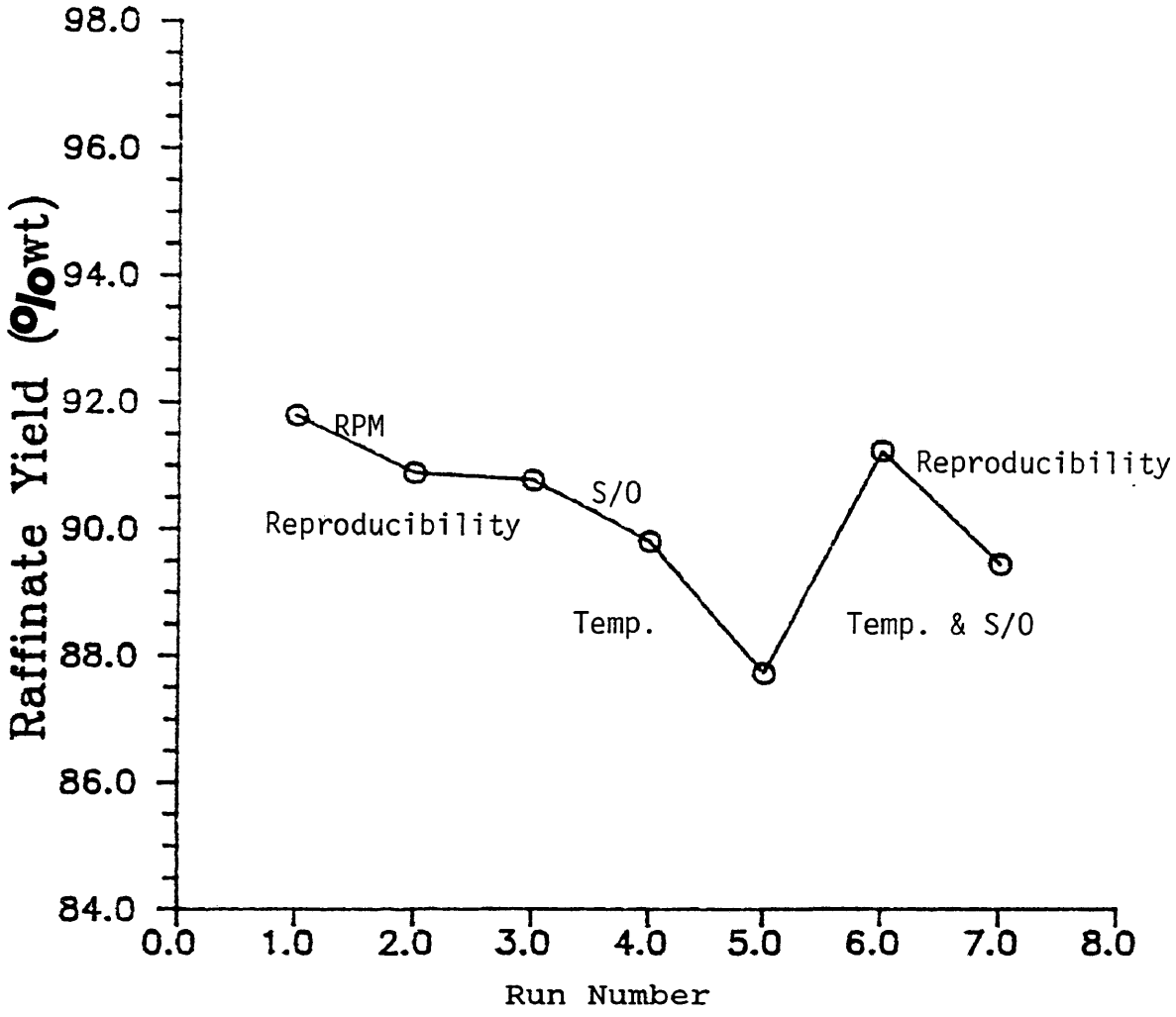


Figure 29

Run Number vs. Raffinate Yield

the extraction temperature. The sharpest rise in yield occurred when the temperature was raise from 214 ^{o}F (yield of 8.95%) to 230 ^{o}F (yield of 11.30%). The second most important operating parameter was the rotor speed. Extract yields varied from 7.99% at 100 RPM to 8.98% at 300 RPM, and to 9.15% at 800 RPM all other operating variables being constant.

RECOMMENDATIONS

The following are recommendations to improve the operation and/or performance of the continuous solvent extraction system:

1.- Use of a reflux line to the RDC column to allow for a better control of the temperature gradient in the unit and to improve the quality and efficiency of the operation.

2.- Use of rotor speeds equal or greater than 800 RPM to ensure the toroidal flow pattern required to improve overall mass transfer rate.

3.- Use of several side streams along the RDC column that will allow the operator to take samples to determine the location of the interface when operating at conditions that do not produce clear phase separation.

4.- Installation of multiple power outlets in strategic points in the laboratory, especially, close to the Preheat and RDC sections to avoid having wires all over the place improve the safety of the operation.

5.- Installation of a ventilation system on top of the RDC column to avoid inhalation of the gases

produced during the solvent extraction operation.

6.- Stocking of necessary amounts of solvent and reduced crude previous to the runs to avoid unnecessary delays and to allow the student to optimize the research planning.

7.- Include elemental analysis of samples such as: nitrogen content, hydrogen/carbon ratio, iron content, and salts and arsenic contents.

8.- Use different solvents and solvent-polar component pairings and same operating conditions used in this research work to study and compare products properties and yields.

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APPENDIX A

Table A-1

Total Mass Balance for the Extraction Operation (Run 1)

Mass In (lbs)		Mass Out (lbs)	
Solvent	22.135	Extract (bulk)	20.501
Reduced Crude	7.675	Raffinate (bulk)	8.115
		Extract Samples (R1-E)	0.360
		Raffinate Samples (R1-R)	0.430
Total Mass In	29.810	Total Mass Out	29.406

Mass Out as % of Mass In = 98.64%

* 90% TTEG - 10% Water

Table A-2

Hydrocarbon Balance (Run 1)

Total mass of extract collected = 20.861 lbs

Percent solvent contained in extract = 97.06%

Mass of solvent-free extract = 0.6133 lbs

Total mass of raffinate collected = 8.545 Lbs

Percent solvent contained in raffinate = 19.37%

Mass of solvent-free raffinate = 6.8898 lbs

Total mass of solvent-free material out = 7.5031 lbs

Total mass of solvent-free material in = 7.675 lbs

$$\text{Recovery} = \frac{7.5031}{7.6750} = 97.80\ \%$$

Table A-3

Total Mass Balance for the Extraction Operation (Run 2)

Mass In (lbs)		Mass Out (lbs)	
Solvent	23.818	Extract (bulk)	21.098
Reduced Crude	6.790	Raffinate (bulk)	7.370
		Extract Samples (R2-E1, R2-E2)	0.510
		Raffinate Samples (R2-R1, R2-R2)	0.420
Total Mass In	30.608	Total Mass Out	29.398

Mass Out as % of Mass In = 96.04%

* 90% TTEG - 10% Water

Table A-4

Hydrocarbon Balance (Run 2)

Total Mass of extract collected = 21.608 lbs

Percent solvent contained in extract = 97.17%

Mass of solvent-free extract = 0.6115 lbs

Total mass of raffinate collected = 7.790 lbs

Percent solvent contained in raffinate = 20.01%

Mass of solvent-free raffinate = 6.231 lbs

Total mass of solvent-free material out = 6.8425 lbs

Total mass of solvent-free material in = 6.7900 lbs

$$\text{Recovery} = \frac{6.8425}{6.7900} = 100.8\ \%$$

Table A-5

Total Mass Balance for the Extraction Operation (Run 3)

Mass In (lbs)		Mass Out (lbs)	
Solvent	16.500	Extract (bulk)	14.567
Reduced Crude	4.521	Raffinate (bulk)	4.144
		Extract Samples (T1-E)	0.355
		Raffinate Samples (T1-R)	0.420
Total Mass In	21.021	Total Mass Out	19.486

Mass Out as % of Mass In = 92.69%

* 90% TTEG - 10% Water

Table A-6

Hydrocarbon Balance (Run 3)

Total mass of extract collected = 14.922

Percent solvent contained in extract = 97.27%

Mass of solvent-free extract = 0.407 lbs

Total mass of raffinate collected = 4.564 lbs

Percent solvent contained in raffinate = 9.92%

Mass of solvent-free raffinate = 4.111 lbs

Total mass of solvent-free material out = 4.518 lbs

Total mass of solvent-free material in = 4.521 lbs

$$\text{Recovery} = \frac{4.518}{4.521} = 99.93\ \%$$

Table A-7

Total Mass Balance for the Extraction Operation (Run 4)

Mass In (lbs)		Mass Out (lbs)	
Solvent	17.135	Extract (bulk)	16.767
Reduced Crude	2.705	Raffinate (bulk)	2.015
		Extract Samples (R3-E1, R3-E2)	0.278
		Raffinate Samples (R3-R1, R3-R2)	0.477
Total Mass In	19.840	Total Mass Out	19.537

Mass Out as % of Mass In = 98.47%

* 90% TTEG - 10% Water

Table A-8

Hydrocarbon Balance (Run 4)

Total mass of extract collected = 17.045 lbs

Percent solvent contained in extract = 98.42%

Mass of solvent-free extract = 0.269 lbs

Total mass of raffinate collected = 2.592 lbs

Percent solvent contained in raffinate = 9.24%

Mass of solvent-free raffinate = 2.261 lbs

Total mass of solvent-free material out = 2.621 lbs

Total mass of solvent-free material in = 2.705 lbs

$$\text{Recovery} = \frac{2.621}{2.705} = 96.91\ \%$$

Table A-9

Total Mass Balance for the Extraction Operation (Run 5)

Mass In (lbs)		Mass Out (lbs)	
Solvent	33.497	Extract (bulk)	32.936
Reduced Crude	7.022	Raffinate (bulk)	6.308
		Extract Samples (R4-E1, R4-E2)	0.480
		Raffinate Samples (R4-R1, R4-R2)	0.410
Total Mass In	40.519	Total Mass Out	39.934

Mass Out as % of Mass In = 98.55%

* 90% TTEG - 10% Water

Table A-10

Hydrocarbon Balance (Run 5)

Total mass of extract collected = 33.416 lbs

Percent solvent contained in extract = 97.62%

Mass of solvent-free extract = 0.795 lbs

Total mass of raffinate collected = 6.718 lbs

Percent solvent contained in raffinate = 10.71%

Mass of solvent-free raffinate = 5.998 lbs

Total mass of solvent-free material out = 6.793 lbs

Total mass of solvent-free material in = 7.022 lbs

$$\text{Recovery} = \frac{6.793}{7.022} = 96.74\ \%$$

Table A-11

Total Mass Balance for the Extraction Operation (Run 6)

Mass In (lbs)		Mass Out (lbs)	
Solvent	21.934	Extract (bulk)	21.998
Reduced Crude	7.626	Raffinate (bulk)	6.799
		Extract Samples (R5-E1, R5-E2)	0.324
		Raffinate Samples (R5-R1, R5-R2)	0.670
Total Mass In	29.560	Total Mass Out	29.191

Mass Out as % of Mass In = 98.75%

* 95% TTEG - 5% Water

Table A-12

Hydrocarbon Balance (Run 6)

Total mass of extract collected = 22.322 lbs

Percent of solvent contained in extract = 97.04%

Mass of solvent-free extract = 0.660 lbs

Total mass of raffinate collected = 7.449 lbs

Percent of solvent contained in raffinate = 10.12%

Mass of solvent-free raffinate = 6.695 lbs

Total mass of solvent-free material out = 6.147 lbs

Total mass of solvent-free material in = 7.626 lbs

$$\text{Recovery} = \frac{6.695}{7.626} = 87.79\ \%$$

Table A-13

Hydrocarbon Balance (Run 7)

Total mass of extract collected = 39.460 lbs

Percent of solvent contained in extract = 98.06%

Mass of solvent-free extract = 0.765 lbs

Total mass of raffinate collected = 8.202 lbs

Percent of solvent contained in raffinate = 8.53%

Mass of solvent-free raffinate = 7.502 lbs

Total mass of solvent-free material out = 8.267 lbs

Total mass of solvent-free material in = 8.367 lbs

$$\text{Recovery} = \frac{8.267}{8.367} = 98.80\ \%$$

APPENDIX B

Table 6

Physical Properties and Structure of Various Commercially Used Solvents

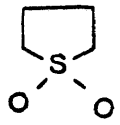
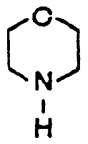
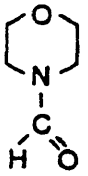
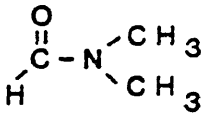
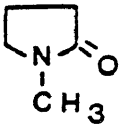
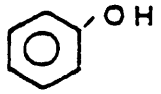
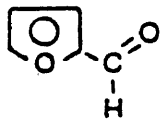
Solvent	Specific Gravity	Boiling Pt. (°C)	Selectivity	Structure
Sulfolane	1.260	276.0	Very Good	
Morpholine	1.000	238.0	Good	
N-formyl-morpholine	1.150	243.0	Very Good	
DMF	0.949	151.0	Good	
NMP	1.030	201.7	Very Good	
Phenol	1.070	181.7	Good	
Furfural	1.150	161.7	Excellent	

Table 7

Physical Properties and Structure of
Tetraethylene Glycol Solvent

Specific Gravity:	1.1248 20°C/20 °C
Freezing Point:	-4.0 °C
Boiling Point:	314.0 °C
Vapor Pressure:	< 0.01 (20 °C)
Lbs/gal:	9.4
Structure:	$O(CH_2CH_2OCH_2CH_2OH)_2$

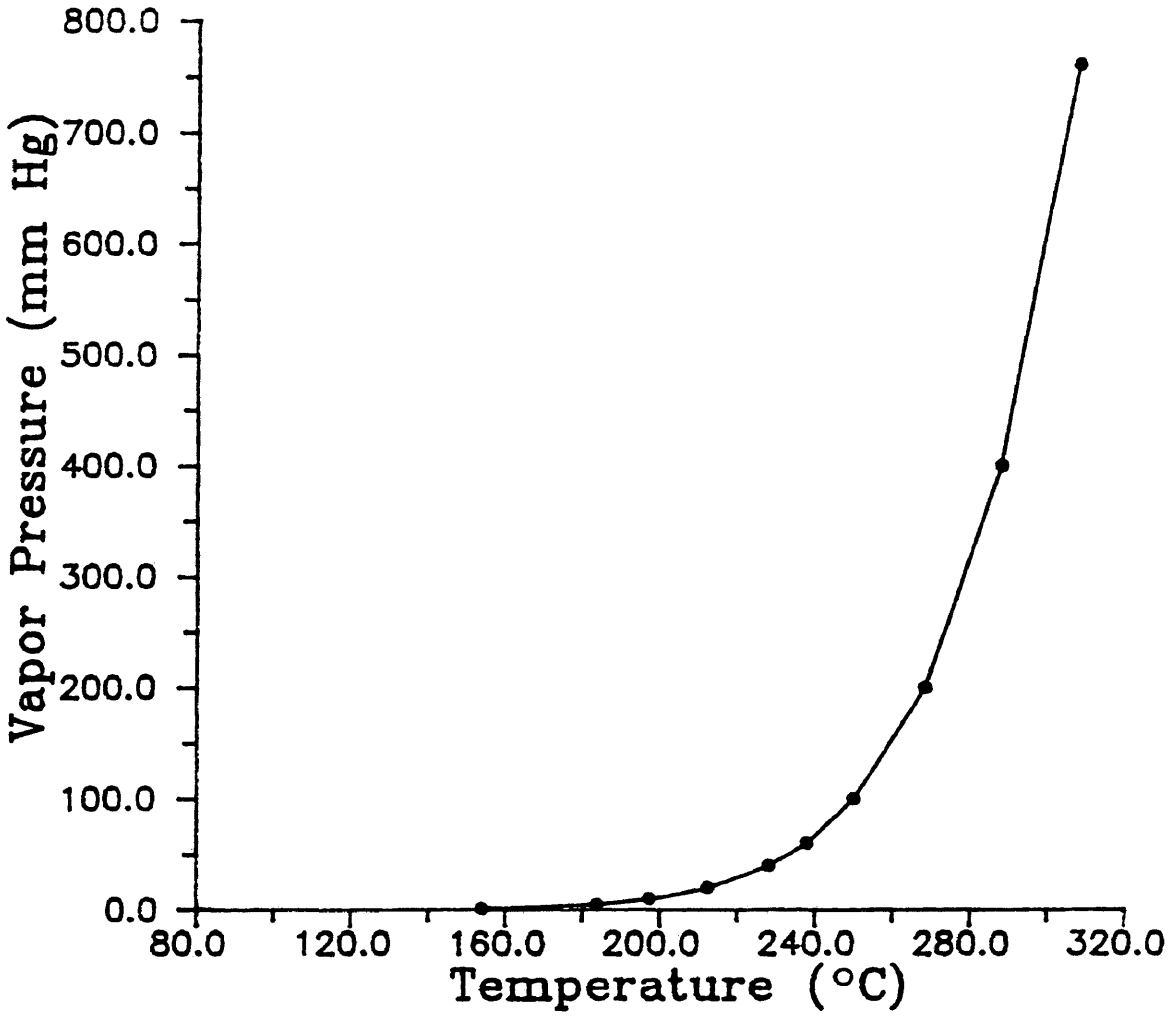


Figure 30

Vapor Pressure vs Temperature for TTEG Solvent