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SOLVENT EXTRACTION OF SHALE OIL

by

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DEDICATION

The thesis study is dedicated to the fulfillment of goals, to Angela, and to my parents, John and Marilyn.

ABSTRACT

The solvent extraction of Paraho shale oil was investigated in a continuous unit employing a rotating disk contactor (RDC) extraction column. Batch extractions were performed to determine the utility of solvents and processing conditions prior to operation of the continuous apparatus.

The continuous extraction system was operated with n-heptane as a deasphalting solvent and with the solvent pair 70% NMP - 30% water as a polar and aromatic molecule selective solvent.

The heptane extractions in the continuous unit were performed at a 4:1 solvent to oil ratio, a RDC rotor speed of 800 r.p.m., and a system pressure of 140 psig. The temperature range was 60 °C to 104.4 °C. Phase separation was not achieved in any of the runs.

The operating conditions for the 70% NMP - 30% water solvent extraction runs consisted of a 4:1 solvent to oil ratio, a rotor speed of 800 r.p.m., and 125 psig pressure. The temperature was varied from 48.9 °C to 110 °C. The raffinate oil yield decreased and the quality of the oil was improved as the extraction temperature was raised. The oil yield at 110 °C was 77.60% by weight with a nitrogen content

of 1.39% reduced from 2.21% in the raw shale oil, and an arsenic content of 18.4 ppm reduced from 54.4 ppm in the raw shale oil.

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INTRODUCTION

Transportation fuels traditionally have been obtained through the refining of petroleum crude oil. In recent years, the consumption of petroleum products in the United States has exceeded domestic production forcing increased dependence on imported oil. The need for the development of new energy sources within the United States is emphasized by the declining world supply of crude oil, the increased cost of this oil, and the threat of a disruption in the flow of Mid-East oil. The need for a secure and reliable source of transportation fuels is vital to a stable economy and to national defense and has lead to an increased interest in alternate domestic hydrocarbon fuels. These alternate fuels include tar sands, shale oil, and coal.

Research and development studies (1,2) have shown that shale oil is one of the best potential alternate sources of middle distillate or transportation fuels. Oil shale deposits are found in many parts of the United States. The Green River oil shales, located in Colorado, Utah and Wyoming, are particularly high grade, containing the equivalent of 1.8 trillion barrels of shale oil (1). It is estimated that 600 billion barrels of this oil is ultimately recoverable. If true, this would be 20 times the proven crude oil reserves.

The organic portion of the Green River oil shale is composed of 0 - 5% bitumen (extractable organics) and 95 - 100% kerogen (unextractable organics). In this instance, extractable is meant to include all organics removeable from the shale matrix by a method other than thermal decomposition. The C/H weight ratio in kerogen (approximately 7.8) is closer to values required in liquid fuels than that of coal (approximately 13.9). It is necessary to heat the shale to approximately 250 °C (900 °F) to thermally decompose the kerogen to give oil (65 - 70%), gas (10 - 15%), coke (15 - 20%), and water (2 -7%) by weight.

Raw shale oil has a high nitrogen content, high C/H ratio, and high levels of arsenic when compared to conventional crudes. The viscosity and pour point are also high. Typical values for shale oil are:

nitrogen wt.%	2.18
C/H ratio	7.5
arsenic ppm.	31
viscosity @ 100 °F (cSt)	53
pour point °F	85

The nitrogen and arsenic are catalyst poisons for conventional cracking, hydroprocessing, and reforming steps. Due to high viscosity and pour point, raw shale oil can not be transported by pipeline.

The location of the Green River formation and the proposed shale oil retorts will require the use of new and existing pipeline networks for transporting the product to refineries or consumers, because of the unattractive economic and environmental problems associated with either rail or truck transport. One alternative is to process the crude shale oil to pipelineable finished products (gasoline, diesel fuel, etc.) on site. Another alternative is to perform a partial upgrading operation to produce a syn-crude, employing coking, hydrotreating, or solvent extraction steps. Thermal coking results in an overall liquid yield loss of approximately 15 - 20% and the production of a significant quantity of coke (3). The coke produced contains high levels of nitrogen, sulfur, and arsenic which lowers the marketability. Further, the coke would have to be transported by either rail or truck to the consumer.

Solvent extraction is one of the options to the shale oil upgrading problem. Solvent extraction allows for the selective removal of undesireable components while avoiding the decomposition and polymerization reactions that occur in the high boiling fractions during thermal processes. Extraction has been used extensively in the refining of conventional crudes since the 1930's.

A research project has been initiated at Colorado School of Mines to investigate the removal of the highly aromatic fraction, polar molecules, and arsenic containing compounds from shale oil utilizing a solvent extraction process. The goal is to achieve a substantial reduction in heteroatom content (N,O,S,As), yielding a product oil capable of refining by conventional technology. The first stage of the research program consisted of the design and construction of a bench scale, continuous solvent extraction apparatus to study the feasibility of reducing heteroatom and arsenic content by selective solvent extraction.

The extraction system was operated with n-heptane at varied temperatures and solvent ratios. A mixture of 70% by volume N-methyl-2-pyrrolidone (NMP) and 30% water was also employed as a selective solvent with temperatures in the range 48.9 °C (110 °F) - 104.4 °C (220 °F). The shale oil used was produced in a direct heat Paraho retort. The effect of solvent type and extraction temperature on product oil yield and quality were examined.

EXPERIMENTAL BASIS

Selective solvents have found application primarily in the areas of refining heavy oils for the production of lubricants, and in the deasphalting of heavy crudes and vacuum residuum to maximize the fraction sent to cracking operations, while minimizing the amount produced as residual fuel oil and asphalt.

Solvent deasphalting, using propane, butane, and pentane, is the treating of residua or heavy crudes with a solvent that solubilizes the desireable fractions of the feed, while rejecting the asphaltic portion. Propane deasphalting is an extraction process involving contacting liquid propane with the heavy oil charge (4 - 8, 11-20). Addition of small volumes of propane initially dilutes the oil but further addition of liquid propane results in a phase separation. The solvent ratio at which a phase separation occurs is termed the critical solvent ratio. Propane has a selective solvency for low molecular weight paraffins. The non-paraffinic (more aromatic) components in an oil remain insoluble and form a second phase along with a small amount of propane.

The unique solvent properties of propane are attributable to the manner in which the specific gravity of propane changes with temperature (21). The specific gravity

of liquid propane changes from 0.50 at 21.1 °C (70 °F) to 0.25 at 94.4°C (202 °F), under its own vapor pressure. Over this range propane changes from a typical liquid to a fluid possessing essentially the properties of a gas. In the temperature range 37.7 °C (100 °F) to 60 °C (140 °F) the heavy, asphaltene fraction is but very slightly soluble in propane; whereas at these same temperatures oils dissolve completely. Instead of behaving as an ordinary liquid and dissolving more of any partially soluble substance as the temperature is raised, propane dissolves less. This is also true of the homologous series including butane, pentane, hexane, and heptane. In general, the heavier compounds are rejected first; but as the physical properties of the solvent become increasingly those of gases it dissolves less and less oil.

Early propane deasphalting units employed mixer-settlers in continuous operation (5,6,7,8,9,22). In such units the reduced crude and liquid propane are mixed and heated to a predetermined temperature which causes asphalt to form a separate phase. The phases are separated continuously in a settling vessel. Additional stages may be added with the mixer-settler operating at a higher temperature to reject an additional fraction of heavy oil. The propane is recovered from flash drums and steam

stripping columns and returned to collection drums.

Since 1940 continuous columns have been used in solvent deasphalting processes (4,11,12,15,16,17,20). Both baffled columns and packed columns are employed. However, it was found that a mechanically agitated column (to be described later) called a rotating disk contactor (RDC) performed more efficiently (4,15,16,20). A comparison of RDC and baffled tower deasphalting, made on pilot plant equipment, showed about a 5% yield improvement for the RDC at a constant quality of deasphalted oil (4). The process generally consists of introducing the feed (at extraction temperature) at the top of the RDC. Liquid propane, introduced near the bottom of the column, is contacted countercurrently with the descending heavy oil. The deasphalted oil solution withdrawn overhead, containing most of the propane, is heated and flashed to remove the solvent. Similarly, the asphalt solution from the bottom of the RDC is heated and flashed to remove propane. Stripping columns for each stream remove the remaining solvent.

Deasphalting with a heavier paraffinic hydrocarbon than propane has also been used commercially. Residua and heavy oil treating with pentane, pentane-hexane mixtures, and n-butane mixtures with i-pentane have been demonstrated successfully (23). The Demex Process licensed by Universal

Oil Products, utilizes normal butane and iso-pentane to produce a deasphalted, demetallized oil (24). Pentane, hexane, and heptane are proposed as the solvent of choice for use in a solvent deasphalting operation on topped crudes and vacuum residues containing high concentrations of metals and asphaltenes (25). The yield of deasphalted oil can be increased dramatically by extracting more high molecular weight fractions through the use of heavier paraffinic solvents, as shown in a laboratory study of various crudes (26). The principle is identical in both propane and heavy paraffinic solvent deasphalting. The extraction column design and solvent recovery systems are also similar, with the difference being the lower vapor pressures of the heavier solvents. Figure 1 (from ref. 2) illustrates the effect of solvent carbon number on the amount of asphalt rejected.

Figure 1

Effect of Solvent Carbon Number on the
Amount of Asphalt Precipitated (From Ref. 2)

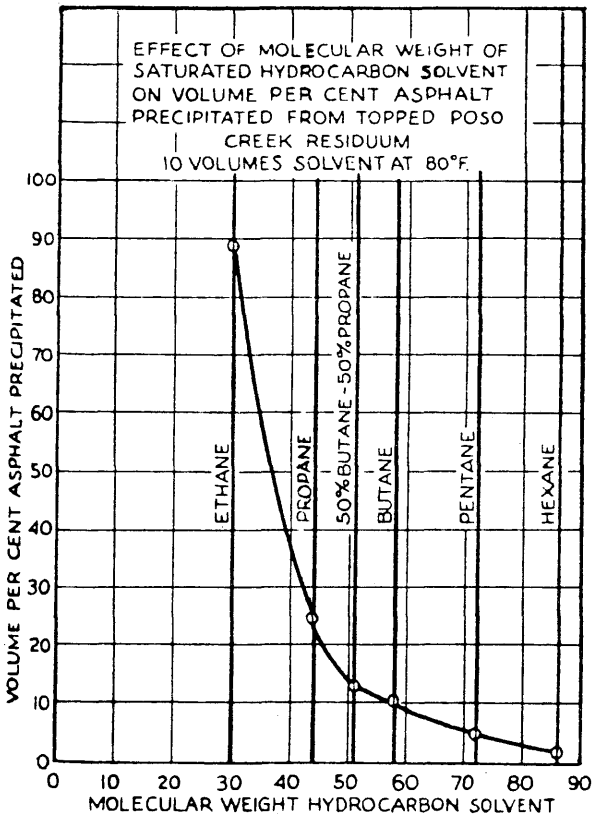


FIG. 1

Another solvent extraction operation that offers possibilities for the treatment of shale oil is the extraction with one of a group of polar solvents that have been previously studied in connection with lubricating oil refining. Solvent extraction provides a means for the removal of aromatics and other undesireable constituents from lubricating oils. The removal of these components improves the viscosity index, color, oxidative stability, and thermal stability of base oils (27). Such a polar solvent, used in the extraction of shale oil, would remove the highly aromatic fraction, polar constituents, and would reduce the concentration of heteroatom compounds. Arsenic containing compounds would also be preferrentially removed.

Many solvents have been proposed for use in the extraction of lube oils. The more common solvents in use as of 1977 were furfural, phenol, liquid sulfur dioxide, and N-methyl-2-pyrrolidone (NMP) (28). Liquid sulfur dioxide was originally introduced in the Edeleanu process for the extraction of kerosene fractions but liquid sulfur dioxide is of limited utility due to its toxicity, pollution control regulations, and the requirement for extraction at fairly low temperatures (due to the pressure required to maintain the liquid phase). The "Duo-Sol" process is a combination deasphalting and phenol extraction process (29,30).

Furfural is used quite extensively in lube oil refining, however it is subject to oxidation and polymerization which complicates the processing apparatus (46). Phenol and NMP both have good selectivity for aromatics and polar compounds, and both are in current use.

Several other solvents bear consideration in choosing a solvent suitable for extracting shale oil. The Udex Process, developed jointly by Dow Chemical Corporation and Universal Oil Products Company, uses di-ethylene glycol as the solvent for extracting aromatics (benzene, toluene, and xylene) from reformates and pyrolysis naphthas (32). NMP is used in the Arosolvan Process for the recovery of BTX aromatics from pyrolysis gasoline (33,34). Sulfolane (tetrahydrothiophene,1-1 dioxide) is used commercially for BTX extraction by the Shell Development Company (35,36,37). Formamide and N,N-dimethyl-formamide (DMF) have also been discussed for extracting aromatics (37). Morpholine (38,39) and N-formylmorpholine have been studied extensively for use in aromatics extraction (40,41,42).

Given the number of solvents proposed for use in pure aromatics (BTX) extraction and in the extraction of aromatics and polar compounds from lube oils, it is instructive to look at the various solvents physical properties. The following list describes desireable solvent

properties for use in shale oil extraction (28).

- High selectivity for aromatics and polar compounds
- Good solvent power -- low solvent to feed ratio
- High extraction temperature -- for good mass transfer
- Easy recovery -- by simple distillation
- Low vapor pressure -- avoid use of pressure equipment
- High density difference -- rapid separation of oil and solvent phases
- Stability -- no chemical or thermal degradation
- Available -- at reasonable cost
- Non-corrosive
- Non-toxic -- environmentally safe

Selectivity and capacity are two factors considered when choosing a solvent. Capacity is defined by the distribution factor, i.e. the aromatics concentration ratio of the solvent phase to raffinate phase. Selectivity is defined by the ratio of the distribution factors of one aromatic component to the distribution factor of one non-aromatic component. This is for any 3 component system of solvent, aromatics, and non-aromatics. The lower the value of the distribution factor (Ka), the higher the capacity of the solvent will be.

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

$$S = Kn/Ka = [\ A\text{-solv}\ ][\ N\text{-raff}\ ]/[\ A\text{-raff}\ ][\ N\text{-solv}\ ]$$

where Ka = distribution factor of aromatic component

Kn = distribution factor of non-aromatic

S = Selectivity

[A-solv] = Solvent phase aromatics concentration

[N-solv] = Solvent phase non-aromatics concentration

[A-raff] = Raffinate aromatics concentration

[N-raff] = Raffinate non-aromatics concentration

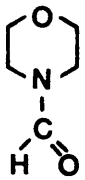
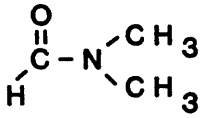
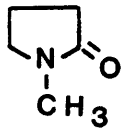
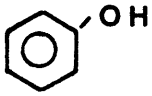
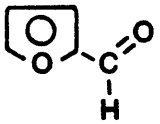
Most solvents with high capacity have a low selectivity and vice versa. A previous study investigated these two properties for many of the solvents listed above (34). Solvents with very low capacities for aromatics require a much greater solvent treatment rate and hence a higher circulation rate for the solvent. This results in increased operating costs due to the larger solvent inventory and the cost associated with solvent recovery. N-methyl-2-pyrrolidone (NMP) exhibited a high capacity but low selectivity; while furfural, phenol, dimethylformamide, morpholine, and sulfolane have low capacities and high selectivities.

Selectivity can be modified by the addition of a polar mixing component, such as water or ethylene glycol, that has a high selectivity and low capacity. The choice of polar mixing components is dictated by availability and the heat requirements of recovering the added component from the solvent.

Table 1 shows the structures and some of the physical properties of the most promising solvents.

Table 1

Comparison of Various Extraction 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	

Looking at the solvents in Table 1, the choice of a suitable solvent for the extraction of shale oil is narrowed down considerably. DMF is impractical as the specific gravity is 0.9487 compared to 0.9352 for shale oil. High boiling points rule out the use of sulfolane, morpholine, and N-formylmorpholine, as they boil above the initial boiling point of shale oil (approximately 206 °C). This prevents distillation and recovery without the simultaneous loss of the shale oil light ends. Phenol, while posessing an adequate difference in specific gravity and a low boiling point (181.7 °C) has a high toxicity and was ruled out on this basis. Furfural also has acceptable values of specific gravity and boiling point, however stability is a problem as it must be kept under an inert atmosphere to avoid oxidation and polymerization. NMP boils at 201.7 °C allowing for recovery by distillation following extraction. It has a specific gravity of 1.03 which is sufficient for rapid separation of the two phases. Further, NMP has a high solvent capacity for aromatics and polar compounds and the selectivity is enhanced considerably with the addition of small amounts of water (28,33,34). It is also non-toxic, non-corrosive, and has excellent thermal and chemical stability.

EXPERIMENTAL EQUIPMENT

A schematic of the bench-scale system used for the continuous solvent extraction of shale oil is shown in Figure 2. The system is divided into:

1) Feed system
2) Preheat - extraction column system
3) Solvent recovery system
    a) Paraffinic hydrocarbon solvent
    b) Polar organic solvent
4) Sample system

Unless otherwise stated all tubing, fittings, and wetted surfaces of the apparatus are of type 316 stainless steel.

Feed System

The metering pump is a reciprocating, positive displacement pump of plunger design. The capacity is linearly adjustable from zero to a maximum of 44.4 liters per hour in the solvent pump head and a maximum of 2.76 liters per hour in the shale oil pump head. The pump produces pulsating flow resulting in pressure surges of 10 percent. The two pump heads powered by a common driver allow for the simultaneous separate pumping of the shale oil and solvent at differing flow rates.

Both solvent and shale oil are fed to the pump inlet in

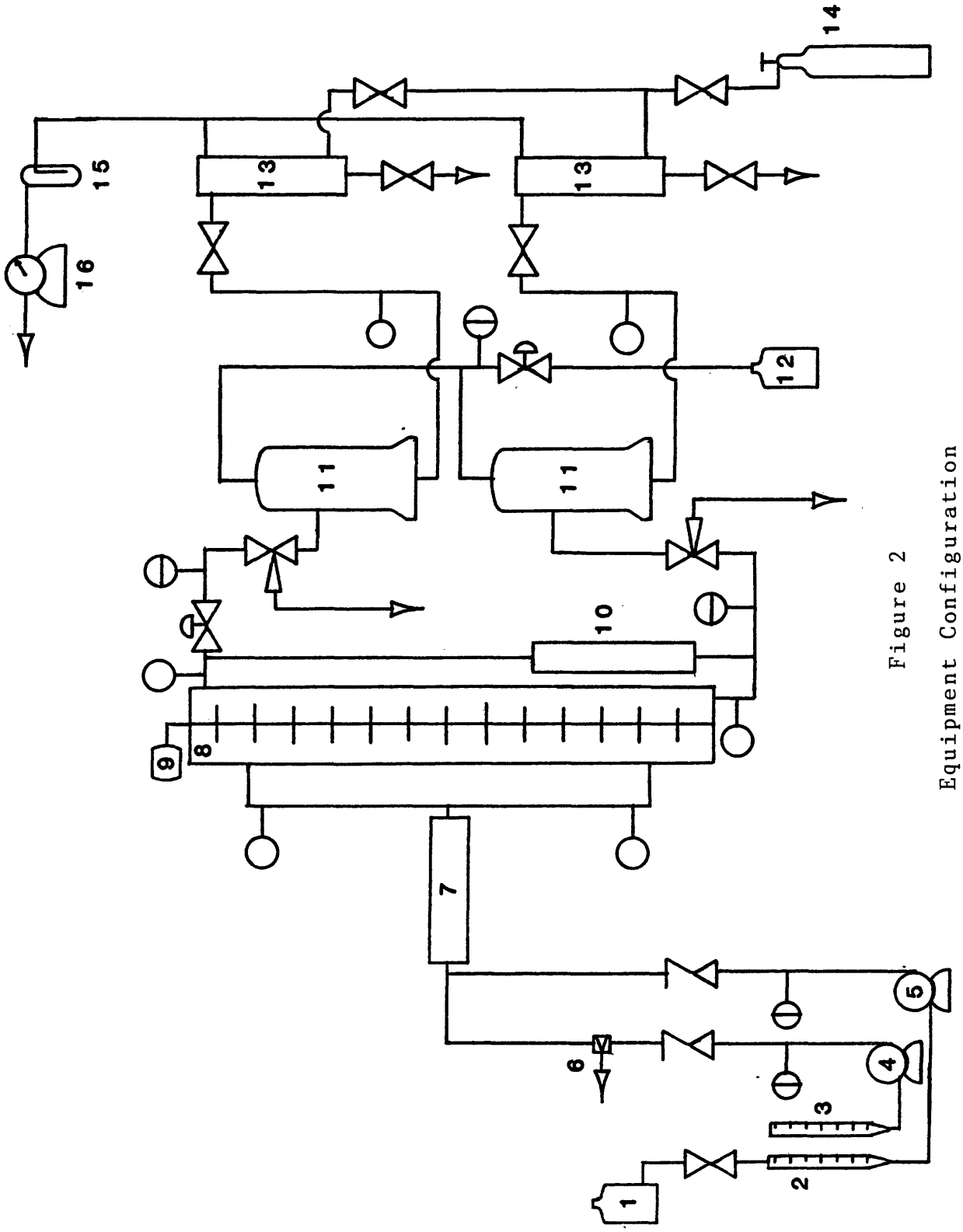


Figure 2
Equipment Configuration

Table 2

Equipment Configuration Diagram Legend

1. Solvent Resevoir Tank
2. Solvent Feed Buret
3. Shale Oil Feed Buret
4. Solvent Pump Head
5. Shale Oil Pump Head
6. Rupture Disc
7. Tube Furnace
8. Rotating Disc Contactor
9. Motor
10. Jerguson Liquid Level Gage
11. Flash Drum
12. Solvent Recovery Drum
13. Stripping Column
14. Nitrogen Cylinder
15. Knock Out Vessel
16. Dry Test Meter

 Valve

 Relief Valve

 Back-Pressure Regulating Valve

 Pressure Gauge

 Thermocouple

 Three Way Valve

one liter volumetric burets. An auxilliary 5 gallon resevoir feeds solvent into the solvent buret through a needle valve. Due to its high pour point, shale oil is heated in the feed buret with heating tape. Heating tape also traces the pump check valves, and the 1/4 inch shale oil suction and discharge lines.

System over-pressure protection is provided by an adjustable, spring-loaded relief valve on both the solvent and shale oil discharge lines. The relief valves both vent into 1/4 inch stainless steel tubes leading to a 30 gallon pressure let-down drum. A vapor relief line of 1/4 inch copper tubing vents to the fume hood.

A calibrated rupture disk provides back-up system over-pressure protection. It is placed on the shale oil discharge line, venting to the same pressure let-down drum described above. The disk is designed to rupture at 516 psig.

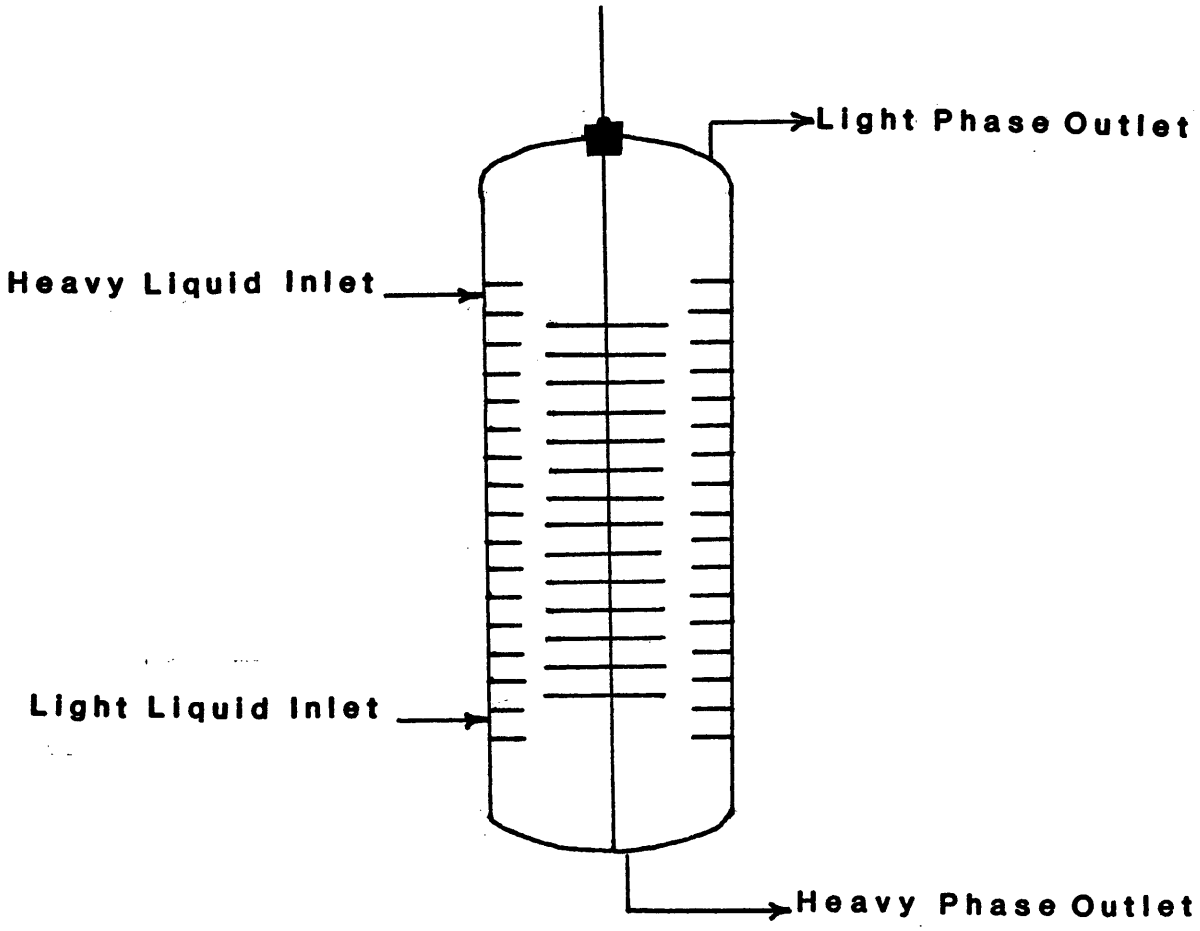
Preheat - Extraction Column System

The shale oil and solvent are pumped through 1/4 inch discharge lines to a mixing tee at the preheat furnace inlet. A 1/2 inch stainless steel tube runs the length of the furnace, providing the residence time necessary to reach the desired extraction temperature. The furnace is a one inch inside diameter by 28 inch long resistance tube

furnace. Power to the furnace is controlled by a variable voltage transformer. The heated feed is split by a tee into two 1/4 inch lines that enter the extraction columns two feed ports. Insulating tape (Zetex) minimizes heat loss along the length of the lines between the furnace and the extraction column. The temperature of both streams is monitored by two in-line type T thermocouples placed immediately prior to entering the extractor. A digital temperature readout and manual selector switch allow for the monitoring of the thermocouples.

The extraction column is a 3 inch inner diameter by 48 inch rotating disk contactor (RDC). The RDC construction and performance is described in the literature (references 43 - 49). The column used in this study was manufactured by York Process Equipment Company of New Jersey. The RDC consists of a number of rotating disks supported on a shaft. Stator rings are positioned on the column wall such that a disk is centered in each compartment formed by a pair of rings. The diameter of the thin disks is smaller than the diameter of the opening in the middle of the stator rings to facilitate removal of the shaft for cleaning. Figure 3 shows a schematic of the RDC.

Figure 3
Rotating Disk Contactor



The RDC shell and internals are 316 stainless steel. Stator ring spacing is 2.25 inches resulting in 18 compartments in the mixing zone and 3.5 inch settling zones at each end. The disk diameter is 1.5 inches and the internal diameter of the stators is 2.25 inches. The rotor is driven by a 1/4 horsepower variable speed electric motor mounted perpendicular to the column. A right angle gearbox connected to the top of the shaft allows for shaft speeds of 0 to 1000 r.p.m..

Mass transfer is increased in a rotating disk column over that observed in a baffled extraction column due to the dispersion of one phase by the mixing action of the disks (4). Liquid flow patterns in the compartments have been investigated previously, and were found to be composed of three movements (44,45,49). Countercurrent flow develops due to the density differences of the two phases. Simultaneously, the liquid mass rotates about the axis of the shaft, while a slower movement of the liquid from the shaft toward the wall occurs near the disks, and from the wall back toward the shaft occurs near the stators. One of the phases becomes dispersed due to the shearing stresses accompanying the toroidal flow pattern in each compartment.

The desired extraction temperature is maintained in the RDC using heat tape, powered by a variable transformer,

wrapped along the length of the column. The column is also covered with a 2 inch layer of foil coated, fiberglass insulation. Type T in-line thermocouples monitor the exit temperature of the extract and raffinate phases.

The interface level in the RDC is monitored with a series T-12, transparent Jerguson liquid level gage mounted in series with the column. The gage is installed so that it reflects the liquid level changes in the bottom 1/3 of the column. The light phase exits the top of the column in a 1/4 inch line leading to a 1/4 inch tee junction. The tee allows flow to the liquid level gage. An adjustable, diaphragm back-pressure regulating valve is placed after the tee junction. The heavy phase exits the bottom of the column in a 1/2 inch line leading to another tee junction, completing the series tubing layout of the column and the Jerguson gage.

All the lines leaving the RDC and entering the liquid level gage are traced with heat tape and insulated with Zetex tape to minimize the loss of heat.

Flow control needed to maintain the position of the interface was accomplished using the back-pressure regulating valve on the light phase draw-off line and a needle valve on the bottom line. The back-pressure regulating valve is adjustable from 100 - 400 psig. The

pressure required to maintain both phases in the liquid state is controlled by the proper adjustment of the valve's set point. At pressures greater than the set point the valve opens and allows light phase draw-off. The interface level is maintained through visual observation in the Jerguson gage and mnaual operation of the needle valve on the heavy phase draw-off line.

Solvent Recovery System

The solvent recovery system is of necessity different for the two classes of solvents investigated. System 1 is employed for low molecular weight hydrocarbon solvents from propane to pentane. System 2 is employed when the solvent is a polar organic with a low vapor pressure such as N-methyl-2-pyrrolidone (NMP). NMP was used with a water content of 30% by volume. System 2 was also used with n-heptane as the solvent.

System 1: Light Phase--Extract, Heavy Phase--Raffinate

This mode of operation allows for the recovery of light hydrocarbon solvents of the series propane through pentane. Hexane and heptane have sufficiently high boiling points to require a simple flash distillation procedure not included in the system.

Both the extract and raffinate phases pass through

identical flash drums and stripping columns to recover the solvent. Following the tee junction at the Jerguson gage, the extract phase flows through a 1/4 inch insulated line at the pressure maintained in the RDC. Prior to expansion across a needle valve into a 4 liter stainless steel flash drum, the temperature and pressure are monitored. The pressure in the drum is controlled by a second back-pressure regulating valve with an operating range of 130-200 psig. The set point for this valve is determined by the vapor pressure of the solvent at the temperature of condensation.

The raffinate phase leaves the tee junction at the Jerguson gage in a 1/2 inch Zetex insulated line at the pressure of the RDC. The temperature and pressure are monitored before expansion into the flash drum. The vaporized solvent streams from both the extract and raffinate flash drums flow in 1/4 inch lines to a tee, and are condensed in the collection vessel. Condensation takes place at the pressure set by the regulating valve. The collection vessel is cooled in a bath at a temperature below the solvent dew point.

The extract oil and raffinate flow through 1/4 inch lines, through a 1/4 inch pressure reducing valve and enter the top of their respective stripping columns. The columns are maintained at close to ambient pressure. The stripping

columns are constructed of 2 inch inside diameter by 2 feet long carbon steel pipes packed with 1/4 inch pyrex glass Raschig rings. Nitrogen flows countercurrent to the oil and strips the remaining solvent from the oil.

In the present study, n-heptane was used as the paraffinic solvent. The solvent recovery system was originally designed to handle solvents whose boiling points did not exceed 37.8 °C (100 °F). Heptane (b.p. 98.4 °C) could not be flashed off or stripped from the oil, necessitating the use of a simple flash distillation column for recovery.

System 2: Light Phase--Raffinate, Heavy Phase--Extract

This mode of operation is used to recover NMP, as its low vapor pressure precludes the use of flash drums and stripping columns for recovery. System tubing is disconnected prior to the extract and raffinate flash drums. Extract and raffinate are collected in 5 gallon drums with the two needle valves prior to the flash drums controlling the flow.

The NMP-water mixture is recovered in a Vigreaux distillation column. NMP with 30% water by volume, has an initial boiling point of 107 °C (250.2 °F). Pure NMP boils at 201.7 °C (395 °F), allowing recovery of the solvent from the shale oil (approximate initial b.p. 206 °C) by

distillation. In order to recover water free NMP for recycling, the NMP-water mixtures boiling in the range 107-201.7 °C were discarded. Both extract and raffinate phases were distilled in this manner.

Sample System

The sample collection method used with a light hydrocarbon solvent consists of the gas sampling system and the liquid products collection. The extract oil and the raffinate are collected in 5 gallon drums as they leave the bottom of the stripping columns. Composition samples are collected in quart-size metal cans protected with a nitrogen blanket.

Nitrogen and the stripped hydrocarbon leave the top of each stripping column in 1/4 inch tubing. Both streams join in a tee and pass into a one liter knockout drum prior to measurement in a calibrated dry test gas meter.

Gas leaving the meter flows to the laboratory hood to be vented. A gas sample can be taken by switching two 3-way valves for about thirty seconds, diverting flow through the sample cylinder.

When operating with the NMP-water solution as the solvent both the extract and raffinate are collected in 5 gallon drums prior to entering the flash drums. Composition samples are collected in quart-size metal cans.

An identical procedure was used when operating with n-heptane as the solvent.

EXPERIMENTAL PROCEDURE: BATCH EXTRACTIONS

Prior to operation of the continuous liquid-liquid extraction system, batch extractions were performed. The batch studies were used to qualitatively evaluate various solvents and solvent to shale oil ratios. Many batch extractions were attempted using n-heptane, n- hexane, and n-pentane at various solvent ratios and temperatures. The other solvents tested were NMP, DMF, phenol, furfural, and morpholine.

The extractions were done in a 500 ml separatory funnel. A water bath was maintained at the desired extraction temperature. The shale oil and the solvent were both heated in the bath until they reached the extraction temperature. The method of contacting, consisted of agitating 200 ml of oil with a measured volume of solvent in a separating funnel. The funnel contents were then allowed to settle facilitating phase separation. The funnel remained in the water bath during the settling time. In most instances a 3:1 solvent ratio and a temperature of 60 °C (140 °F) were used. This temperature was chosen so that the shale oil would be above its pour point. Higher solvent ratios and higher temperatures were employed if phase separation did not occur initially. The results of extractions using n-heptane, hexane, and pentane are shown

in Table 3.

Table 3

Batch Extractions Using Light Hydrocarbons as Solvents

Solvent	Solvent to Oil Ratio	No. of Phases	Temperature °C (°F)
n-Heptane	1:2	1	60 140)
n-Heptane	1:1	1	60 (140)
n-Heptane	2:1	1	60 (140)
n-Heptane	3:1	1	60 (140)
n-Heptane	4:1	1	60 (140)
n-Heptane	4:1	1	70 (158)
n-Heptane	4:1	1	80 (176)
n-Heptane	7:1	1	60 (140)
n-Heptane	10:1	1	60 (140)
n-Hexane	3:1	1	45 (113)
n-Hexane	4:1	1	45 (113)
n-Hexane	7:1	1	45 (113)
n-Pentane	3:1	1	25 (77)
n-Pentane	4:1	1	25 (77)
n-Pentane	10:1	1	25 (77)
n-Pentane	4:1	1	30 (86)

The batch extractions using heptane, hexane, and pentane as solvents failed to produce a second phase. Heptane was used at solvent to oil ratios of 1:2 up to 10:1 at a temperature of 60 °C (140 °F). The shale oil became noticeably thinner and less viscous as the heptane ratio increased. However, even with prolonged settling periods (up to 24 hours) at the desired extraction temperature, phase separation did not occur. Extractions were also carried out at a 4:1 ratio, with increasing temperature levels, to take advantage of the reverse solubility with temperature that is characteristic of paraffinic hydrocarbon solvents. Heptane's boiling point (98.4°C) was the limiting temperature for these batch extractions as the extractions were performed at atmospheric pressure. Even at 80 °C there was no evidence of the presence of two phases.

Similarly, the extractions performed with hexane and pentane failed to produce the desired rejection of a second phase. Hexane was used at 45 °C in ratios ranging from 3:1 to 7:1. Pentane was employed in ratios from 3:1 to 10:1 at 25 °C and 30 °C.

The batch extractions using various polar organic solvents produced more promising results. Table 4 gives the results of extractions using NMP, DMF, furfural, phenol, and morpholine. The temperature was 60 °C (140 °F) and the

solvent to oil ratio was 3:1 in all the tests.

Table 4

Batch Extractions Using Polar Organic Solvents

Solvent	Solvent to Oil Ratio	No. of Phases	Temperature °C (°F)
NMP	3:1	1	60 (140)
0.7 NMP-0.3 Water	3:1	2	60 (140)
DMF	3:1	1	60 (140)
0.9 DMF-0.1 Water	3:1	2	60 (140)
0.9 DMF-0.1 Ethylene Glycol	3:1	2	60 (140)
Furfural	3:1	2	60 (140)
Phenol	3:1	1	60 (140)
0.9 Phenol-0.1 Water	3:1	2	60 (140)
0.9 Phenol-0.1 Ethylene Glycol	3:1	2	60 (140)
Morpholine	3:1	1	60 (140)
0.9 Morpholine-0.1 Water	3:1	2	60 (140)
0.8 Morpholine-0.2 Water	3:1	2	60 (140)
0.8 Morpholine-0.2 Ethylene Glycol	3:1	2	60 (140)

Furfural exhibited the highest selectivity (qualitatively) as it was immiscible with the shale oil

without the addition of a polar mixing component such as water or ethylene glycol. The extract phase appeared brown under natural light.

The other solvents required the addition of either water or ethylene glycol in order to produce a second phase. NMP was miscible with the shale oil at a 3:1 ratio and a temperature of 60 °C. However, the addition of 30% (vol.) distilled water resulted in an immediate phase separation. The interface was very well defined, with the extract phase appearing green in natural light.

A solution of 90% DMF - 10% ethylene glycol (by volume) gave a green extract phase when mixed with the oil. However, the interface was much more defined in a solution of 90% DMF - 10% water.

Morpholine was miscible with shale oil when used alone and also when used with 10% (by volume) distilled water. The addition of 20% distilled water or ethylene glycol to the morpholine however, produced an immiscible phase. The extract phase was green, with a clearly defined interface.

A separation was obtained with a 90% phenol solution containing either 10% ethylene glycol or 10% water as the mixing component. The phase boundary was not as clear as that obtained with either the NMP, DMF, or morpholine solvent solutions.

As discussed earlier, NMP possesses the best combination of physical properties and solvent characteristics of the group of solvents considered for the extraction of shale oil. An additional set of batch extractions with NMP were performed before employing the NMP-water solvent in the continuous extraction system. Table 5 gives the results of additional NMP extractions.

The additional extractions carried out with NMP-water solutions clarified the range of solvent solutions that are feasible for use in the extraction of shale oil. The need for the addition of a polar mixing component is evidenced by the lack of a phase separation when pure NMP is used. This is true, even in solvent to oil ratios up to 4:1.

A series of batch extractions at 60 °C (140 °F) using NMP-water solutions with increasing volume percentages of water were used to determine the quantity of water which gave the clearest separation between the two phases. At a constant 3:1 solvent ratio, extractions were performed at solvent compositions ranging from 95% NMP - 5% water to 70% NMP - 30% water. It was found that at a level of 5% added water the solvent was miscible with the shale oil. However, at levels of 10% -30% added water a second phase formed. The interface increased in clarity as the percentage of water increased. At 30% water (vol.) in the NMP, the

extract phase appeared as a dark green fluid that did not transmit light. The raffinate phase was a dark, brown-black fluid that was also not translucent.

Table 5

Batch Extractions Using NMP Solutions as Solvent

Solvent	Solvent to Oil Ratio	No. of Phases	Temperature °C (°F)
NMP	1:1	1	60 (140)
NMP	2:1	1	60 (140)
NMP	4:1	1	60 (140)
.95 NMP-.05 Water	3:1	1	60 (140)
0.9 NMP-0.1 Water	3:1	2	60 (140)
0.8 NMP-0.2 Water	3:1	2	60 (140)
0.7 NMP-0.3 Water	3:1	2	60 (140)
0.7 NMP-0.3 Water	4:1	2	60 (140)
0.7 NMP-0.3 Water	5:1	2	60 (140)
0.7 NMP-0.3 Water	4:1	2	40 (104)
0.7 NMP-0.3 Water	4:1	2	70 (158)
0.7 NMP-0.3 Water	4:1	2	80 (176)
0.7 NMP-0.3 Water	2:1	2	60 (140)
0.7 NMP-0.3 Water	1:1	1	60 (140)
0.9 NMP-0.1 Ethylene Glycol	3:1	2	60 (140)
0.8 NMP-0.2 Ethylene Glycol	3:1	2	60 (140)
0.7 NMP-0.3 Ethylene Glycol	3:1	2	60 (140)

Next, a number of extractions were carried out at a constant solvent composition of 70% NMP - 30% water, constant temperature of 60 °C, but with varying solvent to oil ratios. At a 1:1 ratio, no separation was observed. This later allowed for the dilution of the shale oil with solvent in a 1:1 ratio as feed to the continuous system. However, at ratios of 2:1 up to 5:1 the solvent phase was immiscible. The appearances of both phases in these extractions were qualitatively identical.

At a constant solvent composition of 70% NMP - 30% water and constant solvent ratio of 4:1, extractions were performed at temperatures from 40 °C (104 °F) to 80 °C (176 °F). These tests showed the existence of two phases throughout this range of temperatures, which allowed further study in the continuous extraction apparatus within approximately the same temperature range.

Ethylene glycol was also studied as an additive to increase the selectivity of NMP. At 60 °C, a 3:1 solvent ratio, and with ethylene glycol levels from 10% - 30% (by volume), two phases were formed. The interface appeared to be slightly less distinct than it was with NMP-water solutions. Ethylene glycol (b.p. 198 °C) can not be separated from solutions containing NMP (b.p. 201.7 °C) by simple distillation due to the close proximity of their

boiling points. For this reason, ethylene glycol was not studied further as a polar mixing component. However, if provisions are made for testing the recycled solvent and adjusting the level of ethylene glycol as necessary, ethylene glycol is suitable as a mixing component.

NMP-water solvent solutions were found to give a good separation when applied in shale oil batch extractions. In particular, a solvent composition of 70% NMP - 30% water used at solvent ratios between 2:1 and 5:1 and temperatures ranging from 40 - 80 °C proved successful in effecting a phase separation. Based on the batch studies, the continuous extraction of shale oil in the RDC system was carried out at a constant solvent to oil ratio of 4:1 and a constant solvent composition of 70% NMP- 30% water. The operating temperature was the variable parameter.

EXPERIMENTAL PROCEDURE: CONTINUOUS UNIT

70% NMP: 30% Water as Solvent

The extract and raffinate bulk collection drums and the quart size sample containter were weighed prior to and after each run. This facilitated the overall mass balance on the system. The refractive index of the NMP was determined to assure 99% purity following distillation and recovery from the products of the previous run. Distilled water was added to the NMP to give a solution containing 30% water by volume. The solvent resevoir tank was then charged with 5 gallons of the NMP-water solution. Nitrogen was used to pressure test the system prior to introduction of the solvent and the oil.

The shale oil feed line heat tape, preheat furnace, and RDC heat tape were turned on and the system was heated to approximately 37.7 °C (100 °F). The shale oil buret heat tape was then turned on and the buret was filled with a 1:1 ratio of shale oil and solvent solution. The shale oil was diluted in the feed buret because the pump check valves became clogged when pure shale oil was fed to the pump. No phase separation occurred at the 1:1 solvent to oil ratio.

The pump was turned on with the shale oil pump head set at the maximum stroke and the solvent head set at zero.

This allowed the system to fill with shale oil at the rate of 2.8 liters per hour. During system filling, the preheat furnace temperature was raised until the desired extraction temperature was reached. The temperature was monitored by the thermocouples placed in the inlet lines to the RDC.

When the RDC filling was complete, the back pressure regulating valve on the light phase outlet was adjusted to maintain the system pressure at 125 psig. At this point the NMP-water solvent flowrate was set and calibrated. The shale oil flowrate was reset and calibrated to achieve the desired 4:1 solvent to oil ratio. The motor driving the shaft in the RDC was now turned on. During this start-up period, the interface developed in the bottom of the column and became visible in the Jerguson gage. The heat tape wrapped around the RDC was adjusted to maintain the temperature that is monitored in the outlet lines $\pm$ 5 °F of the desired extraction temperature.

During start-up, the products were collected and saved in gallon cans for solvent recovery. At the 4:1 solvent to oil ratio the heavy, solvent-rich extract phase was withdrawn approximately four times faster than the raffinate phase, maintaining the interface near the bottom of the column. The total solvent flowrate was 5.3 lit/hr for all runs. The shale oil flowrate was 1.3 lit/hr, giving a total

flowrate of 6.6 lit/hr.

A digital stopwatch was started when the interface, flowrates, and system temperature and pressure were stable. The run was stopped after 4 volumetric throughputs were circulated through the RDC. The length of the runs always exceeded the time needed for 4 volumetric throughputs (3.3 hours). One run was terminated at 3.5 hours due to clogging of the pump check valves on the shale oil line. The average run time was 4.2 hours excluding the shortened run of 3.5 hours.

Flowrate checks were conducted at 1/2 hour intervals. These checks consisted of measuring the time required to pump one liter from the volumetric feed burets. The solvent flowrate remained virtually constant throughout all runs. The shale oil would sometimes decrease slightly in flowrate. If this occurred, the flowrate was then restored by raising the pump stroke length and rechecking the flowrate. These changes in the flowrate were attributed to a gumming of the pump check valves.

The temperatures of the two inlet streams and the two outlet streams of the RDC were recorded at approximately 1/2 hour intervals. The temperature of the inlet streams was maintained $\pm$ 5 °F of the predetermined extraction temperature by adjustment of the power supplied to the

preheat furnace. The RDC outlet stream temperatures were maintained $\pm$ 5 °F of the inlet stream temperatures by manual adjustment of the power to the RDC heat tape.

Pressure was maintained in the system by the back-pressure regulating valve on the raffinate stream. Manual adjustment of the heavy phase draw-off valve regulated the interface level and fine pressure control.

Extract oil and raffinate products were collected in 5 gallon containers. Composition samples were withdrawn after 3 RDC volumetric throughputs (16.7 liters or 2.5 hours) had passed through. The samples were then taken at 20 minute intervals.

At the completion of the run the power supply to the preheat furnace, heat tapes and shaft motor was shut off. Elapsed run time was also recorded. Fresh solvent was pumped through both pump heads flushing the check valves and the RDC feed lines prior to pump shut down. Both the bulk collection drums and the sample cans were weighed.

Prior to the next run the system was drained. The check valves on the shale oil pump head were removed and cleaned in acetone. The back-pressure regulating valve was also cleaned in acetone to remove accumulated residue from the moving parts. NMP was recovered from the extract and raffinate phase prior to the next run.

NMP Recovery

A Vigreaux distillation column was used to distill off the NMP from from both the solvent-rich extract and the raffinate. The recovered NMP was tested for purity by determining the refractive index. The distillation procedure resulted in the recovery of 99% pure NMP.

The composition samples were water washed to remove the NMP that remained following distillation. The extract or raffinate samples were placed in tared 500 ml separatory funnels, re-weighed, and washed with a solution of 90% distilled water and 10% NaCl by weight. The salt solution, containing NMP, was drained and the remaining sample weighed. This procedure was repeated until a clear wash solution was obtained (usually three washes).

The pour point, viscosity and elemental composition were determined for the raffinate oil. The extracted material was tested for elemental composition.

n-Heptane as Solvent

The shale oil feed line heat tape, preheat furnace, and RDC heat tape were turned on and the system was heated to approximately 37 °C (100 °F). The solvent resevoir tank was charged with 5 gallons of n-heptane. The shale oil buret heat tape was then turned on and the buret was filled with a

1:1 ratio of shale oil and heptane.

The system was filled with heptane as the preheat furnace temperature was raised. The back-pressure regulating valve was set to maintain system pressure at least 50 psig greater than the vapor pressure of heptane at the desired extraction temperature. The shale oil pump head was now set and calibrated. The desired heptane to oil ratio was obtained by re-setting the heptane flowrate.

As the shale oil was introduced, the interface theoretically should have formed in the bottom of the RDC. However, the interface was never observed despite the use of varying operating temperatures and different heptane to shale oil ratios.

With n-heptane as the solvent, the light, solvent-rich extract would be withdrawn at a faster rate than the raffinate phase, maintaining the interface in the Jerguson gage. The run was started when the system temperature and pressure were stable.

The run was continued at the operating conditions set for that particular run in the attempt to obtain and locate an interface. The procedure for flowrate checks, temperature recording and product collection was the same as that described for extraction with NMP-water as the solvent.

After 2 to 3 volumetric throughputs without observation

of an interface, the run was stopped. Prior to the next run, the system was drained, and the heptane was recovered from the bulk collection drums. Due to the lack of phase separation, the liquid-liquid extraction did not take place. Instead, the n-heptane diluted the shale oil without rejecting a heavy fraction.

Samples were taken from both streams leaving the RDC and analyzed for evidence of a visually undectable phase separation. Heptane was removed from the samples in a simple flash distillation step prior to the analysis. The pour point and viscosity were then determined. No evidence of a change in the properties of the two streams was found.

n-Heptane Recovery

A simple flash distillation column was used to distill off the n-heptane from the shale oil. The boiling point of the heptane (98.4 °C) was sufficiently below the initial boiling point of the shale oil (approximately 206 °C), to permit recovery of the solvent in this manner. The refractive index of the n-heptane fraction was determined to assure solvent purity.

Emergency Shut-Down Procedure

The main power switch controlling the pump, preheat

furnace, heat tapes, thermocouple temperature display, and shaft motor was turned off. If system pressure was in excess of the rupture disk burst pressure (516 psig) indicating an obstruction in the relief line, pressure could be reduced manually by opening the needle valve on the heavy phase RDC outlet line. Following system pressure stabliization, power could be returned to the temperature display, if there was no danger of fire. This allowed the system temperature in various parts of the apparatus to be monitored. System cool-down was accomplished by pumping solvent through both pump heads and into the RDC inlet lines.

MASS BALANCE CALCULATION PROCEDURE

The overall system mass balance was calculated after each run. The balance was used to calculate the extract and raffinate yields and the percent solvent present in each phase. The two inlet streams, namely solvent and the 1:1 ratio of shale oil and solvent, were balanced against the extract and raffinate products.

Calculation of the Inlet NMP-Water Mass

The mass of solvent introduced into the system during the run was determined using the measured volumetric flowrate and the specific gravity of the solvent. The volumetric flowrate of the solvent was set and monitored throughout the run. Flowrate checks consisted of timing the pumping of 1 liter from the feed buret. Total solvent volume was then calculated using this flowrate and the actual elapsed run time. The solvent density was determined at the temperature of the feed buret (ambient temperature). The mass of solvent introduced was then the product of the volume introduced and the density.

Calculation of the Inlet Shale Oil-Solvent Mass

The volumetric flowrate of the shale oil-solvent mix (monitored in the same manner as the solvent flowrate)

together with the run time determined the volume of the 1:1 shale oil-solvent solution. The density of the solution was determined at the feed temperature, 37.7 °C (100 °F). The mass of the shale oil-solvent solution was then given by the product of the volume introduced and the density.

Determination of the Product Masses

Two 5 gallon drums were used to collect the extract and raffinate products. Samples were withdrawn in quart sample cans. Both the drums and cans were weighed prior to and after the runs. The total extract and raffinate yields were obtained as the sum of the respective sample masses. The overall mass balance was then the sum of the two inlet streams balanced by the sum of the extract and raffinate product.

Determination of the Solvent-Free Extract and Raffinate Yields

The composition samples were distilled in a Vigreaux column to remove most of the NMP-water solvent. Recovered solvent and product weights were determined by difference measurements made on the distillation vessels before and after the distillation. The remaining solvent was removed by washing with a 10 weight percent solution of NaCl in

distilled water. Solvent washing was done in a 500 ml separatory funnel at 60 °C (100 °F). A 3:1 ratio of salt solution to product was used. Extract and raffinate product weights were determined by difference, following weighing of the separatory funnel after successive washings. This procedure allowed calculation of the total percent solvent present in each phase.

The solvent-free extract and raffinate yields obtained from the composition samples were then applied to the total extract and raffinate masses resulting in the solvent-free yields. The percent yield based on inlet shale oil was then calculated.

RESULTS AND DISCUSSION OF RESULTS

Paraho Shale Oil Characterization

The Phillips Oil Company analysis (31) of the Paraho shale oil used in this study is shown in Tables 6 and 7. The API gravity was 19.8, viscosity at 100 °F was 50.9 centistokes and the asphaltene content was 1.8% by weight. Nitrogen and sulfur were 2.21% and 0.77% by weight, and the oil contained 54.4 ppm arsenic. Table 8 gives the averaged physical properties as determined at Colorado School of Mines. The Paraho shale oil was found to have a pour point of 80 F.

The discussion of the results of the batch extractions was given in the previous section. The extractions performed in the continuous rotating disk contactor consisted of two groups of runs. Heptane was used as a deasphalting solvent, while 70% NMP - 30% water was used as a polar and aromatic component selective extraction solvent. The batch extraction results showed that heptane failed to give two phases in solvent ratios up to 10:1 at 60 °C (140 °F) or at temperatures up to 80 °C (176 °F) with a 4:1 solvent ratio. Accordingly, the continuous runs were made under conditions that were more severe (higher temperatures) in the attempt to achieve a phase separation.

Table 6

Characterization of Colorado School Of Mines Paraho Shale Oil (Ref. 31)

API Gravity, 60F	19.8
Specific Gravity, 60/60F	0.9352
BS & W, vol %	Trace
Ash, wt %	0.05
Viscosity, 100F	
Centistokes	50.9
SUS (Saybolt Universal)	236.7
Viscosity, 130F	
Centistokes	22.75
SUS	109.8
Elemental Analysis, wt%	
Carbon	83.28
Hydrogen	12.74
Oxygen	1.63
Nitrogen	2.21
Sulfur	0.77
Arsenic, ppm	54.4
Hydrocarbon Type, wt % (a)	
Saturates	26.5
Aromatics	21.5
Resins	41.9
Asphaltenes	1.8
Distillation Fractions, % (b)	
IBP-400F	2.9
400-650F	23.2
650-1000F	49.4
1000F+	24.5

(a) The SARA analysis does not identify the olefin compounds.

(b) Yields (as area percent) based on simulated distillation by GLC. TBP (GLC) distillation data given in Table 3.

Table 7
Simulated Distillation of Paraho Shale Oil From
Colorado School of Mines
As Determined By Gas Liquid Chromatography

Crude Oil Boiling Point Distribution - Phillips R & D

HG-27755-99-1 (2297) DGF
HP Run #16 Oct/1/81 Time: 02:33:13

%Off	B.P.F.	%Off	B.P.F.	%Off	B.P.F.
IBP	309	30	683	60	881
1	340	31	691	61	888
2	377	32	699	62	895
3	404	33	707	63	902
4	418	34	714	64	909
5	436	35	723	65	916
6	448	36	730	66	923
7	461	37	737	67	930
8	475	38	746	68	937
9	485	39	752	69	944
10	498	40	759	70	951
11	509	41	767	71	959
12	517	42	773	72	966
13	531	43	781	73	974
14	542	44	787	74	982
15	554	45	793	75	990
16	564	46	800		
17	572	47	806		
18	580	48	812		
19	589	49	818		
20	598	50	823		
21	606	51	829		
22	616	52	835		
23	623	53	840		
24	633	54	846		
25	642	55	851		
26	649	56	856		
27	659	57	862		
28	667	58	868		
29	674	59	875		

Table 8

Colorado School of Mines Determined
Physical Properties Paraho Shale Oil

API Gravity 60 °F	20.8
Specific Gravity 60/60F	0.929
Pour Point °F	80.0
Viscosity @ 100 °F	
SUS (Saybolt Universal)	241.0
Centistokes	51.86

Continuous Unit: n-Heptane Solvent

Two runs (#1,#2) were made at conditions that were also used in the batch extractions. These runs also resulted in just a single phase, but they provided corroborating data to the batch studies. The continuous system allows the use of pressure as an additional operating parameter. The pressure was maintained at least 50 psig greater than the vapor pressure of heptane at the extraction temperature.

The remaining runs were carried out at higher temperatures to take advantage of the reverse solubility with temperature that the light paraffin solvents exhibit. Table 9 shows the operating conditions of all the n-heptane continuous unit extractions.

Table 9

Run Operating Parameters

Run No.	T °C (°F)	Rotor (rpm)	Solvent Ratio	P(psig)
1	60 (140)	800	4:1	140
2	60 (140)	800	5:1	140
3	85 (185)	800	4:1	140
4	95 (203)	800	4:1	140
5	104.4 (220)	800	4:1	140

As the operating temperature was increased up to and exceeding the normal boiling point of n-heptane the formation of a second phase still was not observed. Samples were withdrawn from the top and bottom RDC outlet streams periodically to test for a second phase that might be visually undetectable from the first phase. These samples were distilled, removing the heptane, and the gravity and pour point were determined. The results of these sample characterizations shown in Table 10, confirm that there was virtually no difference in the properties of the two streams from the extraction column. This appears to indicate that a single phase consisting of heptane diluted shale oil was present.

It should be noted that a small amount of residue was present as a film on the Jerguson gage and on the walls of the sample containers after the highest temperature run (104.4 °C). The residue was most likely heavy, insoluble asphaltene compounds. However, the residue was very minimal and was not analyzed.

Table 10

Pour Point and Gravity of the RDC Outlet Streams With n-Heptane Solvent

Run No.	Sample	Pour Point (°F)	API
1	Top	80	20.9
1	Bottom	80	20.8
2	Top	81	20.8
2	Bottom	80	21.0
3	Top	80	20.9
3	Bottom	80	21.0
4	Top	81	20.7
4	Bottom	81	20.8
5	Top	80	20.9
5	Bottom	80	20.7

The next logical phase of the study, ie. investigation of hexane, pentanes and butanes as deasphalting solvents was not pursued. This was due to two factors. First, there was little encouraging data from the batch studies with n-hexane and n-pentane to indicate that solvent deasphalting of Paraho shale oil would be successful. The low asphaltene content (1.8 wt. %) is most likely responsible for the observed phase behavior, as a higher level of asphaltenes would enhance phase separation. Second, the continuous extraction system had not been proved, especially at elevated pressures. As the use of the lighter hydrocarbon solvents require substantially higher pressures to maintain them in the liquid state, it was decided to study the selective solvent solution of 70% N-methyl-2-pyrrolidone -- 30% water.

Continuous Unit: 70% NMP - 30% Water

NMP - water solvent solutions formed a distinct second phase when mixed with shale oil in the batch studies. As previously discussed, NMP exhibits increased selectivity with the addition of a polar mixing component (such as water), it is chemically and thermally stable, and it has suitable values of specific gravity and normal boiling point for use in the extraction of shale oil. Further, NMP has

been demonstrated to be an effective solvent for polar and aromatic molecules.

The object of the study was to quantitatively determine the oil yield and the elemental composition of both phases resulting from the continuous extraction with 70% NMP - 30% water in the rotating disk contactor.

Operating Conditions

The process variables include solvent to oil ratio, solvent composition, temperature, pressure, and RDC rotor speed. A 4:1 solvent ratio was employed since the batch study showed a clear phase separation at that ratio, with a solvent composition of 70% NMP - 30% water. The pressure was maintained at 125 psig as this was the lowest pressure easily attained in the system given the operating range of the back-pressure regulating valve (100 - 400 psig). The NMP - water solvent (initial b.p. 107 °C) was effectively maintained in the liquid state at 125 psig for all the runs, including the highest temperature run at 110 °C (230 °F). A rotor speed of 800 r.p.m. was used for all the runs. This corresponds to a peripheral rotor speed of 314 ft./min.. Peripheral rotor speeds greater than 300 ft./min. are generally required to establish torroidal fluid flow patterns in the compartments, rather than a simple rotation

of the whole liquid mass around the rotor shaft of the rotating disk contactor (44). The temperature was the only process variable that was changed in the runs. Table 11 gives the operating parameters for each run.

Table 11

Run Operating Parameters

Run	Temp. °C (°F)	Vol. Frac. Water in NMP	Rotor (rpm)	Solvent Ratio	P(psig)	Time (min.)
2	76.7 (170)	.30	800	4:1	125	258.0
3	76.7 (170)	.30	800	4:1	125	260.5
4	110 (230)	.30	800	4:1	125	210.0
5	48.9 (120)	.30	800	4:1	125	240.0

Solvent Purity

The refractive index of the NMP recovered between runs was determined to assure solvent purity following the distillation and water washing steps. These values are shown in Table 12. The results indicate that the recovery procedure was capable of returning high purity NMP for recycling.

Table 12

Refractive Index of the Recovered NMP Used in Each Run

Run No.	Refractive Index (25 °C)
2	1.4680
3	1.4679
4	1.4677
5	1.4679
NMP (as received)	1.4684
NMP (literature)	1.4690

Mass Balances

The overall mass balance was calculated using the procedure described in the previous section. Table 13 gives the resulting balance for run 5. The balance closed to 99.20% indicating excellent mass accountability for the run. The total extract collected was 81.8% while the raffinate was 18.2% of the total products. These values remained constant within 1% for all the runs. The overall mass balances for all the runs are given in the appendices.

Table 13

Overall Mass Balance Run 5

Mass In (kilograms)		Mass Out (kilograms)	
Solvent*	16.240	Extract (bulk)	18.937
0.5 Shale Oil-0.5 Solvent*	10.014	Raffinate (bulk)	4.140
		Extract Samples (1-3)	2.367
		Raffinate Samples (1-3)	0.600
Total Feed	26.254	Total Products	26.044

Product Mass as % of Feed Mass 99.20%

* Solvent = 70% NMP - 30% Water

Yield Results

The solvent-free extract and raffinate yield calculations are more involved. The interface height must be the same at both the beginning and the end of the run for meaningful yields of the extract and raffinate phases. This is because the interface height is directly controlled by the rate of withdrawal of the heavy phase. The total solvent recovered from the composition samples is the sum of that solvent recovered by distillation and the amount of solvent recovered by the NaCl-water solution washings. Tables 14 and 15 give the percentage of solvent contained in the extract and raffinate phases respectively. The samples were taken at 20 minute intervals with the last sample being taken just prior to stopping the run. The sample numbering corresponds to the order of sampling.

In runs 2 and 4, the E-1 samples were spilled during distillation or during washing and are not reported.

Table 14

Total Solvent Recovered From Extract Samples
(Percent By Weight)

Run	Sample	Wt. %	Avg. Wt. %
2	E-2	92.87	94.69 ± 1.82
2	E-3	96.51	
3	E-1	94.63	
3	E-2	92.66	93.91 ± 1.25
3	E-3	94.45	
4	E-2	88.74	85.47 ± 3.27
4	E-3	82.20	
5	E-1	97.27	
5	E-2	97.65	97.53 ± 0.41
5	E-3	97.68	

Table 15

Total Solvent Recovered From Raffinate Samples
(Percent by Weight)

Run	Sample	Wt. %	Avg. Wt. %
2	R-2	10.92	10.80 ± 0.13
2	R-3	10.67	
3	R-2	9.07	9.12 ± 0.05
3	R-3	9.17	
4	R-2	19.91	20.13 ± 0.23
4	R-3	20.36	
5	R-2	9.94	9.18 ± 0.76
5	R-3	8.42	

The error shown in Tables 14 and 15 is the result of sampling error, transfer losses, and distillation losses.

Looking at the extract samples in Table 14, a trend corresponding to the extraction temperature is apparent. At the lowest temperature (48.9 °C in run 5) the extract phase contained 97.53 + 0.41 % (by weight) solvent. Solvent content was reduced at 76.7 °C (runs 2 and 3) to approximately 94 %, while at the highest temperature (110 °C in run 4) the extract contained 85.47 + 3.27 % solvent. This indicates that as the temperature was increased the solvent phase extracted more material from the shale oil

phase, resulting in a lower percent solvent in the extract phase. The data presented also indicates good reproducibility of runs 2 and 3 which were both at an extraction temperature of 76.7 °C.

Table 15 gives similar results for the raffinate oil. As the temperature increases from 48.9 °C (run 5) to 110 °C (run 4) the corresponding solvent content increase is from 9.18 + 0.76 % to 20.13 + 0.23 %. More oil is extracted at the higher temperature leaving the raffinate phase with a greater solvent content.

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 run. This gave the solvent-free masses of each phase. The raffinate oil yield is then, the solvent-free raffinate mass divided by the inlet shale oil mass for the run. Table 16 gives the oil yields for each run. Oil yields decrease from 90.06 % at 48.9 °C to 77.60 % at 110 °C, indicating enhanced mass transfer with temperature.

Table 16

Raffinate Oil Yields

Run No.	Percent Yield Based On Inlet Shale Oil Mass	T °C (°F)
2	82.76	76.7 (170)
3	87.95	76.7 (170)
4	77.60	110 (230)
5	90.06	48.9 (120)

Elemental Analysis

The composition samples were first stripped of solvent to provide the yield data discussed in the last section. Two samples from each phase were then analyzed at Phillips Oil Company laboratory to determine the elemental composition. The results of the elemental analysis of the extracts is shown in Tables 17 and 18. In Table 17 the E-3 samples were taken at the end of the run, while the E-2 samples were withdrawn 20 minutes earlier. Table 18 gives the average of both samples for each run and the raw shale oil composition is included for comparison. Table 17 shows no consistent trend in elemental composition changes between the samples withdrawn 20 minutes apart in the runs. This supports the assertion that the system had reached steady state.

Table 17

Extracts Elemental Analysis (wt. %)

Run	Sample	C	H	O	N	S	As (ppm by wt.)
2	E-2	81.01	9.29	4.61	4.33	0.76	24.0
2	E-3	80.91	8.67	5.29	4.36	0.78	26.9
3	E-2	81.39	9.44	4.19	4.22	0.76	29.1
3	E-3	82.26	9.53	3.63	3.92	0.66	33.7
4	E-2	82.18	11.02	3.30	2.79	0.72	26.8
4	E-3	82.17	9.80	3.91	3.39	0.73	29.1
5	E-2	79.37	8.50	6.70	4.68	0.75	32.8
5	E-3	79.70	8.50	6.18	4.91	0.70	28.5

Table 18

Extracts Averaged Elemental Analysis (wt.%)

Run	C	H	O	N	S	As (ppm by wt.)	C/H wt. ratio
2	80.96	8.98	4.95	4.35	0.77	25.5	9.02
3	81.33	9.49	3.91	4.07	0.71	31.4	8.62
4	82.18	10.41	3.61	3.09	0.73	30.7	7.89
5	79.54	8.50	6.44	4.80	0.73	30.7	9.36
Raw Oil	83.28	12.74	1.63	2.21	0.77	54.4	6.54

The extract samples were enriched substantially in oxygen and nitrogen over the amount found in the raw shale oil, as shown by Table 18. Nitrogen content was as high as double that found in the raw oil, while the oxygen content was 3 and 4 times higher. Sulfur values remained essentially the same as those in the raw oil indicating that the NMP-water solvent did not selectively extract sulfur containing compounds.

The nitrogen and oxygen show a strong trend with extraction temperature in the extract phase samples. At 48.9 °C nitrogen and oxygen were 3.09 and 3.61 weight percent respectively. At 76.7 °C the nitrogen content increased to approximately 4.20% and the oxygen to approximately 4.45%. These levels were increased further, in the highest temperature extraction (110 °C) to 4.80% and 6.44% for nitrogen and oxygen respectively. The arsenic levels followed a similar trend with temperature, however the values were anomalous in that the arsenic content was lower in the extract phase than in the raw oil (expressed as ppm by weight of the respective basis).

Tables 19 and 20 show that the arsenic content was also lower in the raffinate oil than in the raw oil. Converting from ppm arsenic to total grams of arsenic in run 5, the raw shale oil contained 0.2600g arsenic, the extract phase

Table 19

Raffinates Elemental Analysis (wt. %)

Run	Sample	C	H	O	N	S	As (ppm by wt.)
2	R-2	83.79	12.05	1.73	1.80	0.63	15.8
2	R-3	84.20	11.96	1.37	1.83	0.63	14.9
3	R-2	83.96	12.22	1.60	1.62	0.61	<3.0
3	R-3	84.06	12.35	1.25	1.74	0.60	14.0
4	R-2	84.40	11.89	1.69	1.35	0.67	13.2
4	R-3	84.22	12.25	1.42	1.42	0.70	11.7
5	R-2	83.83	11.84	1.66	1.98	0.68	17.4
5	R-3	84.10	11.92	1.41	1.76	0.81	19.3

Table 20

Raffinates Averaged Elemental Analysis (wt. %)

Run	C	H	O	N	S	As (ppm by wt.)	C/H wt. ratio
2	84.00	12.01	1.55	1.82	0.63	15.4	6.99
3	84.01	12.29	1.43	1.68	0.61	8.5	6.84
4	84.31	12.07	1.56	1.39	0.69	12.5	6.99
5	83.97	12.88	1.54	1.87	0.75	18.4	6.52
Raw Oil	83.28	12.74	1.63	2.21	0.77	54.4	6.54

contained 0.0612g arsenic, and the raffinate oil contained 0.0792g arsenic. Thus in run 5, 0.1646g (63.31%) arsenic is unaccounted for. The other runs had similar amounts of arsenic unaccounted for. By comparison, the nitrogen balance closed to 0.19% and the sulfur balance closed to 1.92% for run 5. It is probable that a portion of the arsenic compounds are soluble in the 10% NaCl-distilled water solution and were lost in the sample washing step (ie. the oxide of trivalent arsenic is slightly soluble in water).

The raffinate oil elemental analysis is given for two samples per run (Table 19) and as the average of the two samples for each run (Table 20). As in the extract samples, the raffinate samples taken at a 20 minute time separation do not show a consistent deviation that would indicate that steady state had not been reached by the time the runs were terminated.

Nitrogen and arsenic levels in the raffinate are reduced substantially over that found in the raw shale oil, as seen in Table 20. Sulfur and oxygen levels in the raffinate oil show modest reductions. The trend with increasing temperature is again evident. At 48.9 °C the product oil contained 1.87 weight percent nitrogen and 18.4 ppm arsenic. The nitrogen dropped to 1.39% and the arsenic

to 12.5 ppm at 110 °C. These values are compared to a nitrogen level of 2.21% and arsenic content of 54.4 ppm in the raw shale oil. However, it appears that some of the arsenic was removed in the sample washing step.

Raffinate Oil : Physical Properties

The gravity, pour point and viscosity of the raffinate oil were determined for each run. These properties, along with the oil yields, are shown in Table 21. The oil viscosity and pour point were essentially unchanged from the raw shale oil. This result was expected, as the high viscosity and pour point of shale oil are due, in large part, to the long chain paraffins present. NMP is selective in the extraction of polar and aromatic compounds, leaving the long chain paraffin fraction unchanged.

The API gravity was raised slightly (specific gravity was lowered) as the extraction temperature was increased. This was due to the extraction of some of the heavier aromatic and nitrogen bearing molecules. However, the increase in API gravity to 22.2 for the run at 110 °C, from the 20.8 of the raw oil is not as large as might be expected considering that the raffinate oil yield was 77.60% in the extraction. This indicates that the NMP-water solvent preferentially extracts molecular types not molecular weight

fractions. Also, it indicates that the nitrogen, oxygen and arsenic are not solely present in the heavier oil fractions.

Table 21

Physical Properties
0.7 NMP - 0.3 Water Solvent Extracted Shale Oil

	Run 2	Run 3	Run 4	Run 5
API Gravity 60 °F	21.1	21.0	22.2	20.9
Specific Gravity	0.9270	0.9279	0.9206	0.9290
Pour Point °F	80	80	79	80
Viscosity @ 100°F				
SUS (Saybolt Univ.)	263.3	237.1	235.2	240.1
Centistokes	50.85	51.02	50.62	51.67
Raffinate Oil Yield (wt. % based on inlet shale oil)	82.76	87.95	77.60	90.06

Sources of Error

The two major sources of experimental error in the determination of the solvent-free raffinate oil yields include the variation of the interface height from the position at the beginning of the run and the fluctuation in the solvent to shale oil ratio that occurred when the pump check valves became fouled. Maintenance of the interface level at a constant height was difficult as the runs proceeded toward completion due to a film build-up on the Jerguson gage.

Error is introduced into the calculation of the phase yields when the interface level changes from the original position as the production of both phases is tied directly to that level. The fluctuations in solvent ratio were minimized by periodically checking the shale oil flow rate and resetting this flow rate if necessary. However, each change in solvent to oil ratio disrupts the steady state operation of the system, and hence introduces error into the yield calculation.

Smaller sources of error include sampling error and transfer losses. Sampling errors arise in the weighing of the composition samples and the bulk products. Transfer losses arise from the distillation and washing steps during the sample work-up.

CONCLUSIONS

Batch solvent extractions performed on Paraho shale oil provided qualitative data on the phase behavior of shale oil:paired solvent systems. Solvent pairs that showed promising results in the batch extractions include: NMP-water, NMP-ethylene glycol, DMF-water, DMF-ethylene glycol, phenol-water, phenol-ethylene glycol, morpholine-water, and morpholine-ethylene glycol. The furfural:shale oil system exhibited two phases without the addition of water or ethylene glycol.

Batch solvent extractions employing n-heptane, n-hexane, and n-pentane as deasphalting solvents failed to produce a phase separation in the shale oil : solvent mixture. Extraction conditions included solvent to oil ratios of 2:1 through 10:1 and temperatures from 25 °C (77 °F) to 80 °C (176 °F).

A continuous solvent extraction unit employing a rotating disk contactor (RDC) was used to obtain quantitative data on shale oil : solvent systems. Heptane was studied as deasphalting solvent and the solvent pair 70% NMP - 30 % water was studied as a selective solvent for the removal of polar and aromatic molecules.

Continuous unit extractions performed with n-heptane as the selective solvent were run at a 4:1 solvent ratio, a

pressure of 140 psig and a RDC rotor speed of 800 r.p.m.. The operating temperature was varied from 60 °C (140 °F) to 104.4 °C (220 °F). Pour point and API gravity determinations of the top and bottom streams leaving the RDC indicated that heptane merely diluted the shale oil and that the second phase necessary for extraction had not formed. The low asphaltene content of the shale oil (1.8 wt. percent) is the probable reason for the lack of phase separation.

Continuous unit extractions employing 70% NMP - 30% water as the solvent were made at a 4:1 solvent ratio, a pressure of 125 psig, and a rotor speed of 800 r.p.m.. The extraction temperatures ranged from 48.9 °C (120 °F) to 110 °C (230 °F). The raffinate oil yield was 90.06% (by weight) at 48.9 °C and decreased to 77.60% at 110 °C, indicating enhanced mass transfer with increasing temperature. The quality of the raffinate oil produced improved with increasing extraction temperature. Nitrogen content in the best case, was reduced to 1.39 weight percent from the 2.21% in the raw shale oil. Arsenic was reduced from 54.4 ppm to 18.4 ppm. As mentioned previously, water soluble arsenic was probably removed in the sample washing step. Sulfur and oxygen reductions were modest. These results indicate that the solvent pair 70% NMP - 30% water is an effective

selective solvent for extracting nitrogen and arsenic containing compounds from raw shale oil.

RECOMMENDATIONS FOR FURTHER STUDY

Several problems were encountered in this study which require consideration prior to further work on this apparatus.

Accurate control of the interface level is required to minimize error in the determination of the phase yields. Small "try" valves mounted directly on the RDC are a possibility for interface height detection.

The pump check valve gumming problem can probably be alleviated through the use of a larger bore pump head for the shale oil. Alternatively, another check valve design could be employed. Also, pressure fluctuations could be minimized through the installation of a pressure dampening cell after the pump.

The flow system should be modified through the preheat furnace. A design allowing for the segrated flow of solvent and oil would be preferrable to the present common tube, mixed flow design. The design must allow sufficient residence time for each liquid stream to reach the desired extraction temperature.

With respect to the NMP-water solvent system, other polar mixing components should be studied in combination with the NMP. Alternatives for modifying the selectivity include ethylene glycol, a simple alcohol, or perhaps a

ketone.

Paraffinic solvents such as combinations of butanes and pentanes should be investigated, as a lighter solvent may prove effective in rejecting a portion of the resins along with the asphaltenes present in the shale oil.

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APPENDIX A

Values Used In Mass Balance Calculations

Density of 70% NMP - 30% water @ 72 °F	1.015 g/ml
Density of 70% NMP - 30% water @ 77 °F	1.015 g/ml
Density of 70% NMP - 30% water @ 81 °F	1.014 g/ml
Density of 50% shale oil - 50% solvent* @ 100 °F	0.9629 g/ml
Density of Paraho shale oil @ 100 °F	0.9193 g/ml

* solvent= 70% NMP - 30% water

APPENDIX B

Experimental Run Mass Balances

Run Number 2:

Mass In (kilograms)		Mass Out (kilograms)	
Solvent*	17.458	Extract (bulk)	20.463
0.5 Shale Oil-0.5 Solvent*	10.764	Raffinate (bulk)	3.556
		Extract Samples (1-3)	2.484
		Raffinate Samples (1-3)	1.211
Total Feed	28.222	Total Products	27.714

Product Mass as % of Feed Mass 98.20%

* Solvent = 70% NMP - 30% Water

Inlet Shale Oil Mass 5.138 kg

Run Number 3:

Mass In (kilograms)		Mass Out (kilograms)	
Solvent*	17.627	Extract (bulk)	20.856
0.5 Shale Oil-0.5 Solvent*	10.868	Raffinate (bulk)	4.010
		Extract Samples (1-3)	2.333
		Raffinate Samples (1-3)	1.011
Total Feed	28.495	Total Products	28.210

Product Mass as % of Feed Mass 99.00%

* Solvent = 70% NMP - 30% Water

Inlet Shale Oil Mass 5.188 kg

Run Number 4:

Mass In (kilograms)		Mass Out (kilograms)	
Solvent*	14.210	Extract (bulk)	16.522
0.5 Shale Oil-0.5 Solvent*	8.761	Raffinate (bulk)	3.074
		Extract Samples (1-3)	2.111
		Raffinate Samples (1-3)	0.989
Total Feed	22.971	Total Products	22.696

Product Mass as % of Feed Mass 98.80%

* Solvent = 70% NMP - 30% Water

Inlet Shale Oil Mass 4.182 kg