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SUPERCRITICAL FLUID FRACTIONATION OF JP-8

James J. Watkins and Val J. Krukonis
Phasex Corporation
360 Merrimack Street
Lawrence, MA 01843

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AERO PROPULSION AND POWER DIRECTORATE
WRIGHT LABORATORY
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO-6563

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Ellen M Steward
ELLEM M. STEWARD, Project Engineer
Fuels Branch
Fuels and Lubrication Division
Aero Propulsion and Power Directorate

Charles L Delaney
CHARLES L. DELANEY, Chief
Fuels Branch
Fuels and Lubrication Division
Aero Propulsion and Power Directorate

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The fractionation of military aviation fuels with supercritical methane for purposes of separating multiring heteroaromatic and multiring aromatic compounds was demonstrated. It was shown that fractionated fuel possesses cleaner combustion properties and it is anticipated that fractionated fuel will demonstrate enhanced thermal stability due to the absence of the heterocyclic compounds.

Because supercritical fluids fractionate on the basis of solute/solvent interactions it is possible to separate compounds of similar vapor pressure but slightly different chemical natures. Trace quantities of heterocyclic and multiring aromatic compounds, therefore, may be removed without significantly altering the balance of the fuel. Distribution coefficients and selectivities (in methane) were obtained for several heteroaromatic compounds in JP-8, and calculations using this data indicate that a 95% reduction in heteroaromatic content with a 97% yield will be possible in a continuous, counter-current extraction column with an effective separation zone of less than 10 feet operating at ambient temperature and at pressures of less than 3800 psi.

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Ellen Steward

22b. TELEPHONE *(Include Area Code)*
(513)255-4027

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19. In addition to providing a means for achieving the enhanced specifications of future Air Force fuels, SCF methane fractionation of fuel could also have application in the commercial sector particularly in the area of reduced emission diesel fuel.

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Executive Summary

Military aviation fuels contain a number of components which ultimately have a deleterious effect on their performance properties. The presence of heteroaromatic compounds has long been associated with thermal instability and multiring aromatic compounds are known to possess deleterious combustion properties which promote soot formation and carbonaceous deposits. The requirements of future aircraft exceed the performance properties of current fuels, most notably in the area of thermal stability. The primary objective of this program was to demonstrate the feasibility of fractionating military aviation fuels with supercritical methane for the purposes of separating the multiring heteroaromatic compounds in order to produce a fuel with superior thermal properties. A secondary objective was to investigate the removal of multiring aromatic hydrocarbons which results in a fuel with cleaner combustion properties.

Several fuels including JP-8, a surrogate JP-8 (which was used for the purposes of simplifying the analysis of components by gas chromatography) and a coal-derived JP-8X were fractionated with methane at ambient temperatures and pressures of up to 3800 psi. In some cases the fuels were spiked with representative heterocyclic compounds such as indole, 1-indanol, and quinoline to determine the extraction profile of the compounds.

Several conclusions can be drawn from the results of these experiments. First, multiring heterocyclic compounds can be preferentially partioned from the bulk of the fuel, including separation from those compounds of nearly identical vapor pressure. In one of the experiments, for example, indole (BP=253°C) was concentrated by a factor of over 50 in the final fraction while the tetradecane (BP=252°C) content of the final fraction was less than that of the parent fuel. This result illustrates the fact that SCF's fractionate on the basis of solute-solvent interactions and, therefore, (unlike distillation) compounds of similar vapor pressure but of slightly different chemical nature may be separated. As a result, objectionable heteroaromatics can be removed while maintaining high yields and without significantly altering the balance of the fuel.

The data from the program also demonstrated it is possible to selectively partion the multiring aromatic species. Samples isolated from a fractionation of JP-8 also showed a dramatic increase in smoke point, which is consistent with the removal of multicyclic compounds.

Finally, the data indicate the fractionation of homologous series of hydrocarbons with respect to carbon number. As expected the fractions demonstrated a progression in freezing point and would, by inference, demonstrate a progression in volatility.

Distribution coefficients and selectivities for several heteroaromatic compounds and naphthalene in JP-8 were determined to provide a basis for a preliminary economic evaluation of supercritical methane extraction of jet fuels. Using this data it is estimated that a 95% reduction in heteroaromatic content with a 97% yield of jet fuel will be possible in a continuous counter-current extraction column with an effective separation zone less than 10 feet; the column would operate at ambient temperatures and at a pressure of less than 3800 psi.

In addition to providing a means for achieving the specifications required by future aircraft, SCF methane fractionation of jet fuels could also have application in the commercial sector, particularly in the area of reduced emissions diesel fuel.

I. INTRODUCTION - Identification of the Problem

Topic solicitation AF90-128 (FY-90 DOD SBIR) sought a means to improve the oxidative thermal stability of JP-8. High temperature fuel stability is a primary requirement for realizing the increasing performance demands of future aircraft. For example, jet fuel is used as a heat sink for dissipating the frictional heat generated by high-speed flight by circulating the fuel beneath the surfaces which require cooling. The present thermal stability of JP-8 is insufficient for the high temperature operation required for mach 3+ flight and the fuel would degrade oxidatively in such an application. Degradation of the fuel results in the formation of deposits and gums which can foul heat exchanger surfaces and clog fuel systems. The Air Force has established two goals for developing thermally stable fuels. The near term goal is JP-8+100 with breakpoint of approximately 425°F (i.e., 100 degrees above the current breakpoint) and JP-900 a fuel of yet to be determined composition with a break point in excess of 900°F.

There are an increasing school of thought and expanding body of evidence that point to certain compounds present in the fuel as the culprits which are responsible for decreased oxidative stability including the nitrogen, oxygen, and sulfur-containing heteroaromatic compounds.[1,2,3,4] Daniel and Worstell sought to isolate the effect of nitrogen heterocycles on deposit formation by doping samples of Jet A with nitrogen containing heteroatoms. They found that addition levels as low as 5 ppm nitrogen led to a deterioration of stability in both JFTOT and accelerated storage tests. Table 1 summarizes the effect of 23 nitrogen heterocycles on deposit formation. Figures 1 and 2 show the effect of total fuel nitrogen on thermal stability. The researchers also demonstrated that the total deposit production in accelerated storage tests was proportional to the nitrogen content.

It is generally agreed that oxygen in the fuel promotes auto-oxidation and subsequent formation of hydroperoxides. Hydroperoxide formation serves as an initiating step for the reactions leading to deposit formation. The mechanism of deposit formation is not well understood, but it has been determined that heteroatoms containing nitrogen, sulphur, oxygen, and copper are the primary culprits.

Elemental analysis of deposits indicates the substantial presence of N, S, and O suggesting that the deposits are composed primarily of heterocyclic compounds or their degradation products. Hazlett performed one such study and his data are incorporated in Figure 3 as a reference. Note the N/C ratio of approximately 0.1, which, interestingly, is about the same atom ratio expected in a parent heterocycle. Additionally the deposits exhibit an aromatic character. The cited work supports the current theory that deposit formation is likely attributable to the presence of heterocycles in fuel. Analogously, elimination of the heterocycles, without altering the balance of the fuel, would likely result in the elimination or significant reduction of deposit formation and result in superior, thermally stable fuel.

To date a number of methods have been investigated for the removal of heteroatoms including clay filtration, hydrotreating, and hydrocracking. Clay filtration successfully removes heteroatoms, but it would likely be prohibitively expensive and difficult to scale up; there are also environmental problems associated with disposal of the spent (i.e., contaminated) clay. Hydrotreating, which reduces aromatic and heteroatom content, and hydrocracking have also been evaluated as a means of producing superior fuels. These processes, however, require high temperatures (typically 700°F but up to 900°F) and moderate pressures (typically 500-800 psi but up to 3000 psi), can be expensive, and they alter the composition of the fuel, i.e., the processes result in a reduction in the monocyclic hydrocarbon aromatics which impart beneficial lubricity and combustion properties to the fuel.

Table I. Deposit Formation (168 hr, 120°C) from Spiked Jet A

Spiking Compound	(g deposit/mm) x 10^7
Control (no spike)	3.4 ± 0.3
Pyrrole	3.5 ± 0.5
N-Methylpyrrole	8.7 ± 0.6
2-Pyrrolidone	4.2 ± 0.8
1,2,5-Trimethylpyrrole	3.7 ± 0.3
Indole	3.9 ± 0.3
N-Methylindole	3.6 ± 0.3
2-Methylindole	5.9 ± 0.3
3-Methylindole	2.3 ± 0.5
Indoline	6.7 ± 0.2
Carbazole	2.6 ± 0.3
N-Ethylcarbazole	4.4 ± 0.6
Pyridine	3.6 ± 0.3
2-Acetylpyridine	3.5 ± 0.5
2-Methylpyridine	7.9 ± 0.8
4-Methylpyridine	8.8 ± 0.5
2-Ethylpyridine	5.9 ± 0.3
2,6-Dimethylpyridine	10.0 ± 1.4
2,4,6-Trimethylpyridine	4.7 ± 0.2
Quinoline	7.7 ± 0.0
2,4-Dimethylquinoline	8.2 ± 0.7
7,8-Benzoquinoline	2.8 ± 0.5
4-Hydroxy-2-methylquinoline	9.1 ± 0.4
8-Hydroxyquinoline	8.1 ± 0.2

The potential for utilizing supercritical fluid technology as an alternative solution for increasing the thermal oxidative stability of JP-8 by selective removal of the heteroaromatics was investigated in this program. It had been shown in feasibility tests prior to submission of the Phase I proposal (which will be discussed in Section II) that it is also possible to remove polycyclic aromatics using supercritical fluid extraction. It has been stated that the heterocyclic compounds responsible for degradation reside in the multiaromatic vapor pressure range.[5] Multiring aromatics are known to possess deleterious combustion properties and result in soot formation and carbonaceous deposits. As a result the Air Force has placed a limitation on the multiring aromatics content as evidenced by smoke point and hydrogen and naphthalene concentration. These specifications are summarized in Table 2.

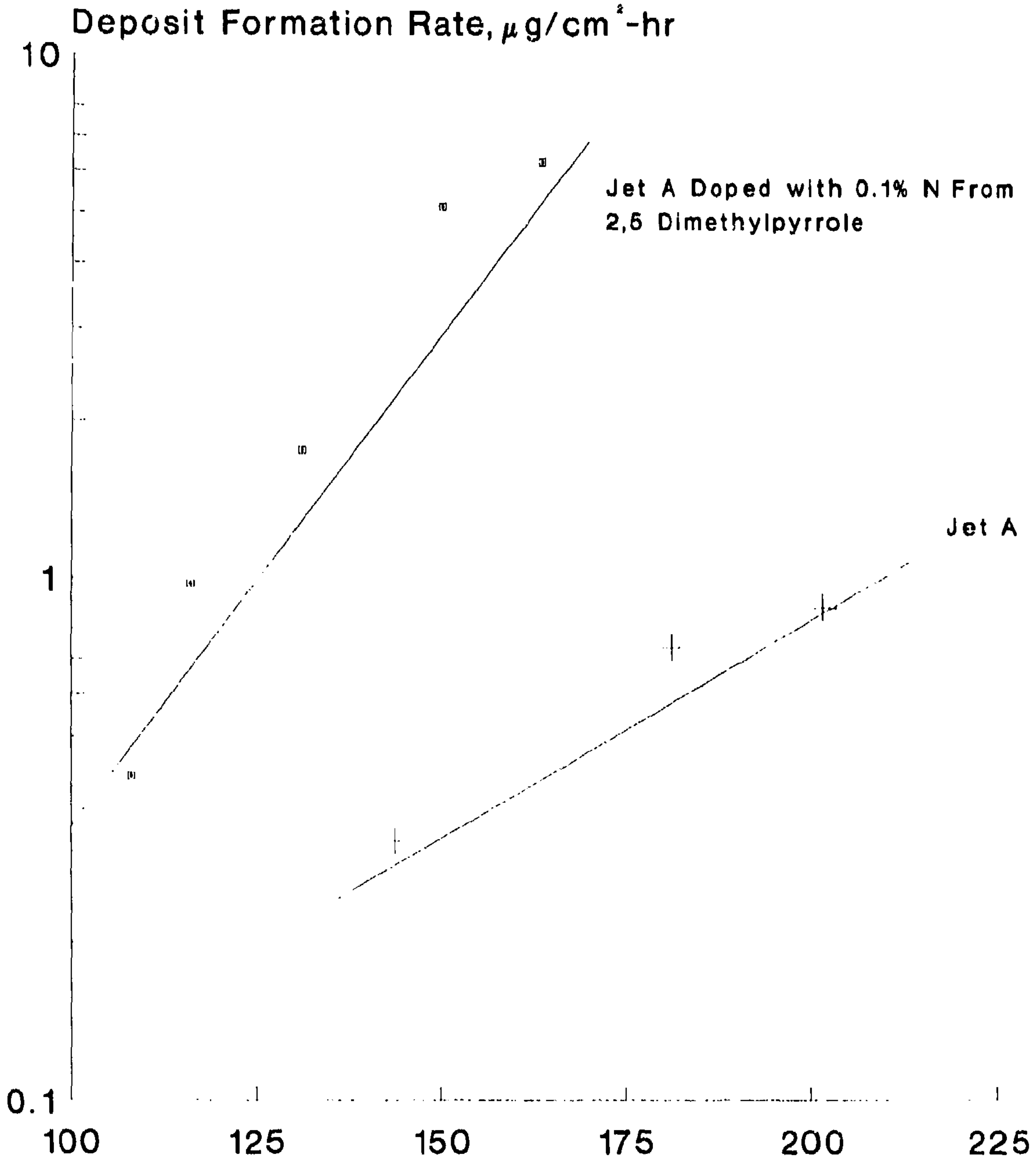


Figure 1. Effect of Fuel Nitrogen Content on Deposit Formation Rate

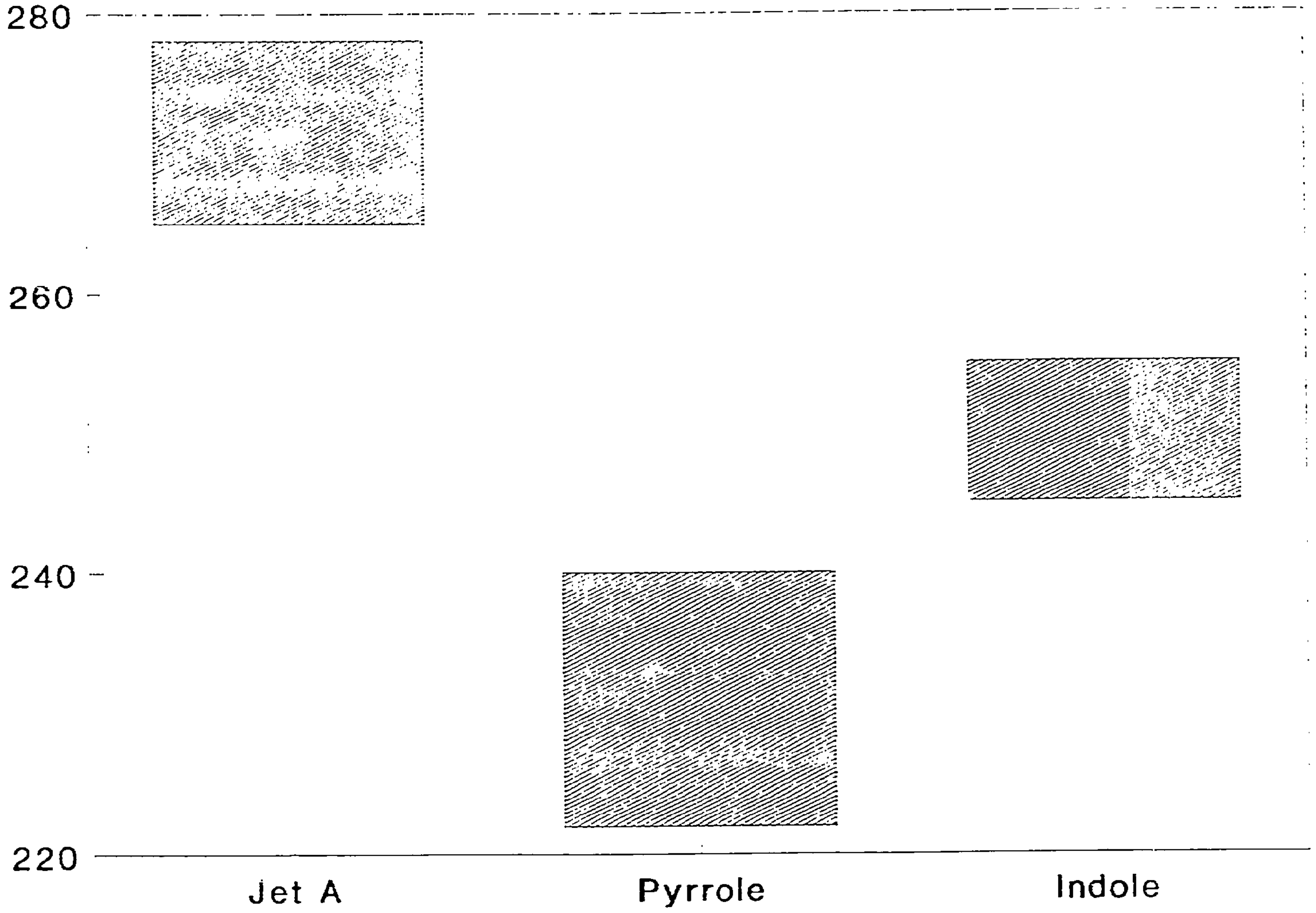


Figure 2. Breakpoint Temperatures of Jet A and Jet A Spiked with Nitrogen Compounds

	Fuel Temp	Atom Ratio			
Tube	°F-In/Out	H/C	N/C	O/C	S/C*
A	286/366	0.7-1.7	0.08-0.13	0.3-0.7	0.02-0.04
B	250/330	1.4-2.4	0.08-0.11	0.8-1.2	----
C	260/340	1.1-1.5	0.11-0.18	0.3-0.5	0.04-0.12
D	260/340	0.5-0.8	0.03-0.04	**	----

* Limited data for S/C

** Data not reliable

Figure 3. Analysis of NAPTC Heat Exchanger Deposits

Table 2. Combustion Specifications of JP-8

Combustion

	(1) Hydrogen Content wt% min	13.6
or	(2) Smoke Point mm min	25.0
or	(3) Smoke Point mm min and	20.0
	Naphthalene, vol% max	3.0

Supercritical fluid extraction may also be used for fractionating single distillation cuts of jet fuel. The fractions will possess combustion, stability, and other performance properties such as freeze point and volatility which are different from the parent material and may be useful in developing the next generation JP-900 fuel.

II. Principles of Supercritical Fluid Extraction

A. Background on Supercritical Fluid Solubility

The phenomenon of solubility in supercritical fluids has been well covered in the literature, in symposia proceedings (6,7) in books (8,9) and in many journals (e.g., 10, 11, 12, 13), but a brief background is presented here primarily for purposes of completeness. These articles have described the advantages of supercritical fluid extraction in a broad range of applications, such as coffee decaffeination, spice extraction, and lipids purification. The processing principles have also long been well known and practiced in the polymer industry, especially in the operation of the high pressure polyethylene process which was developed in the late 1930s (6).

A gas or liquid at ambient conditions becomes a supercritical fluid (SCF) when it is compressed and heated to conditions of temperature and pressure above its critical point. In the critical region a gas exhibits a liquid-like density and a much increased solvent capacity that is pressure-dependent. The variable solvent capacity of a supercritical fluid is the basis on which separation processes can be devised.

The critical temperatures of gases and liquids can differ by hundreds of degrees, and this difference suggests the use of specific supercritical fluids in specific applications. For example, because the critical temperatures of carbon dioxide, ethane, and ethylene are near ambient, they are attractive solvents for processing heat-sensitive flavors, pharmaceuticals, labile lipids, and reactive monomers and macromonomers. Substances that are less temperature-sensitive, such as most industrial chemicals and polymers, are readily treated with the C-3 and C-4 hydrocarbons with critical temperatures in the range of 100-150°C; the C-3 and C-4 hydrocarbons are generally better solvents for polymers than the C-2 hydrocarbons.

In historical development of supercritical fluid solubility, Hannay and Hogarth (14) are credited as the first investigators to examine the unique solvent properties of supercritical fluids. They found that certain alkali halide salts remained dissolved in ethanol when the temperature and pressure were raised to conditions above the critical point of the solution. They found, furthermore, that in the region near the critical point, pressure alone could be used to control the solubility of the salts. When the system pressure was lowered isothermally, the dissolved salt precipitated from solution, and when the pressure was raised isothermally, the precipitated salt redissolved. At the end of their paper Hannay and Hogarth wrote: "We have, then, the phenomenon of a solid with no measurable vapor pressure, dissolving in a gas... When the solid is precipitated by suddenly reducing the pressure, ... it may be brought down as a 'snow' in the gas...." Based on these now more than 100-year-old findings, separation processes using the pressure-dependent dissolving power of supercritical fluids are being developed.

Knowledge of the solubility behavior of a material in a supercritical fluid is important in assessing the processing potential of these solvents. Figure 4 shows the solubility behavior of one compound, naphthalene, in two gases, ethylene and carbon dioxide. At low pressures (< 1-2 MPa or 10-20 bar) the solubility of naphthalene in both gases is low, as might be expected, and is readily calculable from solely vapor pressure considerations. As the pressure is increased and as the critical pressure of each gas is approached, the solubility begins to increase rapidly, and as the pressure is raised still further, the solubility of naphthalene rises dramatically to high levels. The rapid rise in solubility occurs at about the critical pressure of each gas (5.04 MPa or 50.4 bar for ethylene and

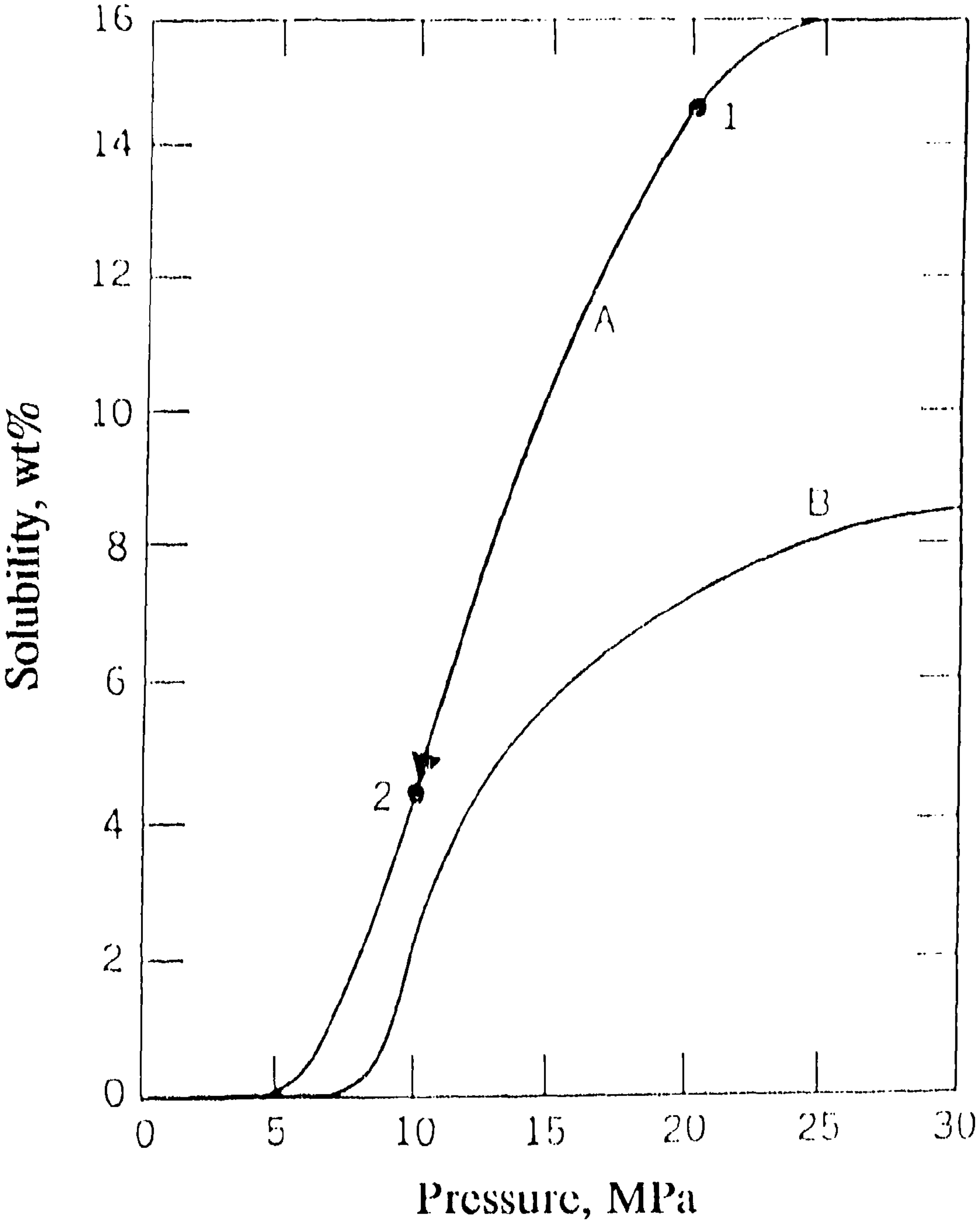


Figure 4. Solubility of Naphthalene in Ethylene, 35 °C (A) and Carbon Dioxide, 45 °C (B)

7.38 MPa or 73.8 bar for carbon dioxide).

The solubility behavior depicted in Figure 4 is, to a first approximation, attributable to changes in the gas density. As the critical pressure is approached, the density of a gas increases rapidly, and at high density conditions the solvent power is greatly increased because of increased intramolecular forces related to molecule-molecule proximity considerations. Numerous authors have shown that this increase in solubility is not merely the result of a hydrostatic pressure effect on the solid, i.e., a raising of its vapor pressure. Instead, the rise in solubility near the critical point is a result of increased dispersion forces operating in dense gases. This behavior can frequently be calculated accurately with a simple cubic equation of state (15), which accounts for interactions of the specific solvents and solutes; other factors such as acid-base complexing and hydrogen bonding can also be operative in the critical region (16). For example, carbon dioxide although strictly a nonpolar molecule, has a strong quadrapole moment that gives it the ability to solvate polar compounds such as methanol.

Figure 1 shows that at pressures higher than the respective critical pressures the solubility of naphthalene is higher in ethylene than in carbon dioxide. A priori it might be anticipated that naphthalene (and other solutes) would dissolve to different concentrations in the two gases, just as it would be anticipated that, for example, polymers would dissolve to different extents in different liquid organic solvents.

The solubility behavior shown in Figure 4 is general and is exhibited by any liquid or solid material that dissolves in a supercritical fluid, and this general solubility behavior can be exploited in separation processes. For example, using the pressure-dependent dissolving power of a supercritical fluid, a compound can be dissolved, extracted, or purified. A specific illustration is the condition at Point 1 (~20 MPa or 200 bar, 35°C) on the naphthalene-ethylene solubility curve in Figure 4. Naphthalene can be dissolved in ethylene at this condition and extracted from some other insoluble (or slightly soluble) compounds. Isothermally lowering the pressure to Point 2 (~10 MPa or 100 bar, 35°C) greatly reduces naphthalene solubility, resulting in precipitation from the ethylene solution; it drops out as a "snow". The naphthalene snow can be collected in a suitable separator vessel, and the ethylene can be recompressed and delivered to the extractor vessel to continue the extraction-separation cycle. A generic extraction process using the pressure-dependent solvent properties of supercritical fluid solvents was explicitly described by Todd and Elgin in 1955 (17), and a description of the process operation is given below.

B. Supercritical Fluid Extraction Process Operation

There are many operations that can be carried out with supercritical fluids. Because of its simplicity a batch extraction of solid materials is described first.

1. Batch Extraction of Solid Materials

A schematic diagram of the extraction process described by Todd and Elgin is shown in Figure 5. Four major pieces of equipment are shown in the figure, viz., an extraction vessel, a pressure-reduction valve, a separator, and a compressor. (For simplicity ancillary pieces of equipment, such as gauges, controls, facilities for storing gas, etc., are not shown in the figure.) The solubility behavior of naphthalene-CO_2 is also shown in Figure 5 as a function of temperature and pressure; solubility isobars from 70 to 300 atm are given. Several directed lines, e.g., line segments

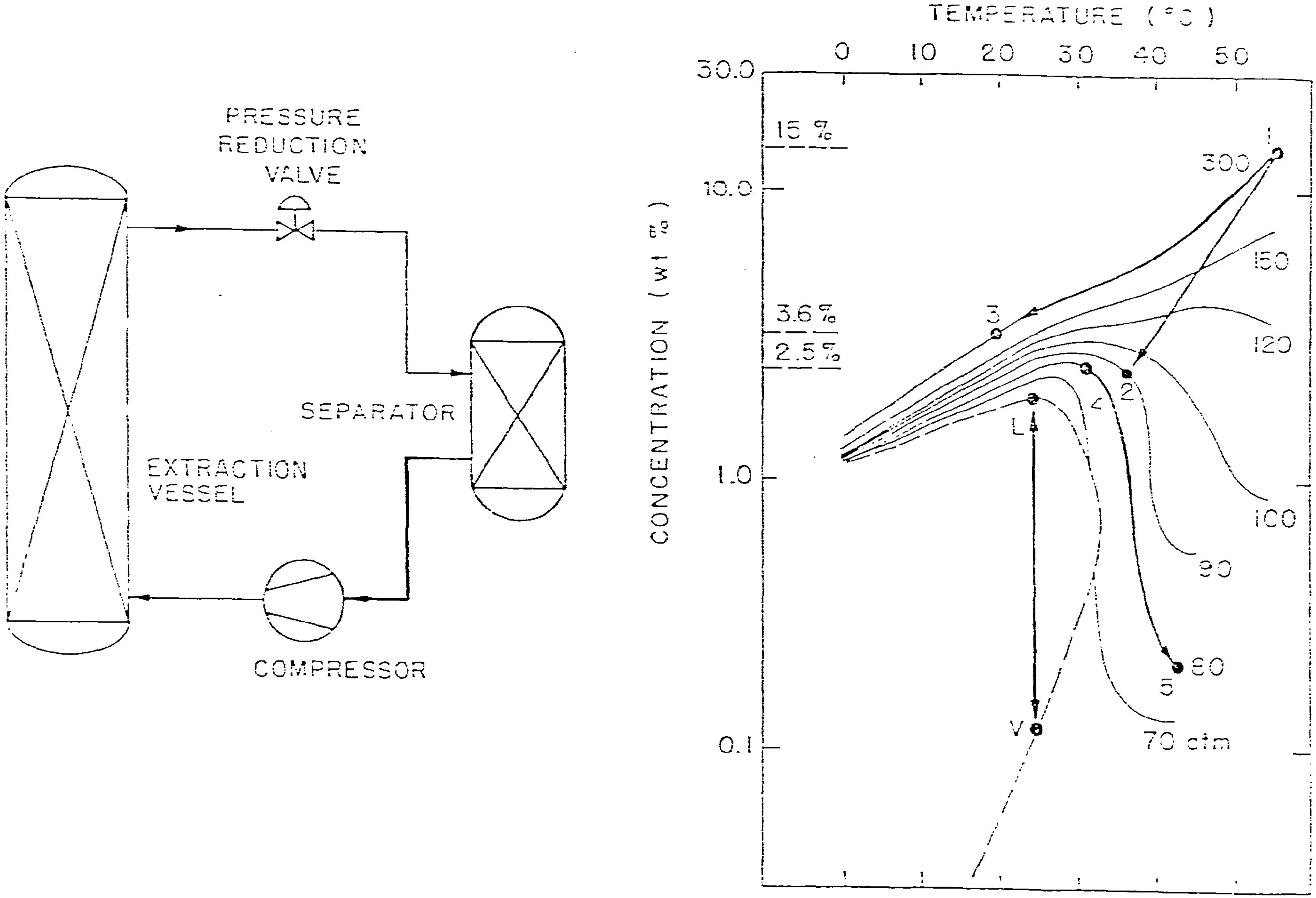


Figure 5. Extraction Process Operation (Using Naphthalene Solubility Behavior in CO_2)

1-2, 1-3, are also given in the figure and the end points of the segments represent extraction and solute separation conditions.

To illustrate the operation of the process, assume that the extractor has been filled with a 50/50 mixture of naphthalene and some insoluble material, e.g., powdered chalk. Chalk, Calcium/Magnesium Carbonate, does not dissolve in carbon dioxide. Incidentally, the filling of the vessel with the solid mixture, although "an engineering detail" for this discussion, is not necessarily an easy task and is, furthermore, not without substantial capital and operating costs in the overall separation process. The mixture is probably not continuously "pumpable" into the extraction vessel during high-pressure operation; it instead will probably be charged in a batch mode through quick-acting gate valves or through some other motor-activated opening. Because the filling and extraction operations are done in a batch mode, it might be desirable to have two or three extraction vessels in parallel, and these concepts are easily extrapolated to a multivessel system with different substances and different gas solvents.

Once the naphthalene-chalk dust mixture is charged to the vessel and the vessel sealed, carbon dioxide is compressed and heated to the desired operating conditions. When the pressure reaches the desired operating level, the pressure-reduction valve is actuated and CO_2 flow commences. Using the data in Figure 5 operation with extraction conditions at 300 atm and 55°C will be described. As carbon dioxide flows through the vessel, naphthalene dissolves in the stream of CO_2 to a concentration level of 15 wt-% (see point 1 in Figure 5). The loaded CO_2 phase leaving the extractor is expanded, for purposes of illustration, to 90 atm through the pressure-reduction valve. When the pressure is lowered, naphthalene precipitates from solution. An isenthalpic expansion of the carbon dioxide-rich stream, causes a drop in temperature of about 19°C (as calculated from thermodynamic data for pure carbon dioxide), and, thus, the expansion path on the naphthalene solubility diagram is shown as an oblique line. At 90 atm and 36°C the equilibrium solubility of naphthalene in CO_2 is only 2.5 wt-%. The naphthalene that has precipitated is collected in the separator, and the carbon dioxide stream is recompressed to the initial extraction conditions of 55°C and 300 atm and is recycled to the extractor.

It is informative to follow the process cycle on a carbon dioxide Mollier diagram for the purpose of determining the energy requirements of this SCF process relative to some other process for separating the two materials and the extraction will be compared to the vaporization of the naphthalene at its boiling point (218°C). An enlarged view of the pertinent section of the temperature-entropy diagram of carbon dioxide is given in Figure 6. The arrows on this figure trace the path of CO_2 in the process cycle. As previously described, the extraction step occurs at 55°C and 300 atm (point 1 in Figure 6). The CO_2-naphthalene solution leaving the extractor is isenthalpically expanded across the pressure-reduction valve to 90 atm (to point 2). During the expansion step, the temperature of the CO_2 solution falls about 19°C (the heat effects associated with the formation of solid naphthalene are ignored for this discussion). The stream of carbon dioxide leaving the separator is now at 36°C and 90 atm. As this stream is isentropically compressed to 300 atm, its temperature rises to 72°C. The energy required to compress CO_2 to 300 atm, can be read directly from the Mollier diagram; the energy is 7 kcal/kg (12.6 Btu/lb) of CO_2. In completing the process cycle the CO_2 stream is isobarically cooled to 55°C, the initial extraction temperature (and no attempt is made here to integrate the heat-exchange steps in this process to improve the energy efficiency). Since the expansion of CO_2 results in a solubility decrease from 15 wt-% to 2.5 wt-%, it is readily calculated that it is necessary to recycle about 7 pounds of CO_2 to extract 1 pound of naphthalene.

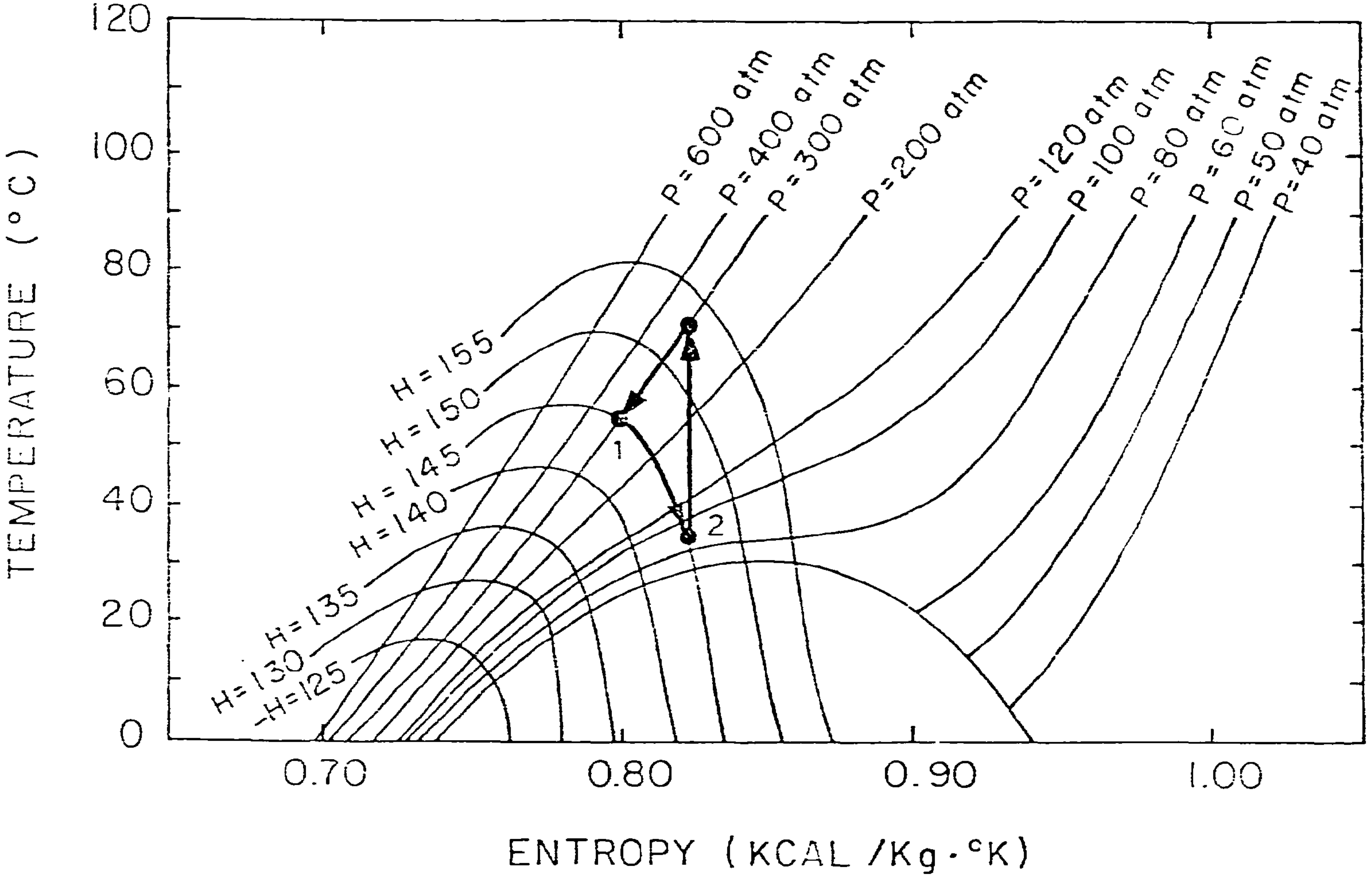


Figure 6. Tracing the Extraction Process on a Mollier (Temperature-Entropy) Diagram

The energy required to extract naphthalene via the Path 1-2 is compared to the energy needed to vaporize naphthalene from the chalk dust mixture. The electrical energy required to compress 6.7 lbs of CO_2 in the recycle stream (at 12.6 Btu/lb CO_2) is 84.4 Btu, i.e., the electrical energy input to the process to extract 1 pound of naphthalene, and the equivalent thermal energy of this step is about 222 Btu assuming 38% Carnot efficiency, i.e., the conversion of heat of combustion energy from natural gas or coal to electrical energy is 38%. The vaporization process for naphthalene separation requires energy input for latent and sensible heat. The heat of vaporization is 84 Btu/lb naphthalene, and in order to raise the bed temperature from ambient to 218°C (the boiling point of naphthalene), a sensible heat input of 350 Btu/lb naphthalene is required. Thus, the total thermal energy requirement for the vaporization process is 434 Btu/lb naphthalene, while in this separation, the example extraction with supercritical carbon dioxide requires only about one half the energy of the vaporization process. It is seen from Figure 5 that the solubility of naphthalene in CO_2 is also influenced by temperature. Changing the temperature of a system can have a dramatic or moderate effect on the solubility behavior, depending on the region of the solubility diagram in which the change occurs. Thus, as an alternative to extraction and separation using pressure reduction, the process can operate isobarically using changes in temperature. For example, starting at point 1 of Figure 5, the stream leaving the extractor can flow through a heat exchanger (which is not shown in the figure) instead of a pressure-reduction valve and it can be cooled to 20°C, as indicated by the arrow on the 300-atm isobar. As the CO_2-rich stream is cooled, the concentration of naphthalene decreases from 15 wt-% to 3.6 wt-%, as shown by point 3. The carbon dioxide leaving the separator can then be heated back to 55°C and recycled to the extractor. This isobaric mode of operation employs a blower, as compared with the compressor required in the previously described pressure-decrease mode of operation. The recycle ratio, as calculated from the solubility data shown in Figure 5, for this mode of operation is about 7.5 pounds of CO_2 per pound of naphthalene.

Temperature variations can be used advantageously in another region of the solubility diagram, the "low"-pressure region or retrograde-condensation region where increasing temperature causes a decrease in solubility. Specifically, for the case of the naphthalene-chalk dust separation, the process can operate isobarically between points 4 and 5 in Figure 5. Extraction occurs at 80 atm and 32°C and is then recycled to the extractor. The solubility levels are lower, but so are the operating pressure levels, and the economics of this mode of operation must be compared with the previous modes for each specific case.

A fourth alternative for carrying out the naphthalene extraction utilizes the dissolving capacity of near-critical liquid carbon dioxide. This operating mode is illustrated in Figure 5 by the L-V tie line. Liquid carbon dioxide is employed to dissolve and extract the naphthalene from the mixture, and the solution leaving the extractor is heated to vaporize the carbon dioxide and recover the naphthalene. The CO_2 is then condensed and recycled to the extractor.

In summary of extraction with gases, there exist four modes of operating the extraction of solid (or other) substances. The specific mode employed in any instance is a function of many factors, for example, the sensitivity of the material(s) to temperature and the ease of condensation or nucleation. Many facets and parameters must be considered and evaluated before a process and operating conditions are selected for any type of process; supercritical fluid extraction is no exception to this rule.

2. Counter-Current Continuous SCF Processing of Liquid Products

The simple extraction process described above for solid materials can be extended and indeed simplified when the feed material is in the liquid state. Figure 7 shows a schematic of a continuous process as it might be applied to the purification of jet fuel.

A continuous counter-current extraction process has the substantial advantage over a batch-continuous process in that many equilibrium stages may be utilized for a more efficient and precise fractionation rather than utilizing only the single "quasi" equilibrium stage encountered in batch continuous operation.

The fuel is fed at or near the top of the column and is in contact with the supercritical fluid solvent which is fed at the bottom of the column and typically rises through the column because it is less dense than the feed. The extract phase exiting the top of the column contains those components which have dissolved to their solubility levels at the conditions within the vessel. The overhead stream is expanded to some condition of lower solubility where the "product" devoid of multiaromatics and heterocyclics is separated from the gas and can be drawn off as is or concentrated and returned to the column as a reflux stream. The solute-free solvent is then recycled to the process. The raffinate stream, which contains those components not dissolved in the fluid, can be drawn off directly.

Counter-current extraction using supercritical fluids has been applied to many problems in industry including the removal of monomers and oligomers from polymers, fractionation of polymers, removal of cholesterol from butter oil and the extraction of phenol from waste water.

3. Supercritical Fluid Extraction vs. Distillation

At first glance, the process depicted in Figure 7 resembles a distillation process; for example, there is a feed stream near the top of the column, there is an overhead stream which is condensed and may be drawn off as product and, if necessary, partially returned as a reflux stream; and there is a raffinate stream which may be drawn off the bottom. The principles of SCF extractions, however, are wholly different than those of distillation; and therefore, the separation resulting from each process is very different.

Supercritical fluid extraction does not separate by vapor pressure, but instead by solute-solvent interaction phenomena. In very broad terms SCF extraction is similar to a liquid-liquid extraction process in which the strength of the extracting solvent is tunable by pressure. It is possible to remove heteroaromatics from fuels in a liquid-liquid extraction using phenol and NMP, but the liquid extraction process is nonselective and removes all of the aromatics including single and multiring hydrocarbons. The removal of monocyclic hydrocarbon aromatics has a negative impact on the lubricity and combustion properties of the fuel.

JP-8 is a boiling cut from distillation whose concentration of aromatics, aliphatics, olefins, naphthlenes and heterocyclics is determined, in part, from their concentration-vapor pressure relationships. Because SCF extraction can separate based on solute-solvent interactions, it should be possible to fractionate single distillation cuts based on differences in component properties including polarity, size and functionality. The polarity of the heterocyclics, as evidenced by the polar contributions to their Hansen solubility parameters, will likely result in reduced solubility as

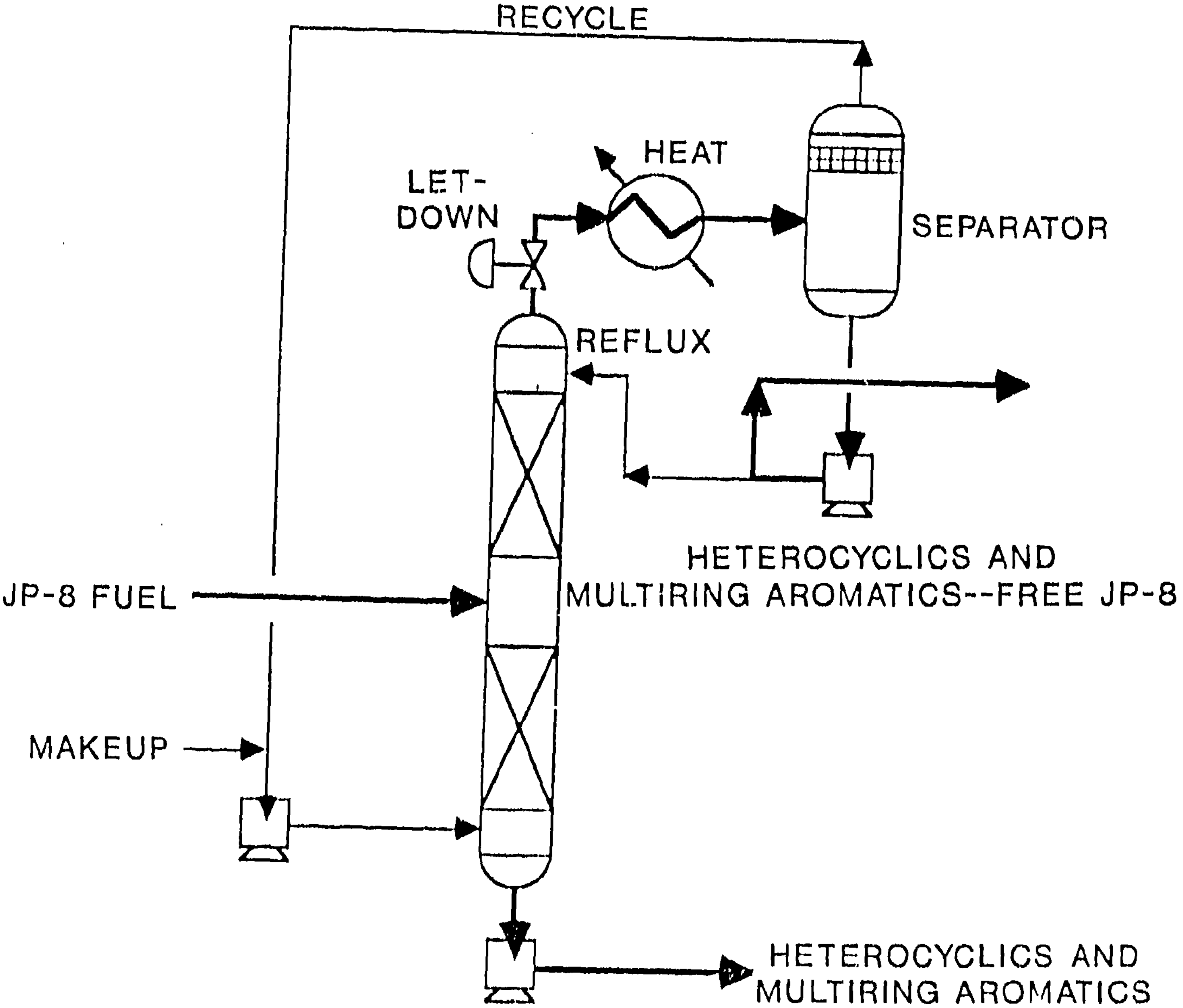


Figure 7. Schematic of a Continuous Counter-Current Extraction Unit

compared to their hydrocarbon analogues in "hydrocarbon-like" solvents such as methane. This hypothesis is supported by the results of the experiments discussed in Section IV.

III. Previous Work

Prior to submission of the Phase I proposal, several tests were performed to determine the feasibility of fractionating jet fuels using methane. Jet A was separated into six fractions and an off-spec JP-5 separated into five fractions by SCF extraction using the methods detailed in Section IV. Several of the fractions were analyzed by HPLC and their compositions are given below.

Table 3. Analysis of Feed and Fractions of JP-A Processed by Supercritical Fluid Extraction

Fraction	Saturates	Monoaromatics	Diaromatics
Feed	79%	18	3
Fraction 1	86	13	1
Fraction 6	70	20	9.8

Another test was carried out with a military fuel, JP-5, containing 9% diaromatics and an unknown amount of heterocyclic compounds. The high diaromatic content of this fuel would likely result in unacceptable smoke points. The results are shown in Table 4.

Table 4. Analysis of Feed and Fractions of JP-5 Processed by Supercritical Fluid Extraction

Fraction	Saturates	Monoaromatics	Diaromatics
Feed	69%	23	9
Fraction 2	76	21	2
Fraction 5	51	26	23*

* This fraction was thought to contain multi and single ring heterocyclics but mass spectroscopy analysis was not quantitative.

Both experiments, one with commercial jet fuel and the other with military jet fuel, demonstrate that supercritical fluid extraction can reduce diaromatic content while maintaining an essentially constant composition of saturates and monoaromatics. Reduction in diaromatics content by SCF extraction can be used to produce an exceptionally clean burning fuel which far exceeds current specifications on the process which may be used to upgrade fuels which do not meet current specifications.

By inference, the multiring aromatics are concentrated in the later fractions and Naval Research Lab personnel, who performed the analysis, believe this fraction also contained the single ring heteroaromatic compounds. Partioning the single ring heteroaromatics in the later fractions is consistent with their polar nature.

The objective of the program described in this report was to further investigate the potential of supercritical fluid extraction for separating heterocyclic and multiring aromatics from jet fuels.

IV. Experimental Methods and Results

A. Phase I Experimental Overview

The objective of the Phase I program was to demonstrate the feasibility of fractionating jet fuels and selectively removing the heterocyclic and multicyclic compounds. Experiments were performed with three jet fuels, JP-8, surrogate JP-8, and coal-derived JP-8X. The surrogate, which is a mixture of 12 components, mimics many of the performance properties of JP-8. The surrogate fuel was used because the composition of fractions may be rapidly determined by gas chromatography. JP-8 analysis is complicated by the complexity of the fuel. JP-8 and surrogate JP-8 were also spiked with nitrogen heterocycles to determine the partioning of these compounds resulting from supercritical fluid fractionation.

All of the experiments were performed in a single-stage batch continuous laboratory extraction system described in the following section. A single equilibrium stage system, while not providing a highly efficient separation, is useful for obtaining fundamental process information such as distribution coefficients, selectivity and solubility.

B. Apparatus, Techniques, and Results

1. Experimental Equipment

A schematic of the apparatus used for the fractionation of the fuels is given in Figure 8. A complete description of the equipment is provided elsewhere (8) and therefore is only briefly described here. The primary components of the system include the gas supply, a diaphragm compressor and pressure controller, a surge tank/preheater, a 60-ml extraction vessel, a cooling coil, and U-tube collectors for recovery of the fuel. Gas flow rate is measured by a rotameter and total gas flow by a dry test meter.

The fuels were fractionated in a laboratory scale batch continuous manner by both isothermal pressure profiling and a constant pressure, isothermal separation. In a typical fractionation by pressure profiling, the fuel is loaded in the extractor and solvent admitted to the vessel from the surge tank/preheater. The solvent preferentially dissolves the material of high solubility as it traverses the column. Upon exiting the column the fluid is expanded via the pressure reduction valve resulting in the precipitation and collection of the solute in the U-tube collectors. The solvent rapidly dissipates and may be recycled to the gas supply or vented. The cooling coil is used to minimize aerosoling of the fuel during precipitation. In general a given pressure level is maintained until the fraction which is soluble at that condition is depleted as evidenced by the cessation of material precipitating from the expanded solvent. Pressure is then increased incrementally and the next fraction collected.

It was determined that the pressures encountered during the fractionation of the fuel were well below the expected convergence pressure of the solvent and the majority of the components comprising the fuel. Additionally the fuel exhibited a limited solubility (approximately 3%) in the solvent at conditions of moderate pressure (3000-4000 psi). Based on these observations it was concluded that a constant pressure separation (by preferential dissolution) may be possible. Several constant pressure experiments were performed and are discussed subsequently.

2. Supercritical Fluid Fractionation of JP-8

JP-8 was fractionated by both an isothermal pressure profile (at room temperature) and an isothermal "constant" pressure fractionation (also at room temperature). The samples were analyzed by gas chromatography and HPLC at Wright-Patterson AFB. A chromatogram of the control sample is presented in Figure 9. A sufficient quantity of fuel was processed in the constant pressure fractionation to permit smoke point and freeze point determination of the fractions to be carried out.

a. Fractionation of JP-8 by Isothermal Pressure Profiling

A 15-gram sample of JP-8 was charged to the extraction system shown in Figure 8 and separated into 9 fractions at pressure levels between 2300 and 4200 psi. A final fraction was collected in CO_2 at 40°C for expedience. Carbon dioxide is an excellent solvent for all the components found in JP-8 including the high molecular weight aromatic and heterocyclic compounds. (In fact CO_2 cannot be used in a practical jet fuel separation process because it is essentially nonselective, i.e., it dissolves everything rather than fractionating the fuel as is possible using methane.) The experiment, designated WP-1, is summarized in Table 5.

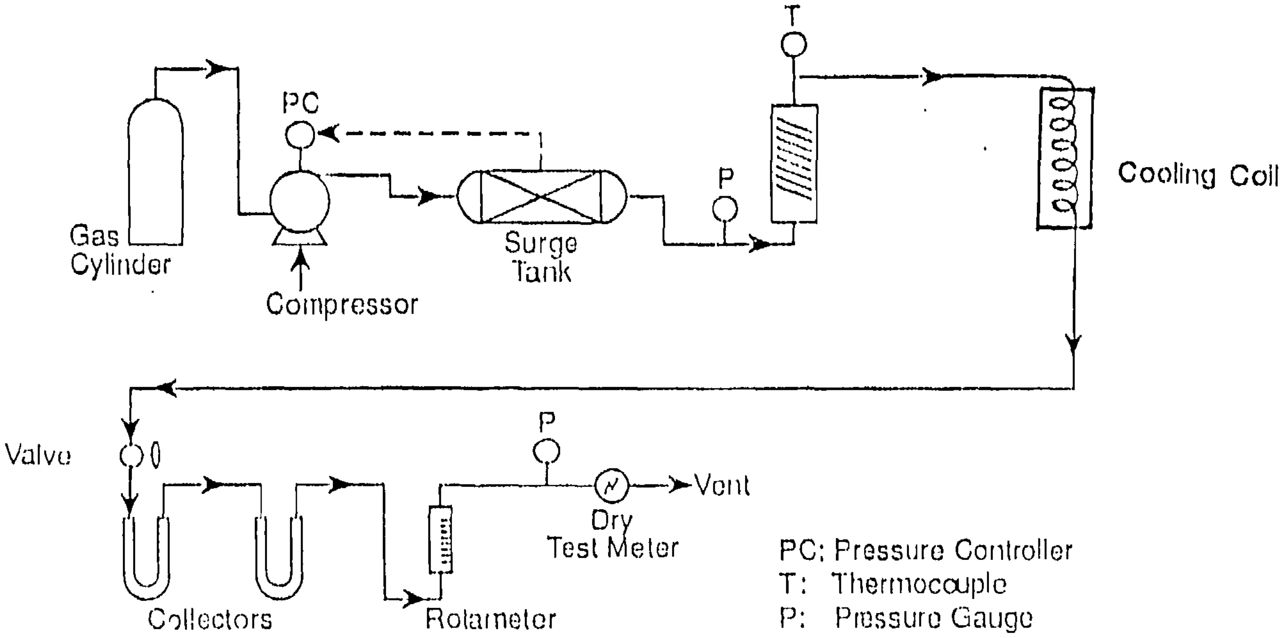


Figure 8. Schematic of a Bench Top, Batch Continuous, SCF Extraction Unit

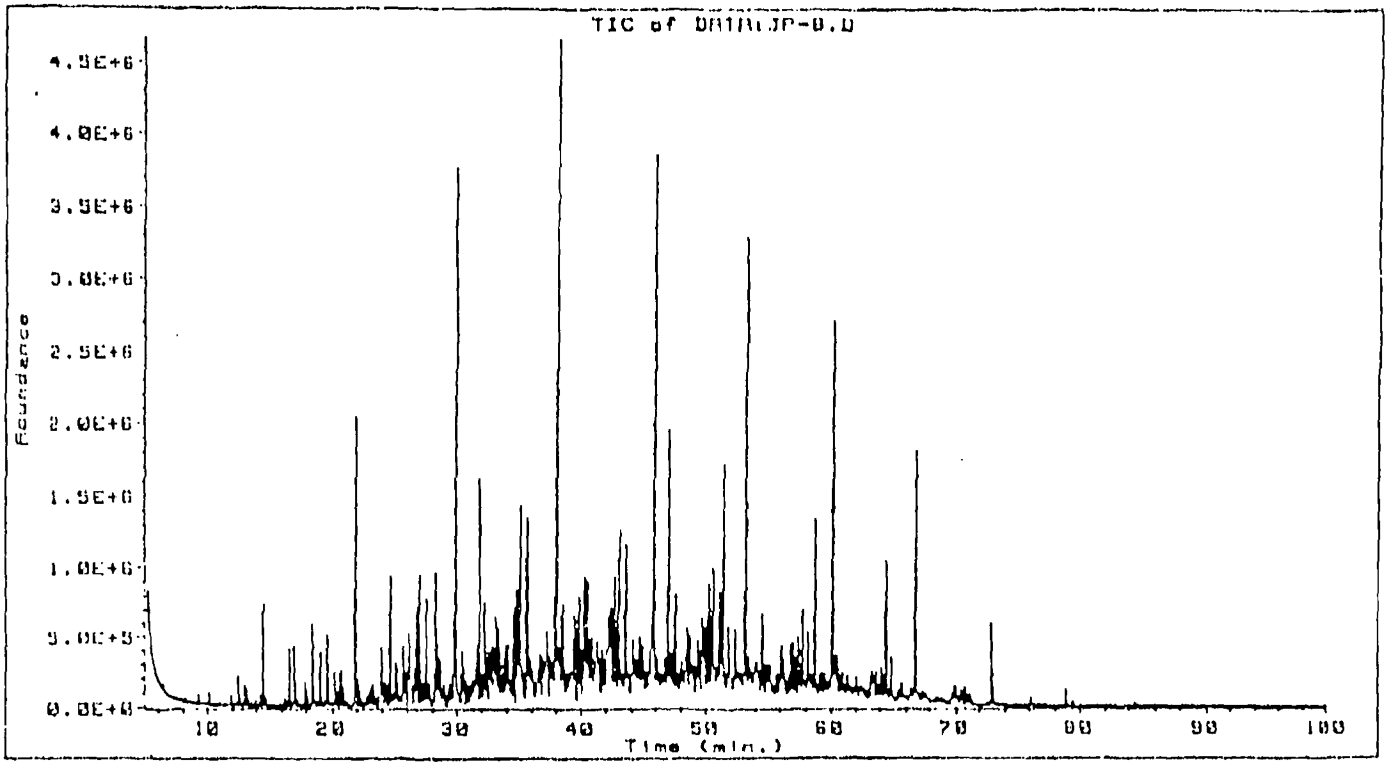


Figure 9. G.C. Chromatogram of Parent JP-8

Table 5. WP-1: Isothermal Fractionation of JP-8 by Pressure Profiling
T=22°C, Charge=15.18g

Fraction	Pressure Range	Standard Liters	Mass (g)	Σwi (%)
1	2300	200	1.19	8.1
2	2300-2500	200	0.97	14.7
3	2400-2700	200	1.08	22.1
4	2700-3000	200	1.57	32.7
5	3000-3200	200	1.88	45.5
6	3200-3450	200	2.30	61.2
7	3400-3600	200	1.97	74.6
8	3600-3800	200	1.93	87.7
9	3800-4200	200	1.61	98.7
10*	3700-4500	150	0.19	100.0
			14.69	

* CO_2 at 40°C

$$\text{recovery} = \frac{14.69}{15.18} = 97\%$$

It can be seen that a recovery of 97% was achieved using the cooling coil. Chromatograms of the control, Fraction 1 and Fraction 9, are presented in Figure 10 and they confirm that the fuel has been successfully fractionated. (The peaks eluted at approximately 116 min are thought to be outside impurities.)

The fractions were also analyzed by HPLC to determine the concentration of saturates and unsaturates of the samples. From the data obtained during the JP-5 and JP-A fractionations that were carried out prior to the start of the program and that were reported in Section III, it is reasonable to conclude the significant increase in unsaturates content in Fraction 9 is attributable to a concentration of the multiring aromatics in Fraction 9.

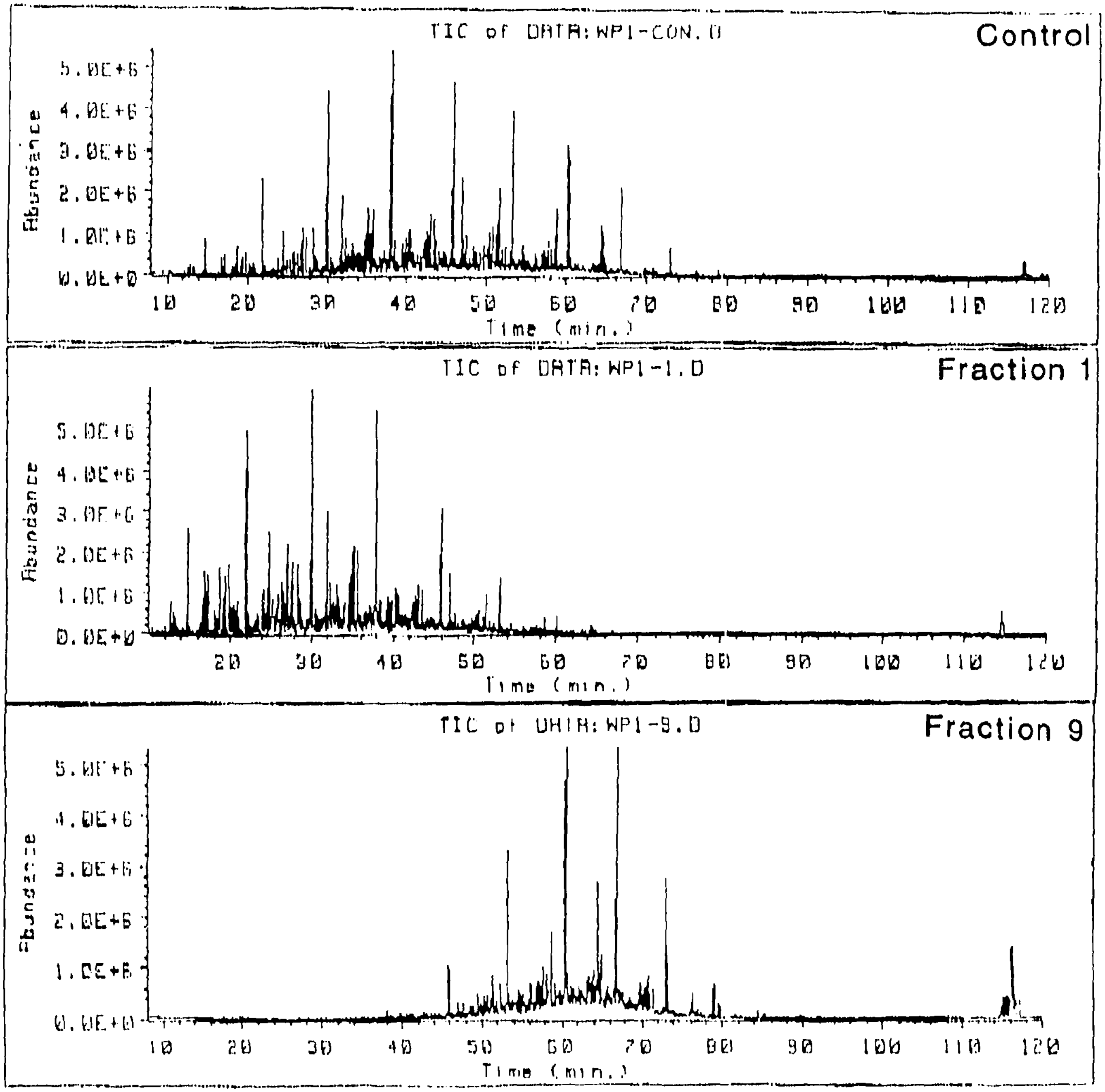


Figure 10. G.C. Chromatograms of Selected Fractions from JP-8 Fractionation (WP-1)

Table 6*. HPLC-DCD Analyses of WP-1 Fractions

Sample	Saturates (Vol %)	Unsaturates (Vol %)	Cumulative wt-%
JP-8 Parent	81.10	18.90	---
WP-1-1	84.30	15.70	8.1
WP-1-2	84.25	15.75	14.7
WP-1-3	84.45	15.55	22.1
WP-1-4	83.40	16.60	32.7
WP-1-5	82.22	17.78	45.5
WP-1-6	82.58	17.42	61.2
WP-1-7	82.66	17.34	74.6
WP-1-8	80.39	19.61	87.7
WP-1-9	74.17	25.83	98.7

*Analyses reported are the average of at least two runs in volume percent using a dielectric constant detector (DCD).

b. Isothermal, Constant Pressure Separations of JP-8

After it was determined that the fractionation pressure was well below the convergence pressure for the solvent and the vast majority of the components in JP-8, a constant pressure separation of the fuel was tested. The constant pressure separation has the obvious advantage of simplicity as compared to a multiple pressure scenario. The constant pressure separation is much like a liquid-liquid extraction in a single counter-current continuous column. Additionally, because the separations are performed near the solubility maximum (of the fuel in the solvent), the solvent-to-feed ratio is minimized.

Approximately 206 grams of JP-8 were changed to an extraction system similar to that shown in Figure 8 and separated into 10 fractions in a batch continuous manner at room temperature. A single increment in pressure range was utilized after the third fraction. Again, CO_2 was used as an expedient to remove Fractions 9 and 10. The experiment, designated WP-4, is summarized in Table 7.

Table 7. WP-4: "Constant" Pressure Separation of JP-8
Charge = 205.7g

Fraction	Pressure Range	Standard Liters	Mass
1	3300-3500	920	22.57
2	3300-3500	890	14.88
3	3500-3800	1030	21.50
4	3500-3800	450	9.17
5	3500-3800	1090	22.11
6	3500-3800	1190	21.20
7	3500-3800	1270	20.46
8	3500-3800	825	11.81
9-CO_2	3300-3800/40°C	450	51.17
10-CO_2	3300-3800	500	3.33
			198.20

$$\frac{198.2}{205.7} = 96.4\%$$

The fractions were analyzed by G.C. to verify fractionation by the constant pressure method. Chromatograms of Fractions 1, 5, and 9 are shown in Figure 11 and indicate selectivity comparable to that of the pressure profiling method. The fractions were analyzed by HPLC to determine the unsaturate content of each fraction and the results are shown graphically in Figure 12. Fractions 1-8 were water-white. Fractions 9 and 10, however, exhibited a strong yellow tint. The coloring of the later samples is consistent with the concentration of polycyclic heteroatoms.

Every other fraction was combined with the fraction preceding it for freeze point and smoke point determination. The freezing point data are presented graphically in Figure 13. The increase in freezing point across the fractions is consistent with the partioning of the heavier components in the latter fractions. These data indicate that desirable freeze point and volatility modifications to current fuels are possible by means of supercritical fluid extraction.

The data from smoke point determinations are presented graphically in Figure 14. Each of the fractions, except for the last, demonstrates substantial improvement in smoke point indicating a significant improvement in combustion properties. The low smoke point values of Fractions 9 and 10 are consistent with high concentrations of multicyclic compounds. It should be noted that no particular attempt was made to optimize the separation of the multicyclic compounds and optimization, including separation in a counter-current column will likely produce a cleaner separation (i.e., a more concentrated fraction of multiring compound in a smaller fraction of the fuel).

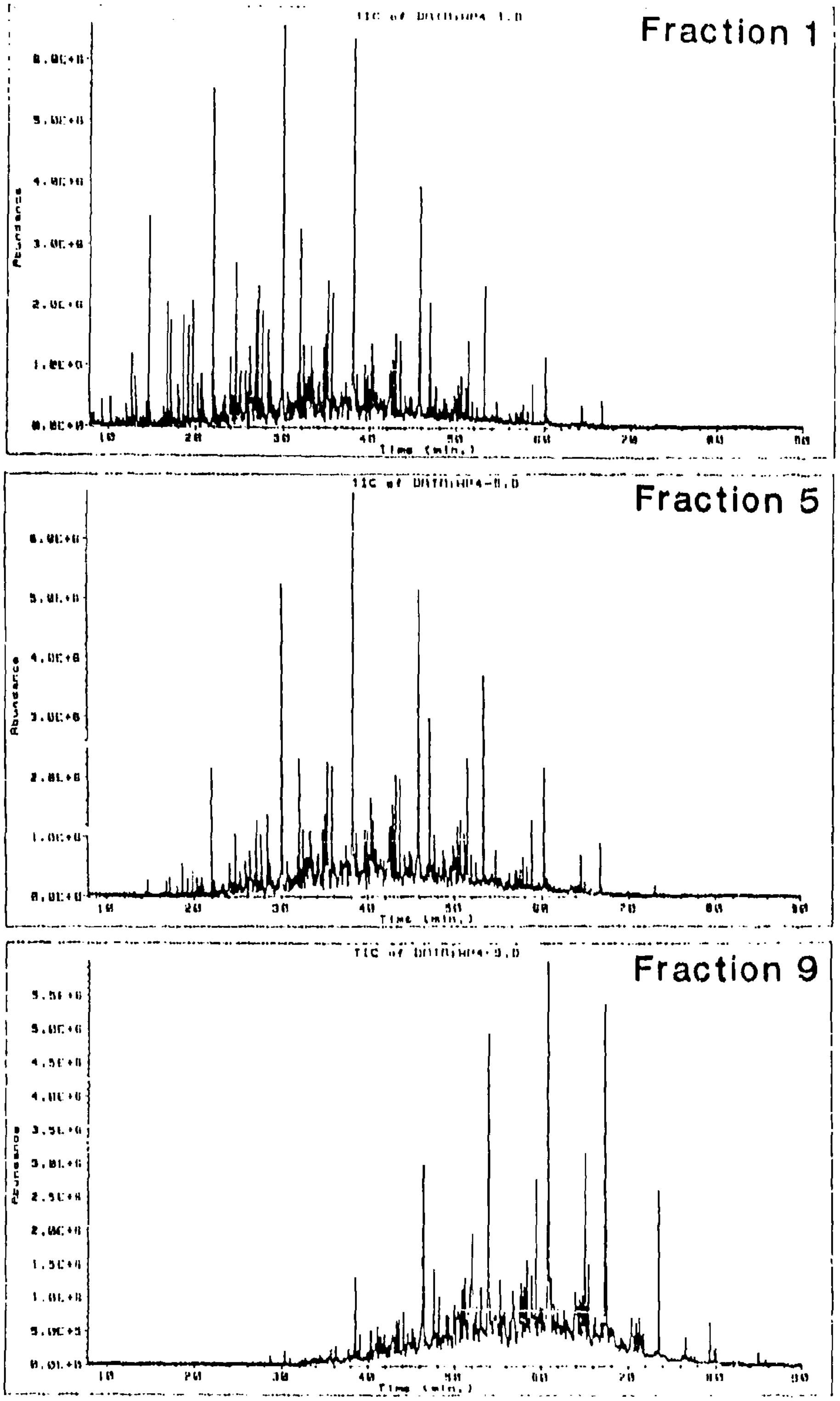


Figure 11. G.C. Chromatograms of Selected, Constant Pressure JP-8 Fractions (WP-4)

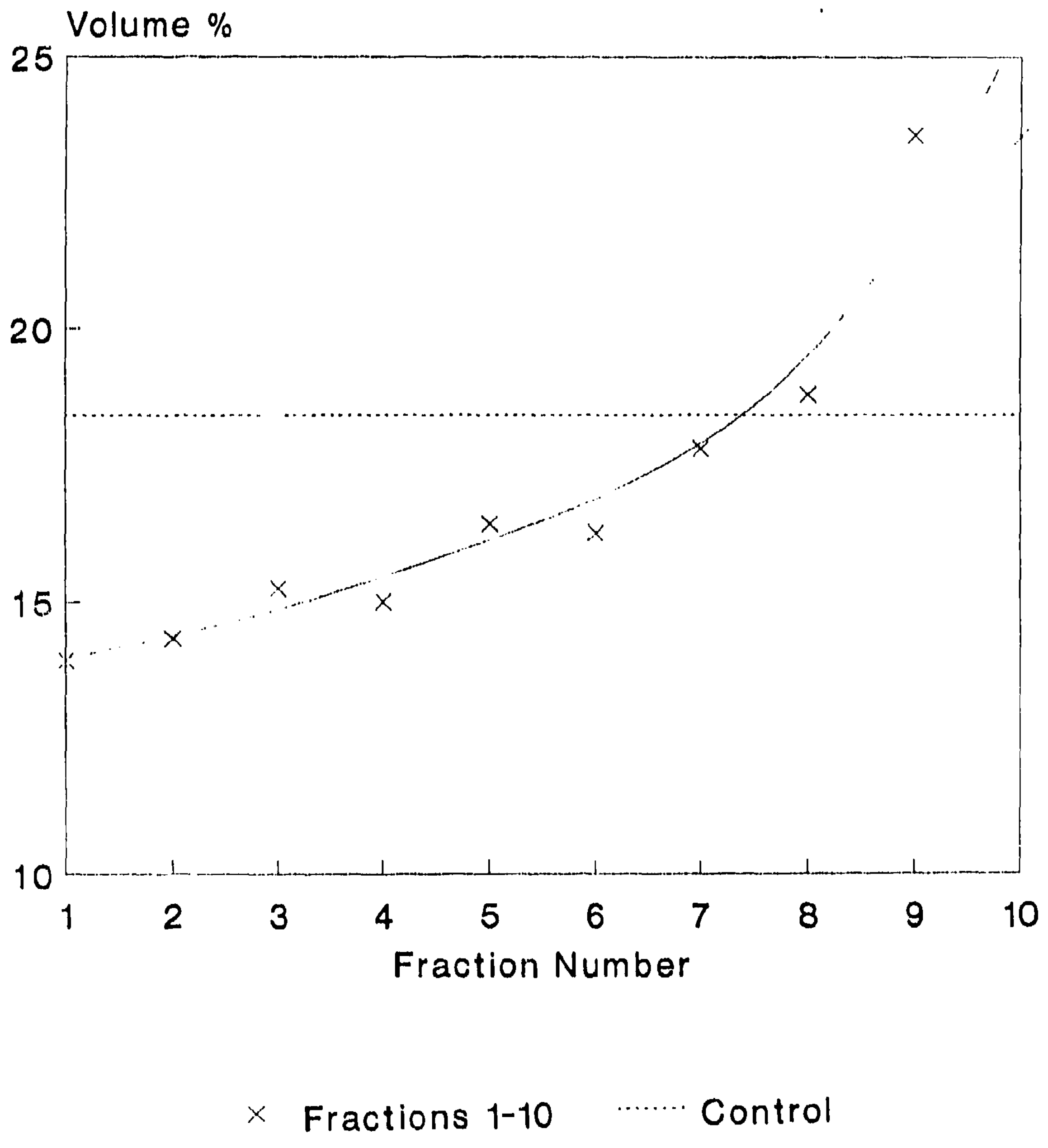
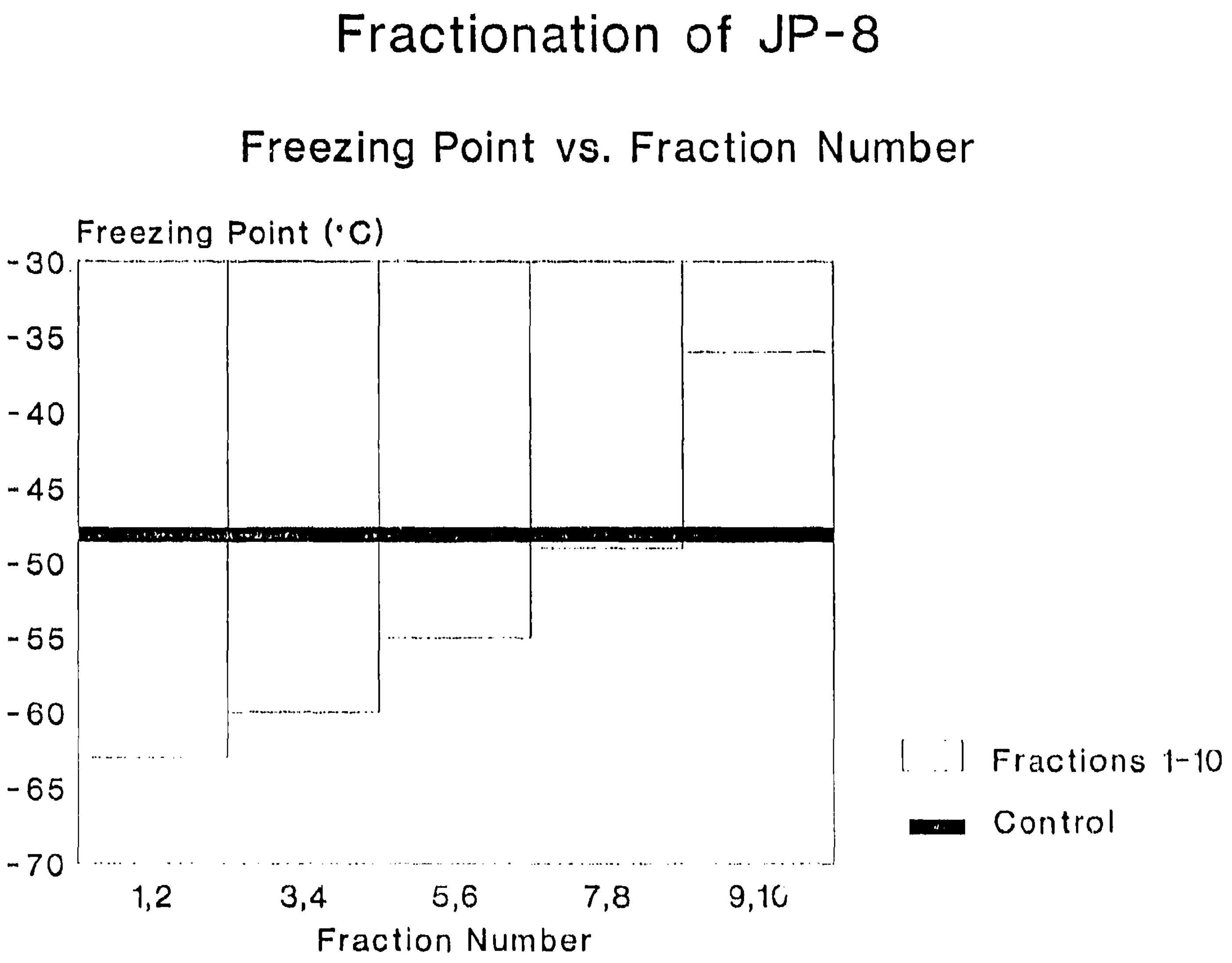


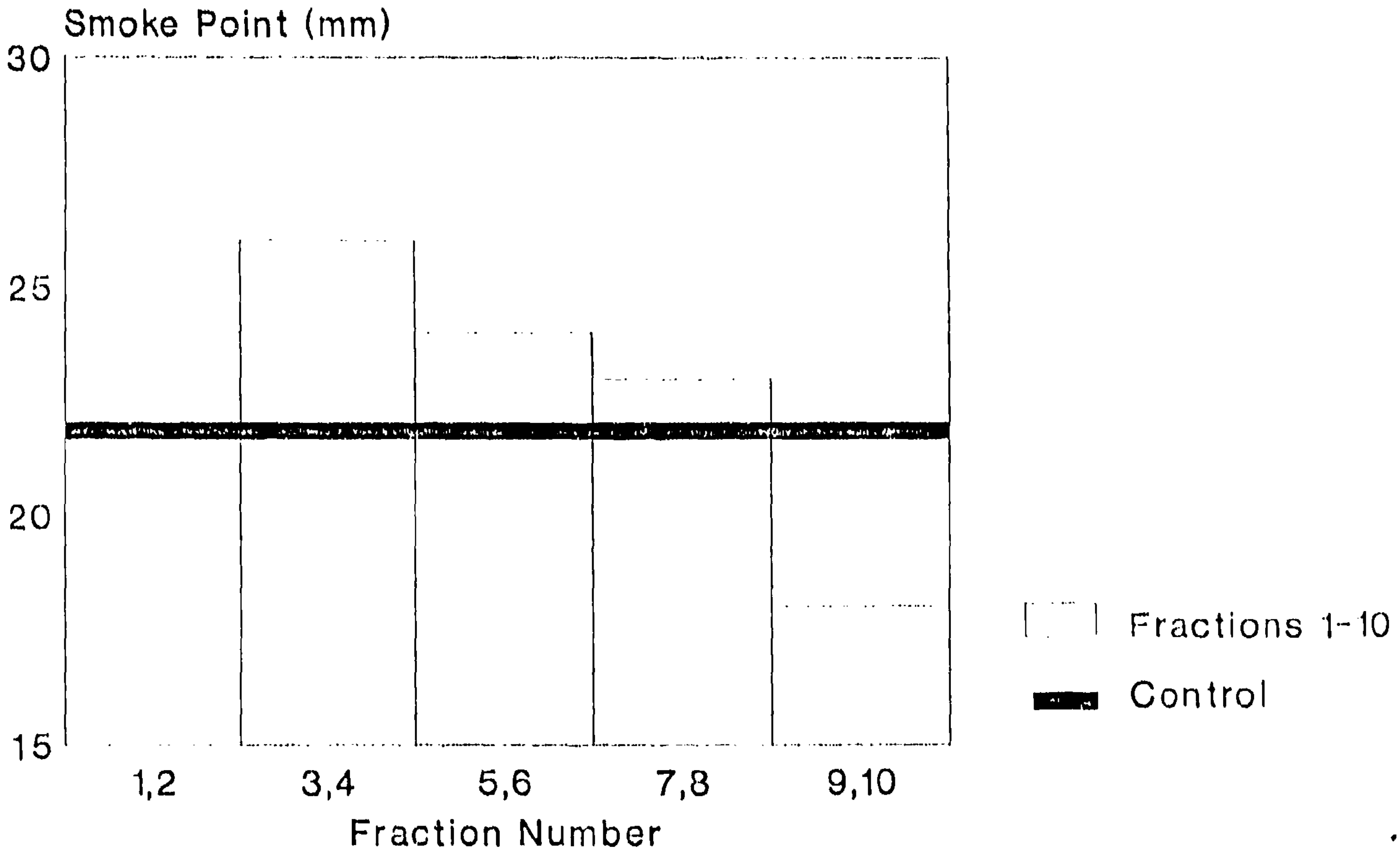
Figure 12. Unsaturates Content vs. Fraction Number for JP-8 Fractions (WP-4)



Fractionation of JP-8

Freezing Point vs. Fraction Number

Figure 13. Freezing Point vs. Fraction Number for JP-8 Fractions (WP-4)



Fractionation of JP-8

Smoke Point vs. Fraction Number

Figure 14. Smoke Point vs. Fraction Number for JP-8 Fractions (WP-4)

c. Fractionation of Spiked JP-8

JP-8 spiked with indole, 1-indanol, quinoline, and naphthalene was fractionated with supercritical methane for the purpose of determining the distribution coefficients (DC's) and selectivities of these compounds in an actual sample of fuel.* The determinations of these parameters are vital for assessing the potential for a successful scaleup of the fractionation to production scale. The fractionation and results are summarized below. The determination of DCs and selectivities and their relevance to determining the technical and economic viability for a commercial process are discussed in Section V, Potential for Scale Up to a Viable Industrial Process.

The concentrations of the spiking agents in the parent fuel are given in Table 8.

Table 8. Concentrations of Spiking Agents in JP-8

indole	0.45%*
1-indanol	0.65%**
quinoline	1.08%**
naphthalene	0.81%**

* determined gravimetrically

** determined by mass spectroscopy

Approximately 13 grams of spiked fuel were fractionated. A summary of the conditions is provided in Table 9.

Table 9. WP-7: Fractionation of Spiked JP-8
T = 28°C, Charge = 12.93g

Fraction	Pressure Range	Standard Liters	Mass (g)	Σw_i (%)
1	2900-3100	150	1.28	11.4
2	3100-3300	150	1.67	26.2
3	3300-3500	150	1.74	41.7
4	3300-3500	150	1.60	55.7
5	3400-3600	150	1.52	69.4
6	3400-3600	200	1.48	82.5
7	3500-3700	200	1.22	93.3
8	3500-3700	150*	0.75	100.0

*CO_2 at 40°C

yield $\frac{11.26}{12.93}$ = 87%

---

* Chronologically speaking the experiment was the final fractionation run on this program; however, it is presented here to maintain a consistent grouping (by fuel type) of the experiments.

Each of the fractions was analyzed by GC-mass spectroscopy to determine the concentration of each of the spiking agents. The results of this analysis are provided in Table 10.

Table 10. Analysis of WP-7 Fractions

Fraction	indole (%)	1-indanol(%)	quinoline(%)	naphthalene (%)
1	trace	nd	0.34	0.60
2	trace	trace	0.42	0.74
3	trace	trace	0.72	0.96
4	trace	0.49	0.88	1.29
5	trace	0.98	1.41	1.73
6	trace	1.04	1.78	2.10
7	trace	1.27	1.92	1.38
8	8.53	4.82	4.97	0.17

Naphthalene was chosen to represent multiring hydrocarbon species in jet fuel. It is anticipated that naphthalene is more soluble (and therefore more difficult to separate from JP-8) than substituted naphthalene and tricyclic and higher aromatic hydrocarbon compounds.

This hypothesis is supported in part by the data of Kurnik, Holla, and Reed who found that 2.6 dimethylnaphthalene is approximately 6.5 times less soluble than naphthalene in CO_2 at 328K and 195 bar.[18]

The data generated above indicate that multiring compounds may effectively be separated from JP-8 via supercritical methane extraction. These data obtained in a single stage batch continuous extraction system can be used to predict the performance of a counter-current continuous separation process as discussed in Section II.

3. Supercritical Fluid Fractionation of Surrogate JP-8

Several experiments were performed using surrogate JP-8. These tests included an isothermal fractionation by pressure profiling, an isothermal fractionation by pressure profiling of a sample of surrogate fuel containing nitrogen heterocycles. Analyses of the surrogate fuel permitted the determination of the partioning of specific compounds to be made (see Section IV.B.3.b). The composition of the parent surrogate fuel is given in Table 11 and a G.C. chromatogram of the parent is shown in Figure 15.

Table 11. Composition of Surrogate JP-8

Compound, Conc. (wt%)	
isooctane	3.66
methylcyclohexane	3.51
m-xylene	3.95
cyclooctane	4.54
decane	16.08
butylbenzene	4.72
1,2,4.5 tetramethylbenzene	4.28
tetralin	4.14
dodecane	22.54
1-methyl naphthalene	3.49
tetradecane	16.87
hexadecane	12.22

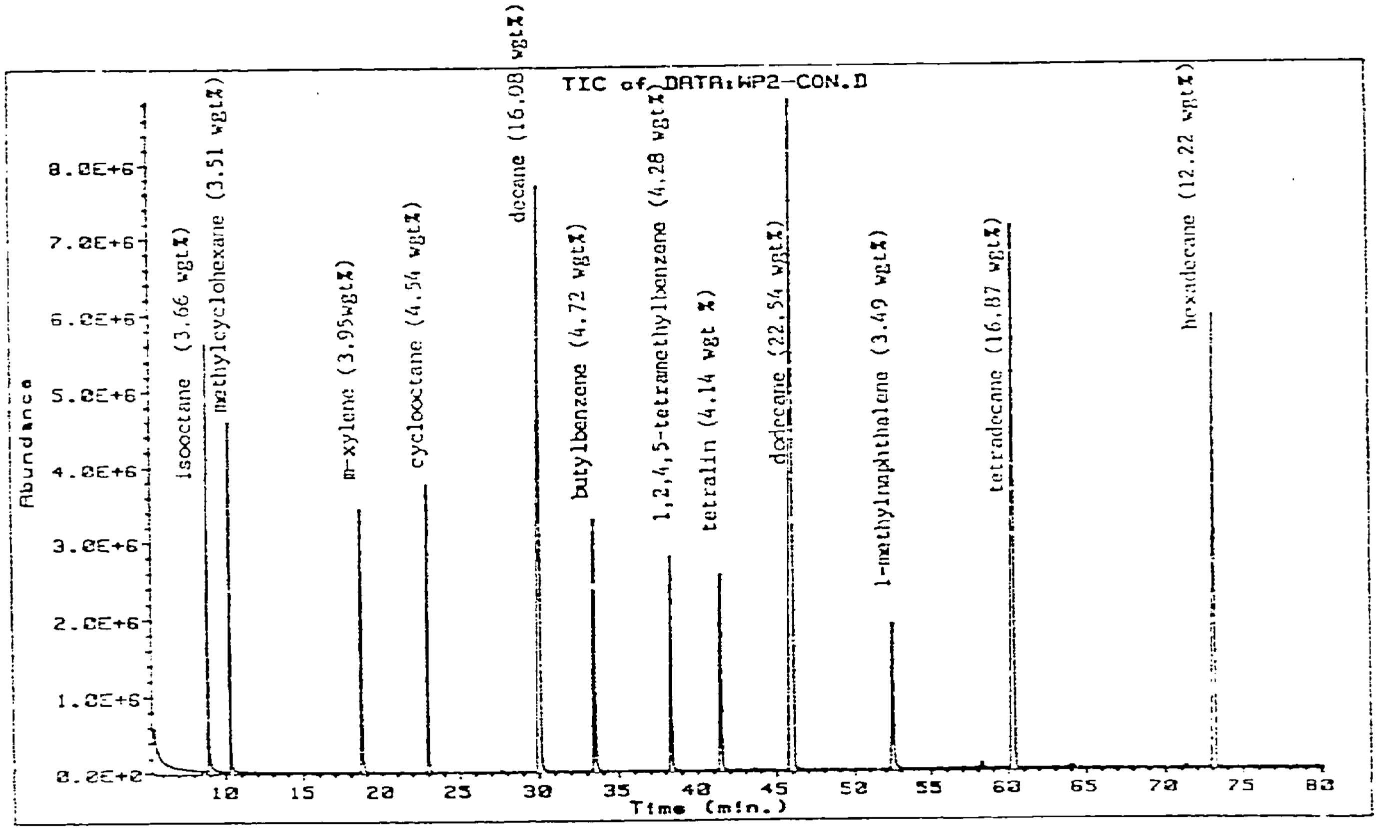


Figure 15. G.C. Chromatogram of Surrogate JP-8

a. Fractionation of Surrogate JP-8 by Isothermal Pressure Profiling

A 15-gram sample of Surrogate JP-8 was fractionated by isothermal pressure profiling in the extraction apparatus shown in Figure 8. Eleven fractions were collected at room temperature (T = 26°C) at pressures between 2200 and 4500 psig. A twelfth fraction was extracted with CO_2 at 50°C and 2000-4000 psig. The test, designated WP-2, is summarized in Table 12.

Table 12. WP-2: Fractionation of Surrogate JP-8 by Isothermal Pressure Profiling
T = 26°C, Charge = 14.88g

Fraction	Pressure Range	Standard Liters	Mass (g)	Σwi (%)
1	2200-2400	200	0.88	7.5
2	2300-2500	150	0.88	15.1
3	2400-2600	200	1.33	26.5
4	2600-2800	170	1.07	35.7
5	2800-3000	200	1.09	45.0
6	3000-3200	200	1.20	55.3
7	3200-3400	200	1.32	66.6
8	3400-3600	200	1.46	79.2
9	3600-3800	200	1.27	90.1
10	3800-4000	200	1.02	98.8
11	4000-4500	250	0.05	99.2
12*	2000-4000	200	0.09	100.0
			11.66	

* CO_2 at 50°C

$$\text{recovery} = \frac{11.66}{14.88} = 78.4\%$$

It is apparent from the data in Table 12 that despite using the cooling coil, the recovery for this test was only ~80%. This problem is common to all the surrogate fuel tests and is attributable to aerosoling of the light components in the fuel (e.g., isooctane, methylcyclohexane, etc.). The yield loss is an artifact of the bench top equipment and would not be a problem in production equipment for processing fuels containing very light components.

Fractions 1 and 10 were analyzed by G.C. and the chromatograms, along with the chromatogram of the control sample are shown in Figure 16. The concentrations of each component in the fraction are shown graphically in Figure 17. It is readily apparent from the figures that the surrogate fuel can be selectively fractionated by SCF extraction. A more detailed analysis of the partioning of components in the individual fraction is given in the following section.

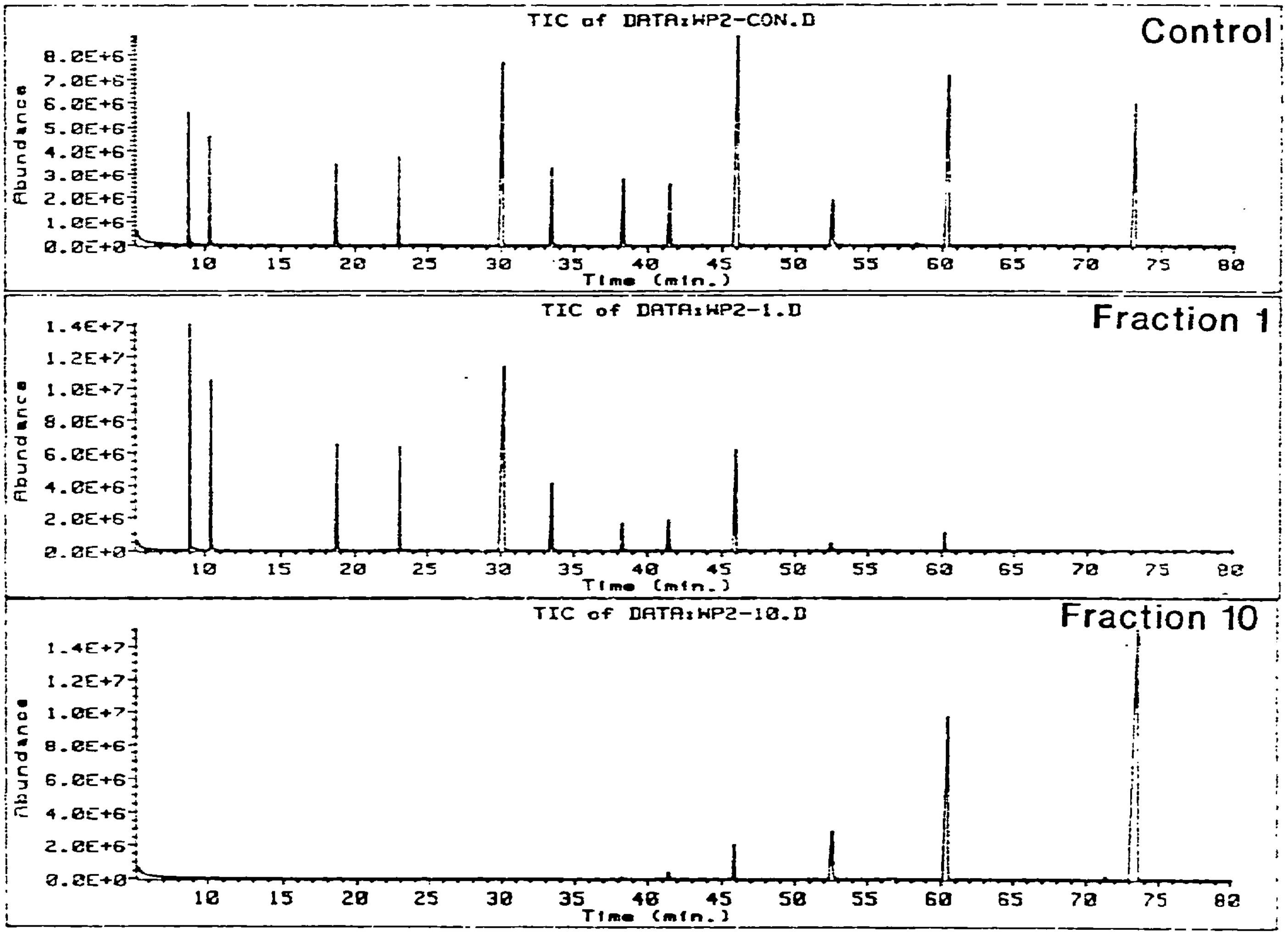


Figure 16. G.C. Chromatograms of Selected Fractions from Surrogate JP-8 Fractionation (WP-2)

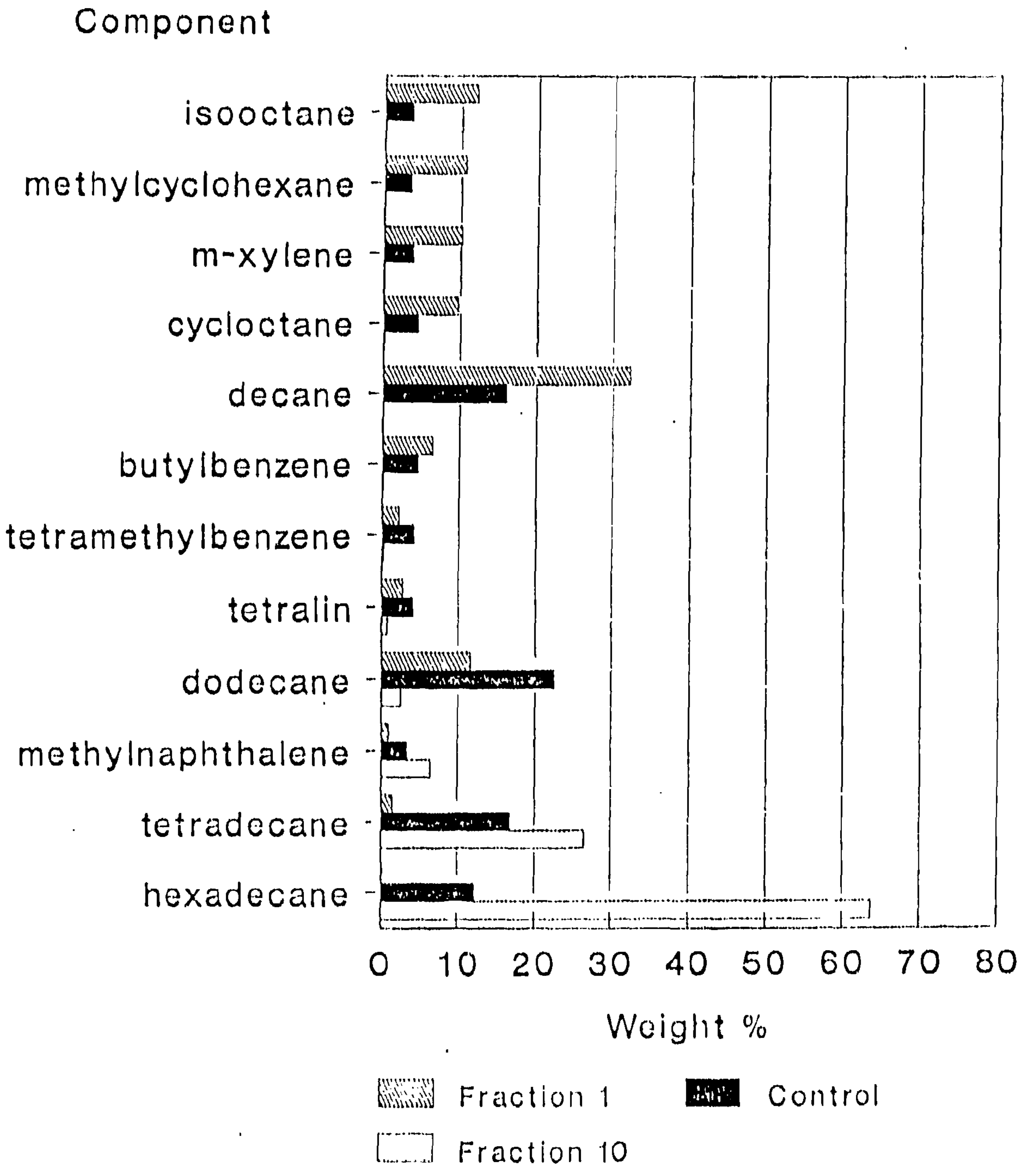


Figure 17. Composition of Surrogate JP-8 Fractions (WP-2)

b. Fractionation of Spiked, Surrogate JP-8 by Isothermal Pressure Profiling

A sample of surrogate JP-8 was spiked with four nitrogen heterocycles, pyrrole, pyridine, quinoline, and indole. The concentration of the spiking agents presented in Table 13 was determined by G.C. Unfortunately, pyridine coelutes with methycyclohexane and, therefore, could not be resolved independently.

Table 13. Concentration of Spiking Agents in Surrogate JP-8

Compound	Conc. %
Pyrrole	0.40
Pyridine	NA
Quinoline	0.29
Indole	0.27

A 14-gram sample of the spiked, surrogate JP-8 was fractionated into 12 cuts in the same manner as WP-2. The test designated, WP-3, is summarized in Table 14. Note that Fraction 12 was removed with CO_2 at 50°C. Again, the yield was low, approximately 80% due to loss of the lights.

Table 14. WP-3: Fractionation of Spiked Surrogate JP-8 by Isothermal Pressure Profiling
T = 23°C, Charge = 14.18g

Fraction	Pressure Range	Standard Liters	Mass (g)	$\sum wi$ (%)
1	<2400	200	1.17	10.2
2	2400-2550	200	1.58	24.0
3	2500-2700	200	1.16	34.2
4	2600-2800	200	1.12	44.0
5	2800-3000	200	1.27	55.1
6	3000-3200	200	1.28	66.3
7	3200-3400	200	1.26	77.3
8	3400-3600	200	1.06	86.5
9	3600-3800	200	0.98	95.1
10	3800-4000	200	0.31	97.8
11	4300-5000	200	0.12	98.9
12	4300-5000	200	0.13	100.0

$$\text{Yield} = \frac{11.44}{14.18} = 81\%$$

The fractions were analyzed by G.C. and the compositions of Fractions 2, 4, 6, 8, 9, 11, and 12 and the control are given in Table 15. The extraction profiles for different groups of compounds, based roughly on compound type, are shown in Figures 18, 19, and 20. Figure 18 shows the partioning of the straight chain hydrocarbons. Figures 19 and 20 show the partioning of some of the cyclic and heterocyclic compounds.

The data indicate substantial enrichment of the indole and quinoline and heavier hydrocarbons in the later fractions. In Fraction 12, for example, the concentration of indole is 13.78% compared to 0.27% for the control and the concentration of quinoline is 3.58% as compared to 0.29% in the control. A quick material balance indicates that approximately 50% of the indole initially present in the control sample is recovered as less than 1% of the fuel. The results point out the potential for concentrating multiring heterocyclic compounds while simultaneously obtaining a high yield of heterocyclic-free fuel.

Another interesting observation is the concentration of impurities arising either from the spiking agents or the parent compounds in the final fraction. These oxygenated impurities including 1-phenylbutanone and 1, 2, 3, 4 tetrahydronaphthenol, and dihydronaphthalenone were not detected in the control samples but note that they are significant peaks in the final fraction. Supercritical fluid fractionation exhibits the potential for concentrating trace impurities in fuels which are often present below detection limits in the parent stream.

Examination of the data illustrates that separation by supercritical fluid extraction is not driven by boiling point or vapor pressure considerations. It is informative to compare the partioning of methyl naphthalene (BP = 240°C) and tetradecane (BP = 252°C) with that of quinoline (BP = 238°C) and indole (BP = 253°C) given in Table 15 and Figure 20. (The concentration of indole in Fraction 2 is suspect as it is out of sequence with the other fractions. Table 16 compares the relative concentration of these components in Fraction 12.)

Table 15. Analysis of Selected Fractions from WP-3

Compound	Cont.	3-2	3-4	3-6	3-8	3-9	3-11	3-12
isooctane	3.80	2.08	----	----	----	----	----	----
MCH	4.19	4.86	0.14	----	----	----	----	----
pyrrole	0.40	0.70	0.06	----	----	----	----	----
m-xylene	3.49	9.17	3.20	0.23	----	----	----	----
cyclooctane	3.96	10.22	5.53	0.84	----	----	----	----
decane	15.42	38.55	30.16	7.31	----	----	----	----
butylbenzene	4.31	6.45	7.71	4.97	0.26	----	----	----
tetramethyl benzene	4.04	2.70	5.57	7.49	1.62	0.24	----	0.07
tetralin	3.83	2.61	4.42	6.06	3.82	0.95	----	0.04
dodecane	22.14	17.79	31.68	43.51	11.27	1.40	4.75	0.34
quinoline	0.29	----	0.20	0.26	0.46	1.62	0.28	3.58
1-phenyl-1-butanone	----	----	----	----	----	----	0.35	0.41
isoquinoline	----	----	----	----	----	----	----	trace
indole	0.27	----	----	0.03	----	1.62	7.00	13.78
1-methyl-naphthalene	3.33	0.60	1.54	3.23	8.45	8.09	2.38	2.94
tetrahydro-naphthenol	----	----	----	----	----	----	----	1.56
dihydro-1-(2H) naphthalenone	----	----	----	----	----	----	----	2.91
tetradecane	17.54	3.71	8.09	21.19	52.77	30.99	10.07	12.67
hexadecane	2.68	0.36	1.65	4.87	21.36	55.04	75.17	61.14
mass	14.18	1.58	1.12	1.28	1.06	0.98	0.12	0.13

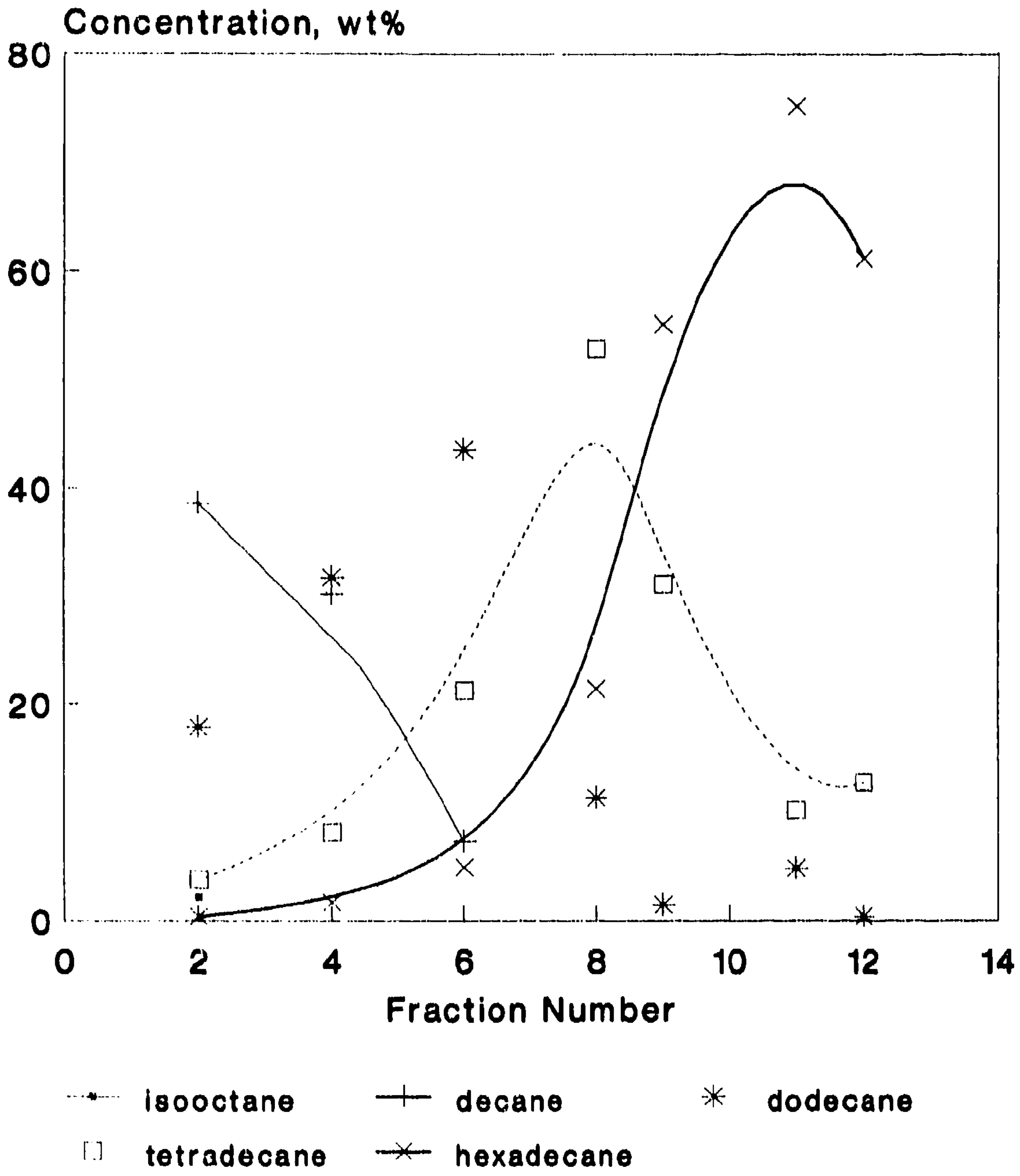


Figure 18. Fractionation of Surrogate JP-8 (WP-3) Partioning of Straight Chain Hydrocarbons

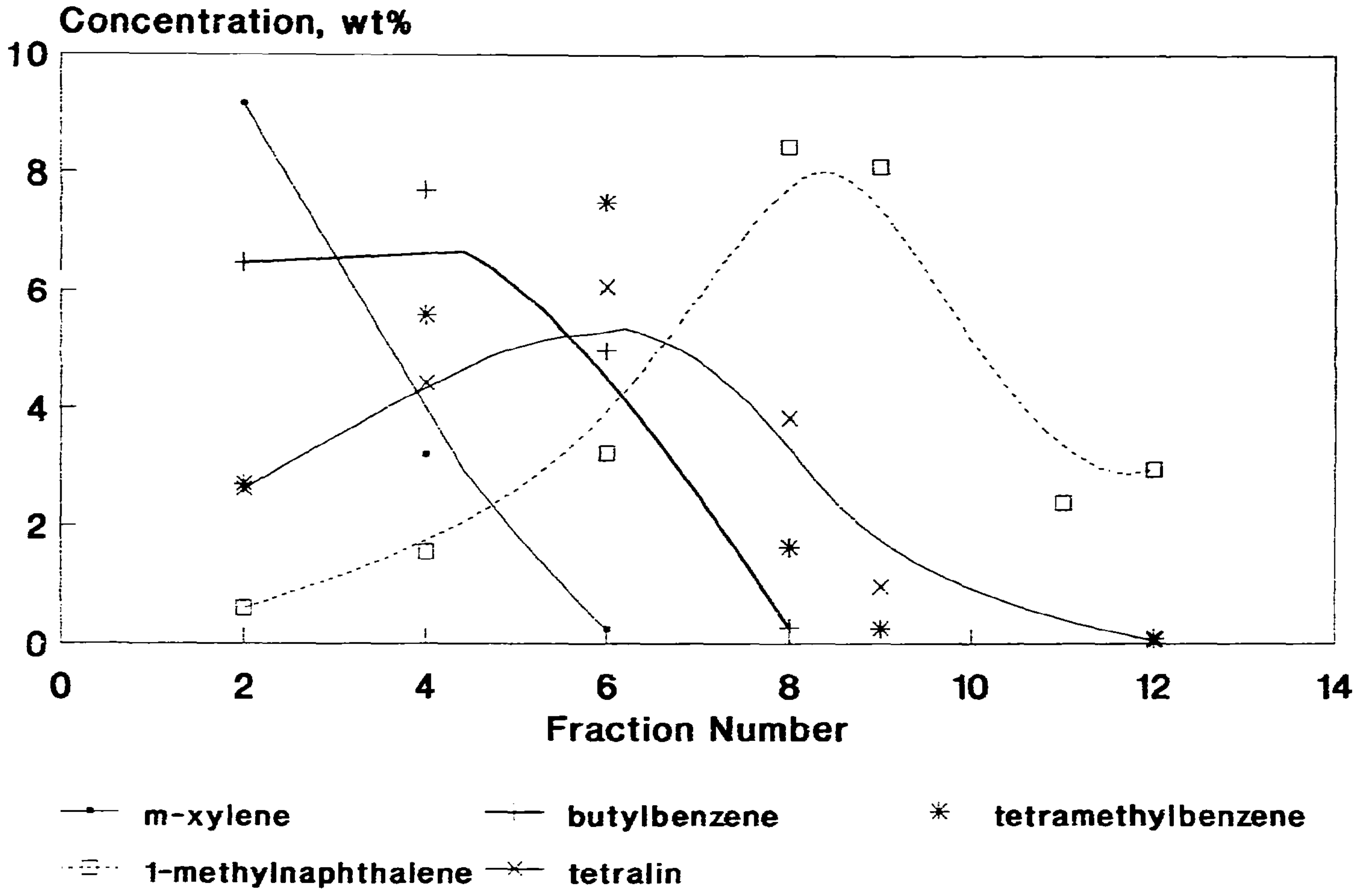


Figure 19. Fractionation of Surrogate JP-8 (WP-3) Partioning of Cyclic Compounds

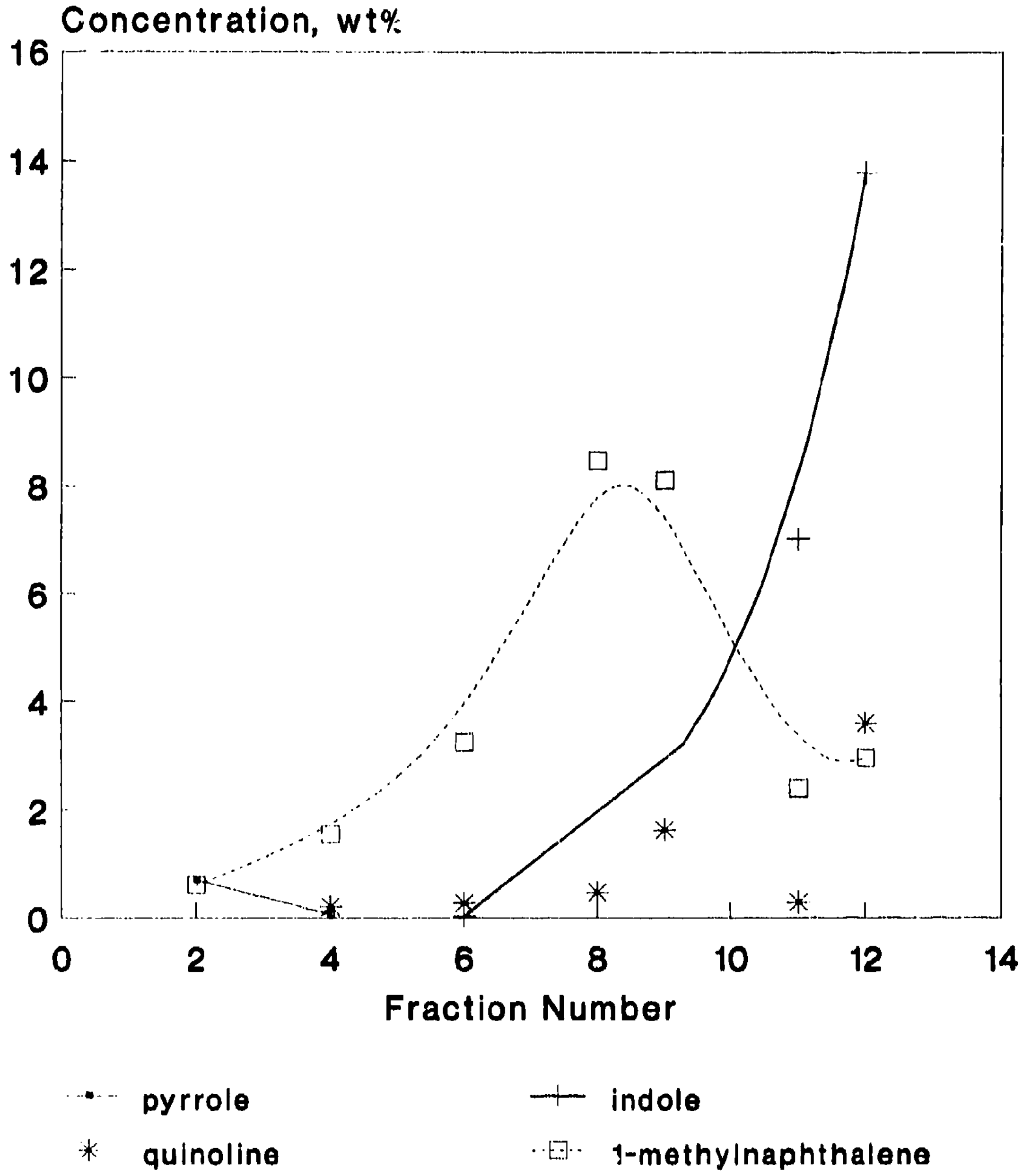


Figure 20. Fractionation of Surrogate JP-8 (WP-3)
Partioning of Cyclic and Heterocyclic Compounds

Table 16. Comparison of the Concentration of Various Components in Fractions WP-3-12

Compound	Boiling Point (°C)	$\frac{\text{Conc. in WP-3-12}}{\text{Conc. in WP-3-Control}}$
Quinoline	238	12.35
Methylnaphthalene	240	0.88
Indole	253	51.04
Tetradecane	252	0.72

The data demonstrate the importance of specific solute-solvent interaction and they indicate that it is possible to separate compounds with nearly identical boiling points but slightly different chemical natures (i.e., polarity, hydrogen bonding, etc.) by SCF extraction which cannot be separated by distillation. It is also interesting to note that the data presented in Figure 18 indicates it is possible to fractionate a homologous series of straight chain hydrocarbons using this SCF extraction.

A number of the samples were analyzed for total nitrogen by ANTEK and the results are presented in Table 17. While all of the fractions analyzed are of a lower nitrogen concentration than the control (which indicates heavy concentration in the later fractions which were not analyzed), Fraction 2 has a relatively substantial concentration of nitrogen and is likely concentrated in pyrrole as evidenced by G.C. analysis. If the concentration of Fraction 3-7 is assumed to be midway between 3-6 and 3-8, a material balance indicates Fractions 9-12 must have an average nitrogen concentration of approximately 2.7%.

Table 17. Total Nitrogen Concentration of Selected Fractions of Spiked, Surrogate JP-8

Sample	%N
WP-3 Control	0.57%
WP-3-1	0.24%
WP-3-2	0.49%
WP-3-3	0.37%
WP-3-4	0.13%
WP-3-5	0.12%
WP-3-6	0.13%
WP-3-7	0.23%

It should be noted that due to the batch-continuous configuration of the experiment, the fuel remaining in the extractor is continually enriched in nitrogen as nitrogen lean fractions are removed and, therefore, the analysis of Fractions 3-4, -5, -6 is particularly encouraging. It should also be noted that while a batch-continuous arrangement is useful for obtaining feasibility information, it is inefficient for precise fractionation because it represents only one equilibrium stage. A continuous counter-current process, such as that which would be used for pilot or commercial scale separations of this type, would employ many equilibrium stages. (Incidently, Phasex has found that in scaling up a variety of processes, in its pilot plant the height of a theoretical stage is only 4-6 inches depending on the system.)

4. Supercritical Fluid Fractionation of Coal-Derived JP-8X

A sample of coal-derived JP-8X produced from tar oil from the Great Plains Coal Gasification Plant was obtained from Wright-Patterson AFB. The fuel was produced for a program to determine the feasibility of converting tar oil to aviation fuel (see AFWAL-TR-87-2042). A G.C. chromatogram for the control sample is shown in Figure 21. The production of jet fuels from tar oil requires extensive hydrotreating and hydrocracking to reduce heteroaromatic and multicyclic compounds to acceptable levels. SCF extraction may represent an alternative for upgrading coal-derived fuels.

a. Fractionation of Coal-Derived JP-8X by Isothermal Pressure Profiling

A sample (19.7 g) of coal-derived JP-8X was fractionated by means of an isothermal pressure profile at room temperature. The experiment, designated WP-5, is summarized in Table 18.

Table 18. WP-5: Fractionation of Coal-Derived, High Density JP-8X* by Isothermal Pressure Profiling, T = 14°C, Charge = 19.73g

Fraction	Pressure Range	Stand. Liters	Mass grams	Σw_i (%)
1	2100	545	1.50	8.3
2	2300-2500	400	1.70	17.7
3	2600-2900	500	3.01	34.5
4	2800-3100	300	1.81	44.4
5	3000-3300	300	2.07	55.9
6	3200-3500	300	1.87	66.3
7	3450-3700	300	1.85	76.6
8	3600-3900	300	2.02	87.7
9	3900-4300	300	1.01	93.4
10**	4000-4400	150	1.20	100.0
			18.04	

* 88-POSF-2658, ** = CO_2 at 60°C, Recovery = 18.04/19.73 = 91.4%

Again, CO_2 was used as an expedient for removing the final fraction. Fractions 1, 5, and 10 were analyzed by gas chromatography and the chromatograms are presented in Figure 22. It may be seen from the data that the fuel was selectively fractionated by supercritical fluid extraction. It is interesting to note the substantial increase in concentration of the compounds eluting after 90 minutes in Fraction 10 which are barely discernible in the control chromatogram (for completeness, the scale used in Fraction 10 is slightly expanded compared to that in the other fractions, but the concentration factor is nevertheless pronounced).

All 10 fractions were analyzed for aromatics content and the results are presented in Figure 23. It can be seen that the aromatics content of the fractions increases steadily across the distribution.

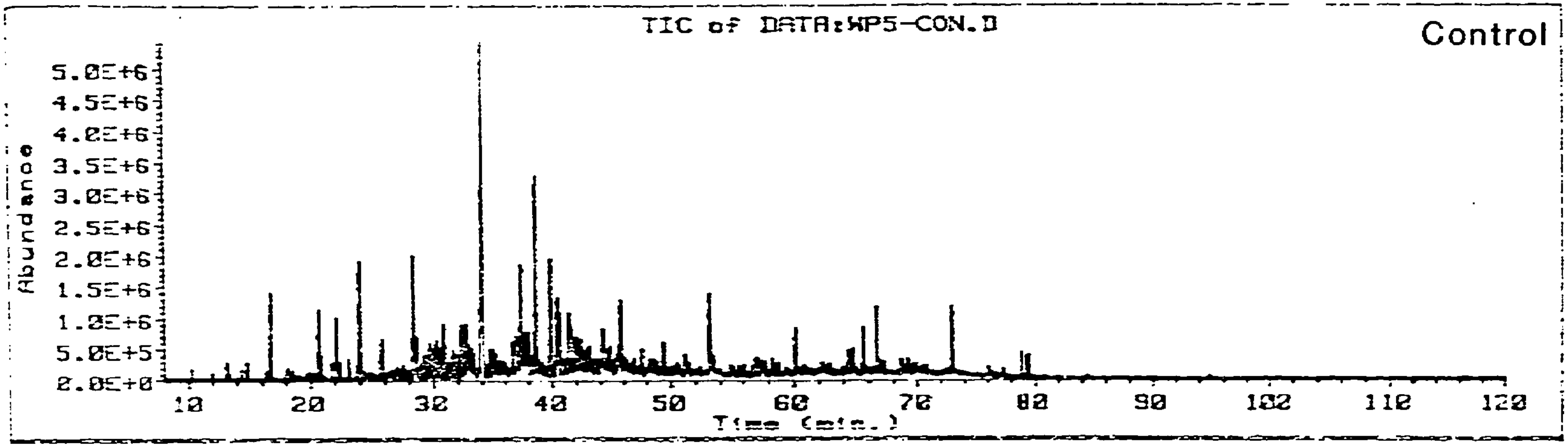


Figure 21. G.C. Chromatogram of Coal-Derived JP-8X Parent

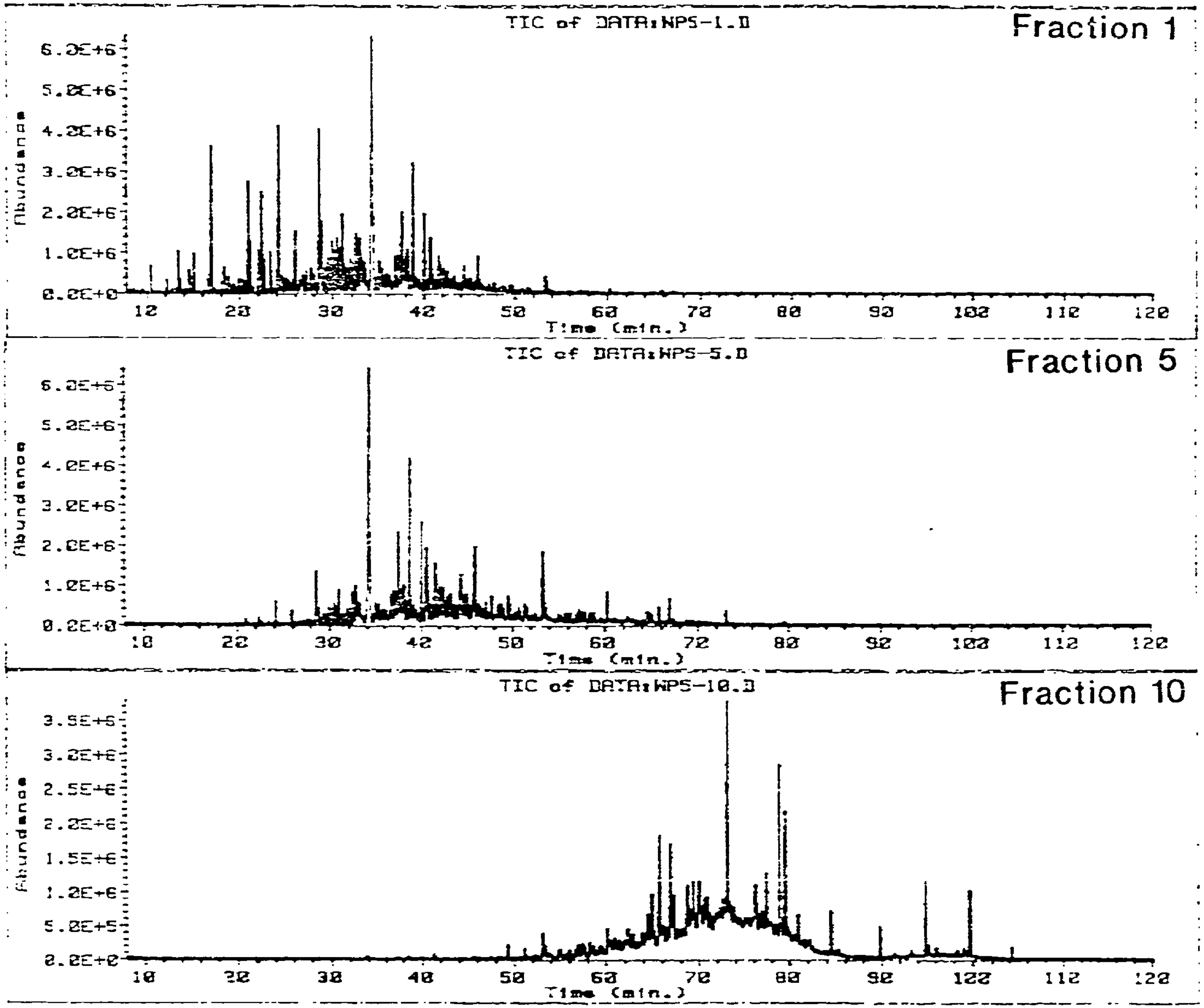


Figure 22. G.C. Chromatograms of Coal-Derived JP-8X Fractions (WP-5)_

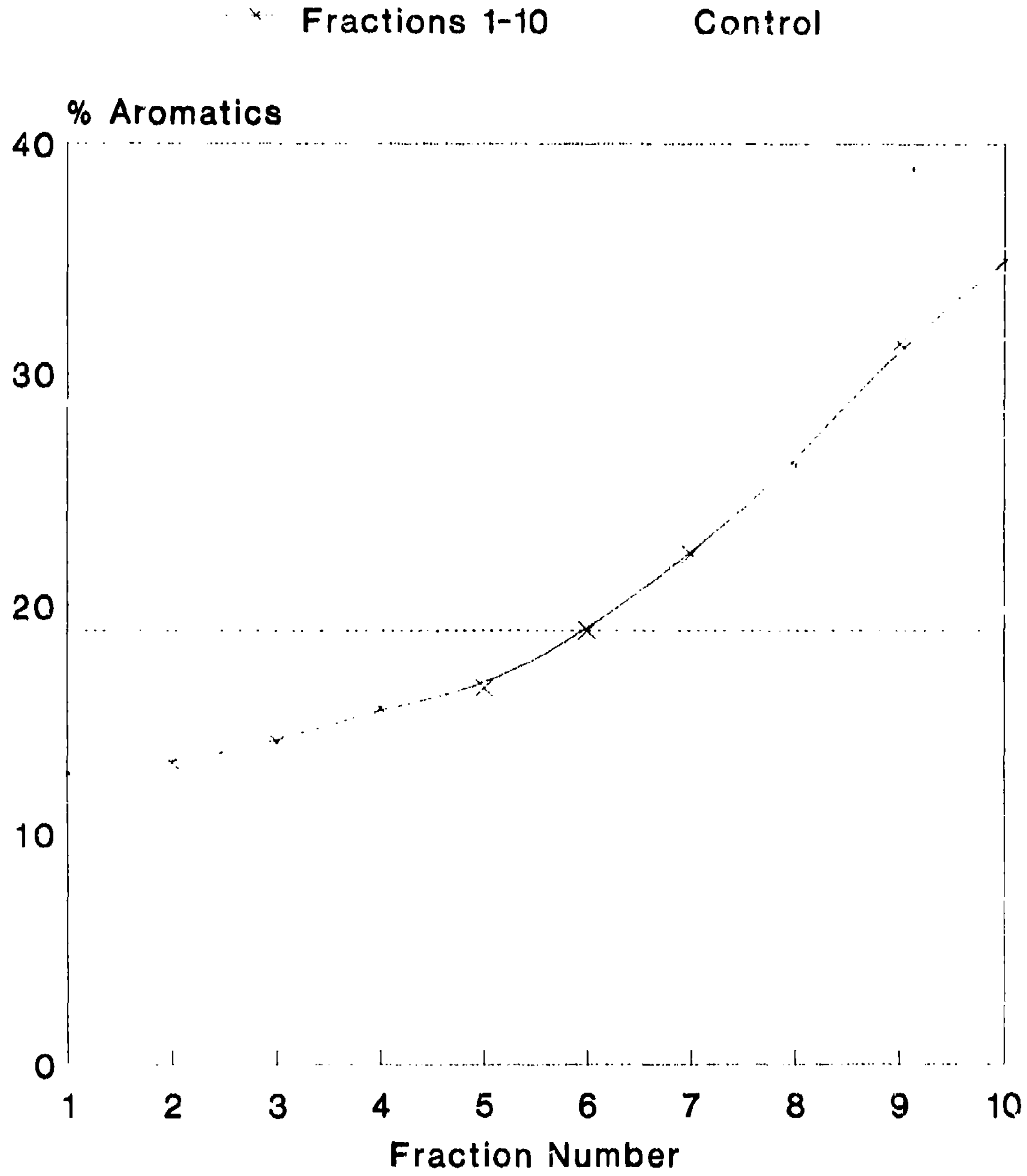


Figure 23. Fractionation of Coal-Derived JP-8X Aromatics Content vs. Fraction Number

V. Potential for Scale-up to a Viable Commercial Process

A. Principles

As related earlier in this report, the feasibility experiments performed over the course of this program were of a batch-continuous configuration. While extremely useful for obtaining feasibility information, batch-continuous separation, which comprises a single equilibrium stage, is not the preferred means of scaling up a liquid-SCF extraction process to pilot or production scale. A more efficient means for this type of separation, including the processing of jet fuels, is the use of a continuous counter-current process. This type of arrangement not only eliminates cumbersome, costly batch processing, but also employs multiple equilibrium stages for an efficient separation.

In order to establish a reasonable basis for assessing the economic viability of a supercritical fluid extraction process, several parameters which describe the equilibrium partioning of components between the bulk phase to be separated and the solvent must be determined. The two most important parameters are the distribution coefficient (*DC*) and the selectivity (β) of the component(s) of interest.

Distribution coefficients are a measure of the extractability of a compound from a mixture of components. Physical chemistry texts define the distribution coefficient as:

$$DC = y_e / x_e \qquad (1)$$

where:

DC is the distribution coefficient,

y_e is the concentration of the desired component in the solvent phase, and

x_e is the concentration of the desired component in the bulk phase in equilibrium with y_e.

Distribution coefficients can be expressed in any consistent units, and weight units will be used for this report.

As is seen from the definition given in Eq. (1), the higher the value of distribution coefficient the higher the concentration of the component that can be transferred from the feed to the solvent phase. The distribution coefficient also provides information about the solvent-to-feed ratio for complete extraction of a component in a counter-current continuous column. In the theoretical limit (i.e., for an infinite number of equilibrium stages), the minimum solvent-to-feed ratio ($R_{\min}$) which is required for the complete extraction of a component is equal to the inverse of the distribution coefficient, i.e.:

$$R_{\min} = DC^{-1} \qquad (2)$$

The advantage of a large distribution coefficient in terms of minimizing R is obvious from the relation given above. As an example of typical distribution coefficients for an industrial process, the value for carbon dioxide extraction of caffeine from coffee liquor is approximately 0.03 - 0.1 depending on temperature and pressure[19].

Distribution coefficients may be determined experimentally in several different ways[20]. For this discussion, distribution coefficients are calculated directly as the concentration of the component in the gas phase divided by concentration of that component in the liquid phase as determined by means of a material balance. In all cases the distribution coefficients calculated are based upon average concentrations at the midpoint of a fraction, i.e.:

$$DC_{av} = \overline{y_e} / \overline{x_e} \qquad (3)$$

where:

$\overline{y_e}$ is the average concentration of the extracted component in the solvent (gas) phase during the course of a fraction. This value is determined by the analysis of the collected fraction and the measured amount of solvent,

$\overline{x_e}$ is the average concentration of the extracted material in solution (i.e., the phase from which the material is extracted) during the course of the fraction, i.e., $\overline{x_w}$ is $(x_{initial} + x_{final})/2$.

Maximizing the distribution coefficient is not the sole consideration when determining operating conditions for a separation process. It is also necessary to optimize in terms of the ability for the solvent to discriminate between or among components. The quantity most often used to define the "separability" of two or more components is the selectivity. Selectivity is usually expressed as the ratio of distribution coefficients, i.e.:

$$\beta_{12} = DC_1 / DC_2 \qquad (4)$$

where:

β_{12} is the selectivity of the solvent for component 1 relative to component 2,

DC_1 is the distribution coefficient of component 1, and

DC_2 is the distribution coefficient of component 2.

Selectivity at a given condition determines the number of theoretical stages required for the separation of components to a given specification.

The process parameters (i.e., solvent-to-feed ratio and number of equilibrium stages) for separating a mixture of known composition to a given specification can be obtained using equilibrium data by the classical McCabe-Thiele method for distillation. Typically the equilibrium curve for two components (y_e vs. x_e) is plotted along with the operating line (typically a value of 1.3 times the minimum R is used) and the number of stages determined by "stepping off" trays. A complete description of this method is provided in many texts.[21] Alternately a computer program may be used; such a program was utilized for the determinations in this report.

B. Determination of Distribution Coefficients and Selectivities for Spiking Agents in JP-8 (WP-7)

As related in the experimental section, JP-8 was spiked with indole, 1-indanol, quinoline, and naphthalene for the purpose of determining distribution coefficients and selectivities of these compounds in an actual sample of JP-8. The complex composition of the fuels leads to a number of complications during these calculations. For example, in addition to removing the undesirable components in the fuel it was demonstrated earlier that the fuel is fractionated with respect to a number of carbon atoms in a homologous series and, therefore, the composition of the fuel is continually changing during the extraction process. For this initial evaluation, distribution coefficients are assumed to be constant in the concentration regimes of interest. Despite the complications described above, the distribution coefficient and selectivities calculated from the data obtained in the experiment will provide a ball park estimate of the solvent-to-feed ratios and number of theoretical equilibrium stages required for a given separation at these conditions; as has been pointed out earlier, the separation conditions are not yet optimized.

The distribution coefficients and selectivities calculated as discussed above are given in Tables 19 and 20. As indicated by the data in Table 10 many of the fractions contained only trace amounts of indole and indanol which were below the concentration limits for quantification on the G.C. Therefore, indole and indanol will partion to a very small extent and the distribution coefficients for the fractions marked with an asterisk as vanishing small. This is not a negative result because of the extremely low values (in fact incalculable values) of the distribution coefficients of indole and indanol in the designated fractions the selectivities of the other compounds relative to indole and indanol by definition approach infinity. Therefore, it can be assumed that a "clean" separation of these components from the fuel can be realized under the designated extraction conditions.

Table 19. Distribution Coefficients of Fuel and Spiking Agents from WP-7

Fraction	Fuel x 10^2	Indole x 10^2	1-Indanol x 10^2	Quinoline x 10^2	Naphthalene x 10^2
1	1.35	*	*	0.33	0.64
2	1.76	*	*	0.47	0.97
3	1.90	*	*	0.74	1.21
4	1.69	*	0.54	0.72	1.41
5	1.60	*	0.86	0.94	1.81
6	1.17	*	0.54	0.74	1.91
7	1.23	*	0.37	0.50	1.81

* extremely low - see text above

Table 20. Selectivity of Fuel with respect to Spiking Agents in WP-7

Fraction	Indole	1-Indanol	Quinoline	Naphthalene
1	**	**	4.1	2.1
2	**	**	3.7	1.8
3	**	**	2.6	1.6
4	**	3.1	2.3	1.2
5	**	1.9	1.7	0.9
6	**	2.2	1.6	0.6
7	**	3.3	2.5	0.7

** very high - see text

C. Test Cases

A computer program has been written at Phasex Corporation for determining the solvent-to-feed ratios and number of stages required for separating a mixture of known composition to a given specification. The program allows for the use of reflux which is usually necessary for situations which require high purity. For purposes of illustration the values obtained in fraction four will be utilized for several test cases. Note that because one of the governing assumptions of a linear equilibrium curve in the regime of low concentration, the percentage reduction in the test cases (i.e., 95% for Case 1) would, in actuality, be independent of the representative concentrations used in the examples. For example, the operating parameters in Case 1 would be the same for a reduction from 0.1% to 0.005% as would be for the stated case of 1% to 0.05%.

Case 1. Reduction of 1-Indanol from 1% to 0.05% Using 1.5 x Minimum Reflux Rate

No. of Stages	11
Feed Stage	6
Yield	97%
Working Reflux Ratio*	0.60
Working Solvent/Feed	95

Case 2. Reduction of Quinoline from 1% to 0.05% Using 1.5 x Minimum Reflux Rate

No. of Stages	14
Feed Stage	7
Yield	97%
Working Reflux Ratio*	0.99
Working Solvent/Feed	118

Case 3. Reduction of Naphthalene from 3% to 1% Using 1.5 x Minimum Reflux Rate

No. of Stages	18
Feed Stage	12
Yield	93%
Working Reflux Ratio*	2.01
Working Solvent/Feed	178

* The working reflux ratio is defined for this report by the ratio of the fraction of distillate returned to the column over the fraction of distillate drawn off as product.

Several comments are made here concerning the values given above. First, these values do not represent an optimum; they are included as a reference from a first case test in order to provide an initial idea of operating parameters and to serve as a basis for an economic assessment. A fractionation at slightly higher pressures, such as those utilized midway through WP-4, resulted in an overall distribution coefficient for the fuel of approximately 0.0271 or about 60% higher than that from WP-7 which is used in the test case. As stated, the separation must be optimized before accurate S/F ratios and number of stages can be established; however, the information generated using the data from this initial trial can be used to provide an initial, worst-case basis for preliminary economic evaluation. In general, Phasex Corporation prefers to use the more pessimistic distribution coefficients and, therefore, the economic assessment is extremely conservative (i.e., pessimistic). Secondly, in the experience of Phasex Corporation it has been found that data obtained in the laboratory on batch continuous extraction systems typically overpredict the required solvent-to-feed ratios by approximately 30%. Finally, it has been found that, in most cases, the height of theoretical stage is approximately 4-6 inches for the separations that have been run in the pilot facility. Therefore, the effective separation length of an extraction column would be a maximum of 9 ft, a very "short" column relative to distillation towers. The fuel drawn off as raffinate, i.e., that fraction with high heterocyclics and aromatics content, may be used to provide energy for the fuel separation plant.

VI. Preliminary Economic Assessment

While a detailed economic analysis is beyond the scope of this report, the Phase I program has provided sufficient information for a rudimentary economic assessment of a supercritical fluid extraction process for producing low heterocyclic content jet fuel. The results of the experiments permit reasonable estimates of many of the operational parameters including temperature (ambient), pressure (3800 psi max), and column height to be made. For simplicity, the supercritical fluid extraction process is assumed to be a separate, stand-alone, unit operation. The estimate, like the Phase I program, does not consider the potential advantages and savings associated with incorporating the SCF process at an earlier stage in the refinery operation, nor does it consider the savings associated with the elimination of hydrotreating.

The following estimate will be based on a 10,000 bbl/day extraction facility. The bases for the operation and design of the supercritical fluid extraction process are:

process throughput	10,000 bbls/day
operating pressure	3800 psi max
operating temperature	ambient
recycle ratio (which also accounts for the JP-8 reflux ratio)	100

The bases fix the recycle compressor size and horsepower, heat exchange requirements, and similar facets of the process; there remains to be specified the extraction column dimensions. Since the extractor, or in most cases multiple extract in parallel, is one of the major pieces of equipment and one of the largest capital cost items, efforts in any experimental program and process design are directed to minimizing its cost. Emphasis is placed on reducing the diameter to a great extent as possible since for pressure vessels of a given vessel volume "length is less expensive than diameter", i.e., the acquisition cost of a long, small diameter column is much less than one with a short, large diameter. The diameter cannot, however, be reduced to a ridiculous extreme merely by ensuring that some given residence time constraint be satisfied with a given volumetric relation, say, a space velocity, because such considerations as density difference, gas velocity, liquid-gas disengagement, etc. intertwine in any given situation.

In a typical industrial liquid-liquid extraction process, the superficial velocity of one liquid or the other is of the order of 0.03 ft/sec,[21] and one of the major reasons for the low velocity resides in the low density difference between most liquid pairs used in industrial extractions. If the velocity of one or both liquids is too high, disengagement of liquid drops and the continuous phase will not occur. In a typical industrial gas-liquid process, e.g., where one component of a gas stream is absorbed by a liquid (gas absorption) or where a gas like air is used to strip a component from a liquid stream (gas stripping), the density difference gas and liquid is usually large, e.g., air at 0.001 g/cc and water at 1.0 g/cc, and there exist no disengagement difficulties; gas velocities of 2-3 ft/sec are commonplace. The column diameter varies as the $\sqrt{velocity}$ so that a factor of 10 diameter ratio is associated with the 3 to 0.03 ft/sec velocities for gas stripping and liquid-liquid extraction.

The brief background on typical liquid-liquid and gas stripping operations in industry was developed for the purpose of providing a means of comparing the supercritical fluid extraction of JP-8 with either liquid-liquid extraction or with gas stripping, and as will be shown subsequently the JP-8 process is more nearly similar to gas stripping; for example, at 3000 psi, 25°C, the density of methane is 0.16 g/cc and JP-8, 0.8 g/cc, this density difference much more nearly modeling the gas stripping case. A conservative gas velocity of only 1 ft/sec (instead of the higher 3 ft/sec used in gas stripping or absorption) will be used for this estimate.

With all the factors and parameters fixed, viz., methane solvent/feed ratio of 100, and extraction column gas velocity of 1 ft/sec, a 10,000 bbl/day facility would require 8 extraction columns each 10 meters (32.8 ft) high by 2 meters (6.6 ft) internal diameter. The stated geometry results in a gas velocity of approximately 0.33 meters/second (1.1 ft/sec) and provides adequate height for settling zones at both ends of the column. Columns of this dimension are consistent with those in present commercial operation (i.e, the decaffeination of coffee and tea). Figure 24 is a copy of a page from a Krupp brochure which gives the cross section of a coffee column in Germany. Incidently the coffee column pictured has a internal volume larger than that of the proposed extraction columns.

It is assumed in the estimate that a pressure reduction step will be utilized for the separation of the purified fuel from the solvent following processing in the extraction column. Incidently, pressure reduction is the mode of separation in commercial carbon dioxide extraction of hops. Based on the observations made during the course of this program, a reduction to 1500-2000 psi would be sufficient to reduce the concentration of components in the solvent stream to negligible levels. While pressure reduction will certainly be effective, there is a substantive energy penalty associated with the recompression and recycle of the solvent. For example for the ideal case of an isenthalpic expansion followed by an isentropic compression and assuming an extraction pressure of 250 bar (at 300 K) and a separator pressure of 100 bar, the energy requirement is approximately 49.7 Btu/lb (115.5 kJ/kg) solvent. The energy requirement as calculated is for an isentropic compressor which does not consider efficiencies; however, for large industrial compressors efficiency is typically 90%. The actual energy requirement is then 49.7 Btu/lb/0.9 or 55.2 Btu/lb (128.3 kJ/kg) solvent. It should be noted that the temperature in the separator would drop approximately 30 K due to Joule-Thompson cooling and this temperature drop would likely improve the separation of fuel from the solvent stream. It is assumed that the heat of compression generated in returning to extraction conditions can be "recycled" to the process by recuperative heat exchange, but this advantageous feature is not included in this estimate.

The power required for the separation plant can either be purchased or provided by an on-site plant. In either case a cost of $2.50/MM Btu, the current price of bulk electricity on the Gulf Coast will be assumed. Using a basis of 100:1 solvent:feed ratio the energy cost, neglecting inefficiencies beyond that of the compressor would be approximately $0.0138/lb of refined fuel or approximately 9.0¢/gallon. A 10,000 bbl/day plant would then require approximately 775 MegW, equivalent to a power facility of moderate size.

An estimate of the other cost factors are provided. Based on conversations with an A&E firm, it is estimated that the capital cost for the 10,000 bbl/day SCF extraction plant is in the neighborhood of $30,000,000 to $50,000,000 dollars. A cost of $40,000,000 will be used for the purposes of this development. Based upon operations of other processes within a refinery, it is assumed the labor requirement is eight persons/shift. While the following analysis is simplistic in scope, a ballpark figure for cost can be determined from it. Once again, it should be noted that estimate does not account for integration of the process further back into the refinery operation nor does it consider the savings associated with the potential elimination of current steps such as hydrotreating.

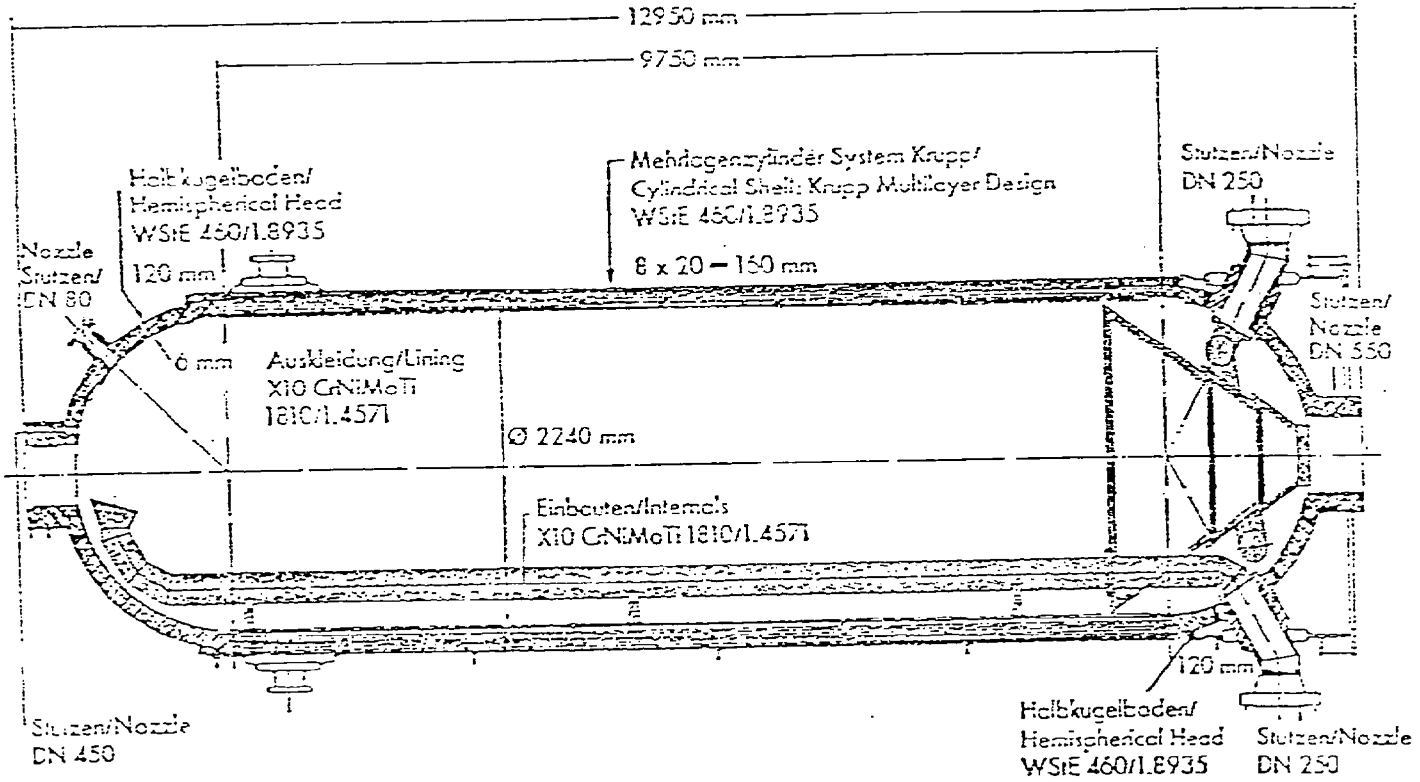


Figure 24. Schematic Diagram of German Coffee Decaffeination Column

Cost Factors

Basis

a. Capital Cost = \$40,000,000
b. Work Schedule = 3 shifts/day, 330 days/yr
c. Throughput = 10,000 bbl/day x 330 day/yr x 277 lbs/bbl
= 9.15×10^8 lbs/yr

Cost Breakdown

1. Labor: 8 persons/shift = 7920 person days/yr
Salaries and Fringes = \$150/day
Labor Cost = (7920 shifts/year x \$150/shift)/9.15×10^8 lbs/yr
= 0.13¢/lb

2. Depreciation Schedule, 10-yr straight line
Capital Costs = \$40 MM/(9.15×10^8 lbs/yr)(10 yrs)
= 0.44¢/lb

3. Buildings, facilities, 20% of capital costs = \$0.088¢/lb

4. Maintenance, 10% of capital costs = 0.044¢/lb

5. Insurance, 10% of capital costs = 0.044¢/lb

6. Supervision, accounting, transfer costs, etc., 100% of labor = 0.13¢/lb

7. Energy = 1.38¢/lb

Total costs = 2.26¢/lb
= 14.9¢/gallon

VII. Conclusions and Recommendations

The feasibility of fractionating jet fuels, specifically as a means of separating multiring aromatic and heterocyclic with supercritical methane, has been demonstrated. The data generated during this program confirm that it is possible to separate components of nearly identical vapor pressure but slightly different chemical nature by SCF extraction; and it is, therefore, possible to fractionate components found in a single distillation cut of fuel. Fractionation has been shown to produce a fuel with "cleaner" combustion properties as evidenced by smoke point testing. The removal of the heterocyclic compounds should result in a fuel with superior thermal stability.

The process parameters required for SCF methane separation of jet fuels are common in the petrochemical industry. A production unit would likely operate counter-currently at ambient temperature and pressures of less than 3800 psi. It is estimated that the separations will require less than 20 stages and that the effective separation length required for extraction column would be less than 10 ft.

A processing cost of 14.9¢/gallon has been determined by a preliminary economic assessment of a 10,000 bbl/day SCF extraction plant. A substantive portion of this cost (~60%) is attributable to the energy consumption required for recompressing methane following expansion and separation of the fuel from the solvent stream. Recovery of the expansion energy via turbocompressors or similar equipment should be considered as a means of reducing energy costs. Additionally, potential savings may be possible by integrating an SCF process further back in refinery operation and replacement of current operations such as hydrotreating should be evaluated in the final economic picture.

Because of the success of the Phase I program it is recommended that the work continue in a Phase II program and that the Phase II effort be staged. Initially the separations should be scaled to the pilot plant level using existing equipment. The samples generated would then be evaluated for thermal stability (JFTOT, flask tests) and combustion properties (smoke point, etc.) to determine the effect of the separations on performance properties. If these results are, as anticipated, positive, the program would then continue for process optimization and intensive economic evaluation.

Fuel fractionation of supercritical methane could also have application in the commercial sector particularly in the production of reduced emission diesel fuels.

VIII. References

1. Hazlett, R. N. "Some Chemical Aspects of Deposit Formation" in Jet Fuel Thermal Stability, W. F. Taylor. Ed., NASA Technical Memorandum 79231, (1979).

2. Peat, A. E., Fuel Thermal Stability. Propulsion and Energetics Panel, Working Group 13 on Alternative Jet Engine Fuels, Vol. 2, R. B. Whyte, Ed., AGARD-AR-181-Vol-2, July 1982, pp. 119-141.

3. Cohen, S. M., Fuels Research - Fuel Thermal Stability Overview. Aircraft Research and Technology for Future Fuels, NASA CP-2146, July 1980, pp. 161-168.

4. Daniel, S. R. and J. H. Worstell, Fuels Research - Fuel Thermal Stability Overview. Aircraft Research and Technology for Future Fuels, NASA CP-2146, July 1980, pp. 185-192.

5. Hardy, D., Personal Communication (1990).

6. Penninger, J. M. L., Radosz, M., McHugh, M. A., and Krukonis, V. J., eds., Supercritical Fluid Technology Elsevier, New York, 1985.

7. Johnston, K. P. and Penninger, J. M. L., eds., Supercritical Fluid Science and Technology, ACS Symp. Series 406 ACS Washington (1989).

8. McHugh, M. A. and Krukonis, V. J., Supercritical Fluid Extraction: Principles and Practice, Butterworth Publishers, Boston, 1986.

9. Stahl, E., Quirin, K. W., and Gerard, D., Dense Gases for Extraction and Refining, Springer-Verlag, New York (1987).

10. Krukonis, V. J. and Kurnik, R. T., Solubility of Aromatic Isomers, J. Chem. Eng. Data, 30, 247 (1985).

11. McHugh, M. A. and Krukonis, V. J., Supercritical Fluids, Encyclopedia of Polymer Science, Mark-Bikales-Overberger-Menges, eds, 16, 368 (1989).

12. Krukonis, V. J., Processing of Polymers with Supercritical Fluids, Polymer News, 11, 7, (1985).

13. Worthy, W., Supercritical Fluids Offer Improved Separations, C&E News, p 16, Aug 2, 1981.

14. Hannay, J. B. and Hogarth, J., On the Solubility of Solids in Gases, Proc. R. Soc. (London), 29, 324 (1879).

15. Peng, D. Y. and Robinson, K. B., A New Two Constant Equation of State, Ind. Eng. Chem. Fundam., 15, 59 (1976).

16. Hyatt, J. A., Liquid and Supercritical CO_2 as Organic Solvents, J. Org. Chem. 49, 5097 (1984).

17. Todd, D. B. and Elgin, J. C., Phase Equilibria in Systems with Ethylene above its Critical Temperature, AIChE J. 1, 20 (1955).

18. Kurnik, R. T., Holla, S. J., and Reid, R. C., Supercritical Fluid Extraction, Paper presented at the 73rd Annual Meeting of the American Institute of Chemical Engineers, Chicago, IL (1980).

19. Margolis, G. and Chiocioni, J., U.S. Patent 4,251,559 (February, 1981).

20. Krukonis, V. J., Supercritical Extraction of Phenolic Wastewater, DOE Technical Report, DOE/PETC/TR-86/7 (DE 86012336).

21. Treybal, R. E., Mass Transfer Operations (Third Ed.), McGraw-Hill Book Company, New York, NY (1980).

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