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THIS NASA INVENTION OFFERS TO HAVE
EXCELLENT COMMERCIAL POTENTIAL
OIL SHALE EXTRACTION USING SUPER-CRITICAL EXTRACTION

The present invention relates to the extraction of oil shale using a supercritical liquid. Conventional separation of an extract from oil shale by retorting produces an unstable petroleum syncrude with a very high nitrogen content and is not cost competitive. In retorting the shale is heated to about 480°C (900°F) in a low oxygen environment. Only about 50% of the organic matter is converted to oil, the remainder to gas and char. The gas is diluted with nitrogen and carbon dioxide and its heat content and efficiency are low. The char is mixed with mineral which endothermically decomposes. Supercritical gas extraction (SCG) has the potential to make the energy in oil shale available in more concentrated form. U.S. Patent No. 4,108,760 discloses SCG extraction of oil shale at 350°C to 500°C, preferably 370°C to 450°C which temperatures are high enough to cause depolymerization and cracking.

It has now been discovered in accordance with the invention that useful extraction can be achieved at temperatures below 450°C, such as 350°C to 425°C, and even at temperatures below 350°C, such as 250°C to 325°C. Residual organic matter after extraction is about one-quarter that left during prototype commercial retorting and less gas and char are produced. These process advantages are achieved by the use of special solvents, particularly those having a Hildebrand solubility parameter differing by less than 1-2 Hildebrands from the solubility parameter for oil shale bitumen. The ratio of solvent to oil shale can be varied over broad ranges. The amount of oil shale can be 1 to 99% by weight of the total mixture of coal and solvent. Use of excess solvent provides increased extraction though it also requires considerable handling at separation effort to recover the extract and the solvent for recycle. Therefore, the amount of shale in the reactor is preferably from 10 to 60% of the total weight of shale plus solvent. The process of the invention is capable of extracting fairly large lumps of shale and it is not believed to be necessary to subdivide and classify the shale below about 5 mesh before processing in accordance with the invention. The process can be practiced over fairly broad pressure ranging from 0.1 to 100 MPa, usually from 5 to 25 MPa. The process can be batch, with or without solvent recycle, or continuous. The oil shale can be restrained in a porous container or freely suspended in a fluidized bed.
1-2 Hildebrands from the solubility parameter for oil shale bitumen. The ratio of solvent to oil shale can be varied over broad ranges. The amount of oil shale can be 1 to 99% by weight of the total mixture of coal and solvent. Use of excess solvent provides increased extraction though it also requires considerable handling and separation effort to recover the extract and the solvent for recycle. Therefore, the amount of shale in the reactor is preferably from 10 to 60% of the total weight of shale plus solvent. The process of the invention is capable of extracting fairly large lumps of shale and it is not believed to be necessary to subdivide and classify the shale below about 5 mesh before processing in accordance with the invention. The process can be practiced over fairly broad pressure ranging from 0.1 to 100 MPa, usually from 5 to 25 MPa. The process can be batch, with or without solvent recycle, or continuous. The oil shale can be restrained in a porous container or freely suspended in a fluidized bed, or held by a grating arrangement. The data for extraction with toluene illustrated in the Figure shows an essentially linear temperature dependence for the percent of total organic matter extracted in the range of 350°C to 390°C.

The results demonstrate the powerful solvent properties of supercritical gases (SCG). Residual organic matter after extracting at 450°C is one-half that left by modified Fischer assay, and it is probably one-quarter or less of that which would be generated during prototype commercial retorting. In addition, the data shows organic matter removal occurring below 450°C can be greater than that found with prototype retorting. Higher solubility parameter solvents are expected to improve these results. Certain process advantages associated with the technique could occur, namely those associated near quantitative removal of organic matter and with the presumably lower gas generation associated with lower temperatures and reduced char formation. In addition the enhanced extraction efficiency and lower temperature of extraction may result in a residual char which contains lower concentrations of mutagenic substances than those found in conventionally produced oil shale char. This possibly would improve the ease of disposal of oil shale char.
Origin of the Invention

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 83-568 (72 Stat 435; 42 USC 2457).

Technical Field

The present invention relates to the extraction of oil shale and, more particularly, to the extraction of oil shale utilizing a supercritical fluid.

The consumption of oil and gas represents about 80% of the consumption of fossil fuels in the United States. At the present time, about one-half of the electric power is generated from natural gas and petroleum. Fuels other than liquid and gaseous hydrocarbons, such as nuclear, hydrogen or methanol are being investigated as are power sources other than internal combustion engines, such as fuel cells, photovoltaic cells or electric storage batteries. However, consumers are accustomed to using liquid fuels and the supply, distribution, power generation and marketing infrastructure are already in place. The demand for liquid hydrocarbon fuels for power generation and transportation is expected to double by the year 2000.

There are large deposits of oil shale in the United States and Canada. The organic portion of oil shale has a higher indigenous hydrogen content than coal. This fossil fuel is a potential source of liquid fuel which would conserve the rapidly depleting
petroleum and natural gas resources for other essential uses as a feedstock for the synthetic rubber and resin industries. The liquid hydrocarbon extract from oil shale could also supply chemical intermediates or serve as a synthetic resin or rubber feedstock.

Green River oil shale in the western United States is considered by many as second only to coal as the largest potential source of fuel in the energy future of the United States. In addition, because of its high indigenous hydrogen content, it is considered superior to coal as a potential feedstock for conversion into liquid fuels. The organic matter in oil shale is conventionally separated by retorting from the inorganics with which it is associated. Temperatures sufficient to crack the organics are used, and a very-high-nitrogen, unstable "petroleum" is produced. It is forecasted by some strategic planners that such oil shale syncrude could enter into the domestic market during the next decade and result in reduction in the nation's dependency on overseas fuel supplies. However, retorting has not yet proven capable of producing a fuel that is truly cost competitive, and present decreases in the price of crude petroleum have reduced at least the short term commercial potential of all synfuels.

Background Art

Oil shale retorting in either above-ground or in-situ retorts centers around heating the material, which is typically 85% rock, to about 480°C (900°F) or higher in a low oxygen environment. The kerogen and bitumen in the rock are decomposed into oil, gas, and a residual char which remains within the rock. Under favorable circumstances in the laboratory, 70 wt% of the organic matter is converted to oil upon heating to 500°C, and
the remainder is converted to about 15% gas and 15% char. These yields change when oil shale is processed in prototype commercial retorts. Oil yield is reduced from 10% to 30% below modified Fischer assay yields, depending on the process, and char and gas yields are correspondingly increased.

The energy content of the organic matter not converted to oil exceeds net process heat requirements for oil shale retorting. The excess depends on the organic content of the shale and the process design, but for well developed processes using a medium grade of shale (roughly 11 to 15 wt% organic matter) the excess can be 100% greater than heat requirements. For instance, the TOSCO II process is based on discarding 100% of the char produced from 11% organic matter shale. The excess can be double or triple this amount when richer material is processed.

The energy contained in the char and gas by-products typically cannot be used efficiently. The gas produced is often greatly diluted with nitrogen and carbon dioxide, and the heat content and its efficiency of usage are greatly reduced. In addition, the energy generated by combustion of the residual char in the rock is considerably less than might be anticipated, because of high temperature endothermic mineral carbonate decompositions which occur when the char is burned. In short, the fuels are in dilute forms and the energy contents have low thermodynamic availability. This severely reduces or eliminates their commercial value. Areas in which western oil shale would be developed contain little or no nearby industrial base which could use such fuel, and the gas and char would require prohibitively costly transport.
This combined with very low value causes char and gas in excess of process fuel requirements to be waste disposal problems, rather than saleable by-products.

The above characteristics of retorting are drawbacks, since energy in saleable form is the desired product. Requirements for heating rock to high temperature, excessive conversion of organic matter to char and gas, and the low value of the diluted energy content of these by-products combine to reduce the net saleable energy to 1/3 to 1/2 below that contained in the raw oil shale.

Solvent extraction with pyrolysis is an alternative to conventional retorting. However, oil shale differs from other carbonaceous-matter bearing material, such as coal, in that the organic material is dispersed throughout a non-porous, inorganic rock matrix. Thus, pore development and mass transfer cannot depend as heavily on solvation of organic matter as in coal. Higher penetration and mass transfer properties are required for the solvent. Dispersal of oil shale inorganics into the extract is also to be avoided. As an example, liquid products of retorting processes are contaminated to varying extents with fine, inorganic particles produced during handling and retorting. The fines interfere with the refining and use of the products. Techniques which alleviate the problem would be useful.

Supercritical gas (SCG) extraction has possible advantages with respect to the above and has the potential to make the energy in oil shale available in more concentrated form than in conventional retorting. This is because of the high solvent extraction ability and solvent behavior of supercritical gases. SCG
extraction has been the subject of a number of recent studies. In the case of coal, simultaneous pyrolysis and extraction of pyrolysis products is effected at temperatures of around 350°C and 450°C. Extract yields in excess of 50% of the organic matter in coal and well in excess of volatile matter contents have been reported when chemically inert SCG solvents are used. The SCG extraction ability is due to near-liquid-density solvent power combined with gas phase mass transfer and penetration properties which inhibit coking reactions that produce char and gas. An outstanding characteristic of the coal extracts is the high molecular weight, a property not characteristic of matter which is simply volatilized from coal.

U.S. Patent No. 4,108,760 discloses extraction of kerogen and bitumen from oil shale or tar sands using a solvent under supercritical conditions. In the case of oil shale, considerable heat is applied to the shale before extraction is effected, and extraction is carried out at a temperature within the ranges of 350°C to 550°C, and preferably 370°C to 450°C. These temperatures are high enough to cause both depolymerization and cracking leading to char and gas, and they involve an unnecessary expenditure of heat. The temperature conditions practiced in this patent are close to the conditions practiced under standard retorting and offer no advantage thereover in terms of heat requirements while adding requirements for high pressure vessels. These conditions were utilized since they were believed necessary to provide useful extraction yields.

Statement of the Invention

It has now been discovered in accordance with the invention that useful extraction can be achieved
at temperatures below 450°C, such as 350°C to 425°C, and even at temperatures below 350°C, such as at 250°C to 325°C. Residual organic matter after extraction is about one-quarter that left during prototype commercial retorting and less gas and char are produced. These process advantages are achieved by the use of special solvents, particularly those having a Hildebrand solubility parameter differing by less than 1-2 Hildebrands from the solubility parameter for oil shale bitumen.

These and many other features and attendant advantages of the invention will become apparent as the invention becomes better understood by reference to the following detailed description when considered in conjunction with the accompanying drawings.

**Brief Description of the Drawing**

The Figure is a graph showing extraction efficiency versus temperature for toluene compared to single temperature results for pyridine and low density nitrogen.

**Description of the Invention**

Several descriptions of the kinetics of oil shale decomposition in inert atmospheres without solvent effects indicate oil shale can be characterized as two materials, kerogen and bitumen, the latter being benzene soluble. Thermal decomposition of the materials can be described by a kinetic mechanism making two consecutive first order reactions:

\[
\text{Kerogen} \xrightarrow{k_1} \text{Bitumen + Gas + Char} \quad (1)
\]

\[
\text{Bitumen} \xrightarrow{k_2} \text{Oil + Gas + Char} \quad (2)
\]

The temperature dependence of both rate constants is
available for the 400°C to 525°C range. Extrapolation of the very linear ln k versus 1/T (°K) dependence of k₁ into the 330° to 393°C range of interest should yield reasonably accurate k₁ values unless a change in the pyrolysis mechanism occurs over the range of the extrapolation. At 350°C, k₁ then equals $3 \times 10^{-3}$ sec⁻¹, and the corresponding first order half life of kerogen during conversion to bitumen would be 230 sec. Rapid and qualitative extraction of the organics in oil shale, even at temperatures of 350°C and below, can be expected with supercritical gases having the proper solvent properties.

Solvent theory is useful in determining the needed supercritical gas (SCG) properties. The theory of SCG extraction is currently approached by treating the dense gas either as a highly compressed gas or as an expanded liquid. It is clear that some success has occurred in predicting single-component solubilities in supercritical gases. However, application has not been made to highly complex hydrocarbon mixtures, such as oil and coal extracts. A useful alternative has been to extend the concept of solubility parameter, which is regularly used in understanding liquid solutions, to supercritical gases.

The solubility parameter concept, developed by Hildebrand and Scatchard is based on the concept of cohesive energy density and the well-tested precept that a correlation exists between cohesive energy density and the mutual solubility of substances. The solubility parameter is defined as:

$$\delta = (E/V)^{1/2}$$  (3)

where $\delta$ in Hildebrand's is $(\text{cal/cm}^3)^{1/2}$. $E$ is the energy required to convert one mole of a given substance from the state of interest to an infinitely expanded gas, the cohesive energy, and $V$ is the molar volume of the
substance in the state of interest. For present purposes E is taken as \(-\Delta H_{\text{vap}} - RT\). It has been shown that the free energy of mixing is minimized and complete miscibility occurs for non-polar liquids when the \(\delta\) of both solvent and solute are equal. Limited solubility occurs when \(\delta\) values diverge sufficiently. The concept has also been extended to solids and polar liquids. In addition, the theoretical evaluation of solubilities based on solubility parameters is developing.

The Van der Waals constant "a" from the equation of state for gases has been used to estimate solubility parameters for liquids, and the success has led to the derivation of the following relation for estimating \(\delta\) values for supercritical gases:

\[
\delta_g = \delta_l \left( \frac{d_g}{d_l} \right)
\]

(4)

where \(\delta_g\) and \(\delta_l\) are the solubility parameters of the gas and the room temperature liquid, and \(d_g\) and \(d_l\) are the densities of the gas and the room temperature liquid. This equation is currently used in the SCG research community. It indicates the solubility parameter of a supercritical gas (SCG) varies directly with density, and there is no provision for temperature. This is a direct result of the use of the Van der Waals equation for the derivation.

The solubility parameter of materials for which values of the cohesive energy and/or molar volume are unavailable, such as oil shale bitumen, can be estimated by using correlations between \(\delta\) and the refractive index. The following estimation is used:

\[
\delta = \left[ c \left( \frac{n^2 - 1}{n^2 + 2} \right) \right]^{0.5}
\]

(5)
where \( n \) is the refractive index and \( C \) is a constant representative of the chemical compound type. \( C \) ranges from a low of approximately 230 for branched aliphatic polymers to a high of 353 for aliphatic ester polymers. The average value of \( C \) over a broad range of compounds, including but not limited to polymers, is about 308. If it is assumed that the bitumen produced in this experiment has about the same elemental distribution as oil shale kerogen, namely \( C_{200H_{300}O_{50N_1}} \), then the material should contain a broad range of chemical functional groups, including large contributions from unsaturated and heteroatomic groups. This assumption is consistent with results from analyses of shale oil which show a rough distribution amounting to 11 wt% saturated hydrocarbons, 18% olefins, 10% aromatics, 36% nitrogen compounds, 6% sulfur compounds, and 19% oxygen compounds. The value of \( C \) used with Equation 5 for the oil shale bitumen is accordingly chosen as the broad range value of 308. The room temperature values for the refractive index of the bitumen and the oil extracted in this work are 1.62 to 1.53, and Equation 5 yields an average room temperature solubility parameter estimate for the compounds comprising the bitumen of 10.4 Hb. The value of 10.4 has been temperature corrected with the following relationship derived for polymeric materials:

\[
\delta_2 = \delta_1 \left[ \frac{d_2}{d_1} \right]^{1.13} \tag{6}
\]

where \( \delta_1 \) and \( \delta_2 \) are the solubility parameters at the reference temperature and the temperature of interest and \( d_1 \) and \( d_2 \) are the respective densities. Basing the density change of the bitumen between room and
experimentation temperatures on the volumetric expansion coefficient for petroleum at 100°C, namely about \(10^{-3}/\text{°C}\), yields estimates of the solubility parameter of the bitumen ranging from 7.7 Hb at 330°C to 7.3 Hb at 393°C. Using an average value of 7.5, the optimum solvents predicted by solubility parameter theory, as shown below, for use in the supercritical gas (SCG) extraction of oil shale in accordance with the invention would have solubility parameters ranging from about 6.0 to about 9.0 Hb, with limited temperature dependent solubility expected at the extremes of the range.

The theory used for prediction is as follows. In general, solubility or miscibility of two substances is to be expected if there is a decrease in the free energy of mixing, i.e.,

\[
\Delta F_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} < 0 \quad (7)
\]

in as much as the entropy of mixing, \(\Delta S_{\text{mix}}\), is always positive (i.e., \(-T \Delta S_{\text{mix}} < 0\)), the enthalpy of mixing, \(\Delta H_{\text{mix}}\), will virtually determine solubility. The latter for nonpolar and some polar substances is positive, and its magnitude is proportional to the square of the difference between the respective solubility parameters, \(\delta\), which are the square roots of the cohesive-energy densities:

\[
\Delta H_{\text{mix}} \approx V (\delta_1 - \delta_2)^2 \quad (8)
\]

The closer the solubility parameter values of the two substances, the smaller the \(\Delta H_{\text{mix}}\) will be; and the decrease in the free energy during mixing will be greater. The following approximation was obtained by Hildebrand and Scott for the condition of immiscibility:

\[
\Delta H_{\text{mix}} \approx V (\delta_1 - \delta_2)^2 > 2RT \quad (9)
\]

When an approximation is made for the effective molar volume of the solution, \(V\), by using the arithmetic mean
of the molar volumes of the pure substances, \( V_1 \) and \( V_2 \), the expression can be rearranged to yield:

\[
\frac{1}{2} \frac{(V_1 + V_2)(\delta_1 - \delta_2)^2}{RT} > 1 \quad (10)
\]

Let \( Q \) denote the left-hand side of equation (10). If \( Q \) is greater than 1 for a given pair of substances, then equation (10) is satisfied, and the substances are likely to be immiscible. Solubility over a limited range of concentrations, however, will still occur.

In the case of oil shale bitumen at 350°C with a solubility parameter of 7.5 Hb and a molar volume of about 1000 cc, equation 10 yields an estimated SCG solubility parameter ranging between 6.0 and 9.0 Hb for complete miscibility between the SCG and bitumen. Extractions outside this range would be expected to show limited and temperature-dependent bitumen solubilities. The values for the end of the complete miscibility range, however, are not exact, because of uncertainties associated with the values of the oil shale bitumen solubility parameter and molar volume. Extractions performed within but near the extremes of this calculated range might show limited and temperature-dependent bitumen solubilities.

The ratio of solvent to oil shale can be varied over broad ranges. The amount of oil shale can be 1 to 99% by weight of the total mixture of coal and solvent. Use of excess solvent provides increased extraction though it also requires considerable handling and separation effort to recover the extract and the solvent for recycle. Therefore, the amount of shale in the reactor is preferably from 10 to 60% of the total weight of shale plus solvent.
The process of the invention is capable of extracting fairly large lumps of shale and it is not believed to be necessary to subdivide and classify the shale below about 5 mesh before processing in accordance with the invention. The process can be practiced over fairly broad pressure ranging from 0.1 to 100 MPa, usually from 5 to 25 MPa. The process can be batch, with or without solvent recycle, or continuous. The oil shale can be restrained in a porous container or freely suspended in the supercritical gas (SCG) solvent suspended in a fluidized bed, or held by a grating arrangement.

Experiments follow:

Experiments were performed with a conventional, supercritical gas (SCG) extraction apparatus. The apparatus is a 300 cc stainless steel reactor with attendant gauging and controls. The oil shale, 8 grams of material with particle diameters ranging between 50 and 188 microns, was enclosed in a fine mesh stainless steel basket located near the top of the reactor and under a fluid circulating stirrer. Experimentation was performed by placing liquid solvent (approximately 150 grams) in the reactor bottom, inserting the extraction basket at the top of the reactor, and then heating reactor and contents to the chosen experimental temperature. The reactor was maintained at constant temperature for four hours and subsequently allowed to cool. Heat-up and cooldown times were both approximately 1 hour. Selected extracts were separated from the condensed SCG by vacuum distillation at 10 torr with a nitrogen flow assist. Raw and extracted shale were analyzed for carbon, hydrogen, and Kjeldahl nitrogen, and results were compared with analyses of raw shale (Table 1)
to derive values of the extraction efficiency of organic matter and H/C ratios of the extracts. It was assumed in these calculations that elemental oxygen and sulfur at a total of about 6 wt% were extracted with the same efficiency as the total efficiency in extracting C, H plus N. Extract molecular weights were determined by gel permeation liquid chromatography using detection by differential refractometry and with methylene chloride as solvent. Separate refractive indices of the bulk extracts were determined by dissolving the bitumens in carbon tetrachloride and extrapolating results to zero solvent content, or by direct determination in the case of the oil.

The results are compared in the Figure and in Table 1:
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temperature (°C)</th>
<th>Pressure (MPa)**</th>
<th>SCG Density (gm/cc)</th>
<th>TOC Removed (wt%)</th>
<th>SCG Solubility Parameter (Hb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene++</td>
<td>330</td>
<td>6.9</td>
<td>0.53</td>
<td>33.8</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>340</td>
<td>7.2</td>
<td>0.53</td>
<td>40.5</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>357</td>
<td>8.3</td>
<td>0.53</td>
<td>54.7</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>385</td>
<td>13.8</td>
<td>0.53</td>
<td>80.1</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>393</td>
<td>15.2</td>
<td>0.53</td>
<td>87.5</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>22.4</td>
<td>0.53</td>
<td>92.5</td>
<td>5.5</td>
</tr>
<tr>
<td>Pyridine++</td>
<td>363</td>
<td>7.6</td>
<td>0.55</td>
<td>63.3</td>
<td>6.0</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>385</td>
<td>0.21</td>
<td>0.0013</td>
<td>16.9</td>
<td>Nil</td>
</tr>
</tbody>
</table>

* Material Extracted: 12.9 wt% organic matter raw oil shale (21 gallon/ton) produced at Anvil Points, Colorado. Organic carbon and hydrogen contents: 10.3 and 1.53 wt%. Kjeldahl nitrogen content: 0.27 wt%.

** 0.101 MPa/Atm

+ Total organic matter

++ Critical parameters: toluene - 319°C, 4.11 MPa; pyridine - 347°C, 5.63 MPa
The data shows that at least 92% of the organic matter in oil shale can be extracted using a supercritical gas (SCG). Results (Figure 1 and Table 1) for toluene show an essentially linear temperature dependence for the percent of total organic matter extracted (extraction efficiency) in the range of 330°C to 393°C. A blank experiment at 385°C using pure low-density nitrogen at 0.21 MPa shows the difference between extraction with a dense gaseous solvent and simple volatilization without solvent effects. Toluene extracts at all temperatures except 450°C are bitumens with molecular weights ranging up to about two thousand. At 450°C the toluene extract is a shale oil with an average molecular weight of about 300. The H/C atom ratio of these extracts averages 1.65.

A comparison between the estimated solubility parameters of the bitumen and supercritical gas (SCG) solvent indicates the observed temperature dependence of the SCG toluene extractions is understandable. For SCG toluene at the 0.53 gm/cc density used, the estimated solubility parameter based on Equation 4 is 5.5, compared to the 7.3 to 7.7 previously estimated for the bitumen. As discussed, these δ values are sufficiently different to allow prediction of a temperature-dependent, limited solubility for the bitumen in supercritical toluene and prediction that greater solubility would occur with solubility parameters above 5.5. Extraction with pyridine at 363°C was performed to determine whether a higher solubility parameter indeed increases extraction. Comparison of results between extraction with toluene and pyridine is included in Figure 1 and Table 1. Extraction efficiency is improved as predicted and is increased by
about 1/6 with pyridine, which has an Equation 4 of 6.0 under experimental conditions. Both organic carbon and organic hydrogen extraction increase by the same amount with pyridine. Additionally, enhanced extraction at temperatures below 400°C is expected with SCG solvents having solubility parameters above 6.0, the minimum δ considered useful below 400°C. A value of 7.0 to 8.0 is considered optimal at temperatures of 400°C and below.

A way to understand how to most efficiently achieve an increased solubility parameter is to consider reduced variables (i.e., pressure, temperature, or density divided by critical pressure, critical temperature or critical density, respectively). Solubility parameters can be increased by increasing the SCG density of a specific compound or by using a different compound with a higher liquid phase solubility parameter (equation 4). In general, extraction with a solvent having a reduced density above around 1.5 results in such high absolute pressures that one normally chooses to start with a compound with a higher liquid phase solubility parameter. This decreases the required reduced density and attendant pressure. At the same time one usually chooses a solvent to match experimental temperatures such that the reduced temperature does not exceed about 1.5. Otherwise, excessively high pressure again results. At the limits of these two constraints the reduced pressure is about 6, corresponding to an absolute range covering roughly 3000 to 6000 psi. These practicalities are evident upon inspection of plots of reduced state, such as for CO₂ (but generalizable to other gases through the law of corresponding states). It is evident that minimizing pressure is important.
if this technology is to be used. However, these constraints might be slightly relaxed in favor of other practical criteria for solvent choice discussed below.

If these constraints are met, the number of compounds which are useful in producing SCG solubility parameters of 6.0 or higher is limited, particularly when certain additional practicalities are considered. The requirement for not exceeding a reduced temperature of 1.5, as an example, corresponds for a 250°C extraction to a requirement for compounds with critical temperatures above 75°C (if the reduced density exceeds 1.0, the lowest acceptable critical temperature might be increased to avoid excessive pressure). In addition, choosing the SCG reduced density to be 1.5 for the preferred example of a SCG solubility parameter between 7 and 8 Hb would require a liquid solubility parameter between 10.9 and 12.4 Hb. Allowing the SCG reduced density to be chosen from a range of values below 1.5 would result in a wider acceptable range of liquid solubility parameters consistent with the required SCG solubility parameter range. Thus, very high solubility parameter compounds, such as ammonia, sulfur dioxide and water, can be used by reducing sufficiently the SCG density.

The range of values for the liquid solubility parameter consistent with a SCG value ranging between 7 and 8 Hb (while maintaining a SCG reduced density equal to 1.5) is based on the following equation:

\[
10.7 \text{ Hb (minimum)} = \frac{(7.0 \text{ Hb}) (2.3)}{1.5} \]
\[
12.4 \text{ Hb (maximum)} = \frac{(8.0 \text{ Hb}) (2.3)}{1.5}
\]

where 2.3 is an approximation for the reduced density of any liquid and 1.5 is roughly the maximum acceptable reduced density of the SCG (as discussed above). As can be seen, reduced densities below 1.5 call for a higher liquid solubility parameter range.
Besides the solubility parameter requirements, the SCG chosen must meet certain practical considerations. The SCG must have acceptable thermal stability under the conditions of extraction (a significant consideration, since many high solubility parameter compounds will decompose, some violently, upon heating to several hundred degrees Centigrade). In addition, the compounds chosen must be available in large quantity and at low cost. Few substances meet all these criteria. Some of the compounds which are believed to meet the criteria for an SCG solubility parameter above 6.0 are listed in Table 2.
TABLE 2

COMPOUNDS POTENTIALLY MEETING SELECTION CRITERIA*

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>CRITICAL TEMPERATURE (°C)</th>
<th>LIQUID SOLUBILITY PARAMETER (Hb)</th>
<th>SCG REDUCED DENSITY ESTIMATED FOR A SCG SOLUBILITY PARAMETER OF 6.0 Hb OF 7.0 Hb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic Acid</td>
<td>321</td>
<td>13.1</td>
<td>1.05</td>
</tr>
<tr>
<td>Acetone</td>
<td>237</td>
<td>9.6</td>
<td>1.44</td>
</tr>
<tr>
<td>Ammonia</td>
<td>132</td>
<td>14.9</td>
<td>0.93</td>
</tr>
<tr>
<td>1,4 Butane diol</td>
<td>--</td>
<td>16.5</td>
<td>0.84</td>
</tr>
<tr>
<td>Benzene</td>
<td>289</td>
<td>9.2</td>
<td>1.5</td>
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<td>Carbon disulphide</td>
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<td>9.9</td>
<td>1.39</td>
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<tr>
<td>Ethanol</td>
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<td>12.8</td>
<td>1.08</td>
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<tr>
<td>Ethylene glycol</td>
<td>--</td>
<td>17.1</td>
<td>.81</td>
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<tr>
<td>Hydrogen cyanide</td>
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<td>1.15</td>
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<tr>
<td>Hydrogen sulphide</td>
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<td>13.3</td>
<td>1.04</td>
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<tr>
<td>Hydrazine</td>
<td>380</td>
<td>18.1</td>
<td>0.76</td>
</tr>
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</table>

*Thermal stability must be verified for specific extraction conditions.
<table>
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<tr>
<th>Substance</th>
<th>Value1</th>
<th>Value2</th>
<th>Value3</th>
<th>Value4</th>
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<td>Methanol</td>
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<tr>
<td>Methyl acetate</td>
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<td>1.45</td>
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<tr>
<td>Monoethanol amine</td>
<td>--</td>
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<td>0.89</td>
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<tr>
<td>1-3 Propane diol</td>
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<td>16.1</td>
<td>0.86</td>
<td>1.00</td>
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<tr>
<td>Propanol</td>
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<tr>
<td>Propylene glycol</td>
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<td>Pyridine</td>
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<tr>
<td>Sulfur dioxide</td>
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<td>14.7</td>
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<tr>
<td>Water</td>
<td>374</td>
<td>23.5</td>
<td>0.59</td>
<td>0.68</td>
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</table>
In general, compounds of use would have critical temperatures above 75°C (minimum extraction temperature 250°C) and liquid phase solubility parameters above 9.3 Hb (minimum SCG solubility parameter of 6.0). Distillation cuts from the SCG oil shale extract or other shale oils, distillates or extracts, from coal tars or bitumens, or from pyrolyzed biomass are expected to be useful SCG solvents so long as the collective solubility parameter and critical constants are near to or within the specified ranges. Other compound classes of particular interest are mono alcohols and thiols with 10 carbons or less, mono-carboxylic acids with 8 carbons or less and diols and triols with less than 8 carbons; aromatic compounds containing up to 10 carbons; alcohol-amines of up to 8 carbons, mono-amines of up to 5 carbons, diamines of up to 8 carbons, ketones of up to 4 carbons, esters of up to 10 carbons, and mixtures thereof. It is of course understood that the identity of the compound is incidental to the criteria established for critical constants and solubility parameter. Any compound meeting these criteria could be used since it is the physical criteria that establish utility.

Extraction above the critical temperature is not a requirement. An extraction system does not have to be at a temperature in excess of the critical temperature of the solvent for the density of the gas phase to be within the established criteria. However, in general, the reduced temperature should be greater than about 0.90 of the critical temperature of the solvent. Otherwise, the density of the gas phase will be too low to allow SCG solubility parameters above the approximate minimum 6.0 Hb, regardless of the solvent chosen.
The results demonstrate the powerful solvent properties of supercritical gases (SCG). Residual organic matter after extracting at 450°C is one-half that left by modified Fischer assay, and it is probably one-quarter or less of that which would be generated during prototype commercial retorting. In addition, the data shows organic matter removal occurring below 450°C can be greater than that found with prototype retorting. Higher solubility parameter solvents are expected to improve these results. Certain process advantages associated with the technique could occur; namely, those associated near quantitative removal of organic matter and with the presumably lower gas generation associated with lower temperatures and reduced char formation. In addition, the enhanced extraction efficiency and lower temperature of extraction may result in a residual char which contains lower concentrations of mutagenic substances than those found in conventionally produced oil shale char. This possibly would improve the ease of disposal of oil shale char.

It is to be realized that only preferred embodiments of the invention have been described and that numerous substitutions, modifications and alterations are permissible without departing from the spirit and scope of the invention as defined in the following claims.
OIL SHALE EXTRACTION USING SUPERCritical EXTRACTION

Significant improvement in oil shale extraction under supercritical conditions is provided by extracting the shale at a temperature below 400°C, such as from about 250°C to about 350°C, with a solvent having a Hildebrand solubility parameter within 1-2 Hb of the solubility parameter for oil shale bitumen.