SUPERCRITICAL GAS EXTRACTION OF OIL SHALE

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INTRODUCTION

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 commerical potential of all synfuels.

Oil shale retorting centers around heating the material, which is typically 85% rock, to about 480°C (900°F) or higher in a low oxygen environment (1). The kerogen and bitumen in the rock are decomposed into oil, gas, and a residual char which remains within the rock. Under favorable circumstances (laboratory analysis by modified Fischer assay) 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 (1,2). 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 (1,3), 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 (1). 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 (1), 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 (4) which occur when the char is burned. In short, the fuels are in dilute forms and the energy contents have low thermodynamic availability. This severly 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 salable byproducts.

The above characteristics of retorting are drawbacks, since energy in salable form is the only 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 salable energy to 1/3 to 1/2 below that contained in the raw oil shale. This is a technical problem contributing to an uncertain future for present schemes, and new technology could be useful.

Supercritical gas (SCG) extraction has the potential to make the energy in oil shale available in more concentrated form, because of the high solvent extraction ability of supercritical gases. SCG extraction has been the subject of a number of papers and reviews (5-8), and extensive study has been made of applications to coal (7-12). In the case of coal, simultaneous pyrolysis and extraction of pyrolysis products is effected at temperatures of around 350°C to 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 (12) 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 (8). An outstanding characteristic of the extracts is the high molecular weight (11), a property not characteristic of matter which is simply volatilized from coal. These results suggest that SCG extraction might be successfully applied to oil shale. In spite of the drawbacks associated with conventional oil shale retorting and the high SCG coal extraction results, description or discussion of SCG oil shale extraction is apparently absent from the literature, with the exception of a recent patent (13).

EXPERIMENTAL

Experimentation was performed with an apparatus similar to that described elsewhere (10). 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. This location eliminated any contact between liquid solvent and the oil shale. 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 cool-down 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 the H/C ratios of the extracts. It was assumed in these calculations that elemental constituents of oil shale organic matter other than C, H and Kjeldahl N [i.e., oxygen and sulfur at a total of about 6 wt% (1)] 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 for the oil.

RESULTS

This work shows that up to 92% of the organic matter in oil shale can be extracted using a supercritical gas. Results (Figure 1 and Table 1) show for toluene an essentially linear temperature dependence for the percent of total

organic matter extracted (extraction efficiency) in the range 330° to 393°C. A blank experiment at 385°C using pure nitrogen at 0.21MPa shows the difference between extraction with a dense gaseous solvent and a 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.

TABLE 1

Extraction Conditions and Results*

Solvent	Temperature (°C)	Pressure (MPa)**	SCG Density (gm/cc)	TOM† Removed (wt%)
Toluene††	330	6.9	0.53	33.8
	340	7.2	0.53	40.5
	357	8.3	0.53	54.7
	385	13.8	0.53	80.1
	393	15.2	0.53	87.5
	450	22.4	0.53	92.5
Pyridine††	363	7.6	0.55	63.3
Nitrogen	385	0.21	0.0013	16.9

* 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

DISCUSSION

The results demonstrate the powerful solvent properties of supercritical gases and provide incentive for further investigation of SCG oil shale extraction. 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 occuring below 450°C can be greater than that found with prototype retorting. Certain process advantages associated with the results could occur, namely those associated with near quantitative removal of organic matter and with the presumably lower gas generation associated with lower temperatures and reduced char formation.

The results are not optimized. Questions regarding temperature, solvent power, solute-solvent ratio, pressure, particle size, and the kinetics associated with reactions in the non-gaseous and SCG phases are open. A question of immediate interest involves the temperature dependence of the data in the 330° to 393°C range. Several descriptions of the kinetics describing oil shale decomposition in inert atmospheres without solvent effects have been published (2,14,15). The work indicates oil shale organic matter 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 involving two consecutive first order reactions:

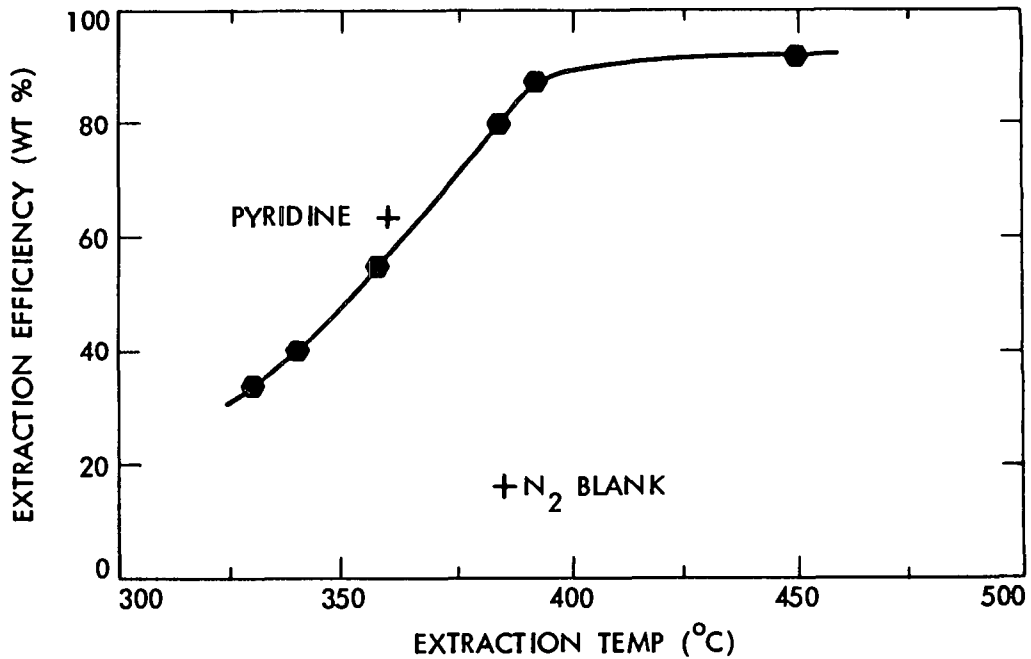

Figure 1. Extraction Efficiency vs. Temperature for Toluene, Compared with Single Temperature Results for Pyridine and Low Density Nitrogen.

$$\text{Kerogen} \xrightarrow{k_1} \text{Bitumen} + \text{Gas} + \text{Char} \qquad 1)$$

$$\text{Bitumen} \xrightarrow{k_2} \text{Oil} + \text{Gas} + \text{Char} \qquad 2)$$

The temperature dependence of both rate constants is available for the 400°C to 525°C range (15). Extrapolation of the very linear ln k versus 1/T (°K) dependence of k_1 into the 330° to 393°C range of interest should yield reasonably accurate k_1 values unless a change in the pyrolysis mechanism occurs over the range of the extrapolation. At 350°, k_1 then equals 3×10^{-3} sec^{-1}, and the corresponding first order half life of kerogen during conversion to bitumen would be 230 sec. Extraction times in this work were approximately 10^4 sec at constant temperature, and the observed temperature dependent extraction yield is not predictable if the indicated kinetics are applicable to these SCG experiments. A temperature dependent SCG extraction mechanism could be present.

Solvent theory is useful in examining this possibility. The theory of SCG extraction is currently approached by treating the dense gas either as a highly compressed gas or as an expanded liquid. The subject has been reviewed recently (5), and 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 (17) and Scatchard (18), 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:

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

where δ is in $(cal/cm^3)^{1/2}$, 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. It has been shown that the free energy of mixing is minimized and complete miscibility occurs for non-polar liquids when the δ of both solvent and solute are equal. Limited solubility occurs when δ 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 (19).

The Van der Waals constant "a" from the equation of state for gases has been used to estimate solubility parameters for liquids (17), and the success has led to the derivation of the following relation for estimating δ values for supercritical gases (20):

$$\delta_g \cong \delta_l (d_g/d_l) \qquad 4)$$

where δ_g and δ_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. The equation indicates the solubility parameter of a 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 in 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 δ and the refractive index (21). The following estimation is used:

$$\delta = \left[C \left(\frac{n^2 - 1}{n^2 + 2} \right) \right]^{0.5} \qquad 5)$$

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 experimentation has about the same atomic makeup as oil shale kerogen, namely $C_{200}H_{300}SN_5O_{11}$ (22), 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 (23). 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 and 1.59, and Equation 5 yields an average room temperature solubility parameter estimate for the compounds comprising the bitumen of 10.4. A somewhat higher value can be derived from a correlation based on the Lorentz-Lorenz function (21). The value of 10.4 has been temperature corrected with the following relationship derived for polymeric materials (24):

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

where δ_1 and δ_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 10^{-3}/°C, yields estimates of the solubility parameter of the bitumen ranging from 7.7 at 330°C to 7.3 at 393°C.

A comparison between the estimated solubility parameters of the bitumen and supercritical gas solvents can now be made to determine if a temperature dependent extraction could be expected. 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 estimated for the bitumen. In normal practice these δ values should be sufficiently different to allow prediction of a temperature-dependent, limited solubility for the bitumen in supercritical toluene. A higher δ SCG might be needed to eliminate temperature dependent extraction effects and increase the overall extraction efficiency at temperatures below 400°C.

Extraction with pyridine at 363°C was performed to test this possibility, and a comparison of results between extraction with toluene and pyridine is included in Figure 1 and Table 1. Extraction efficiency is increased by about 1/6 with pyridine, which has an Equation 4 δ of 6.0 under experimental conditions. This single result needs confirmation. However, both organic carbon and organic hydrogen extraction increase by the same amount with pyridine, and it is concluded that

experimentation with yet a higher solubility parameter SCG might result in additionally enhanced extraction at temperatures below 400°C. Results above 400°C might also be improved, but there is little practical incentive, because of the high extraction efficiency already found.

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