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**Research Investigations in Oil Shale, Tar Sand,
Coal Research, Advanced Exploratory Process
Technology, and Advanced Fuels Research
Volume I -- Base Program**

**Final Report
October 1986 - September 1993**

Verne E. Smith

May 1994

Work Performed Under Contract No.: DE-FC21-86MC11076

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
University of Wyoming Research Corporation
Laramie, Wyoming

MASTER

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**RESEARCH INVESTIGATIONS IN OIL SHALE, TAR SAND, COAL
RESEARCH, ADVANCED EXPLORATORY PROCESS TECHNOLOGY,
AND ADVANCED FUELS RESEARCH
VOLUME I -- BASE PROGRAM**

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Western Research Institute
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FOREWORD

This report summarizes the major research investigations conducted by the Western Research Institute under Cooperative Agreement DE-FC21-86MC11076 with the U.S. Department of Energy (DOE) over the period October 1986 through September 1993. In 1989 a Jointly Sponsored Research Program (JSRP) was incorporated into the agreement whereby some of the investigations were conducted as part of the Base Program and some were undertaken with cosponsorship from the commercial sector or other government agencies in the JSRP.

This report is divided into two volumes: Volume I consists of 28 summaries that describe the principal research efforts conducted under the Base Program in five topic areas. Volume II describes tasks performed within the JSRP. Research conducted under this agreement has resulted in technology transfer of a variety of energy-related research information. A listing of related publications and presentations is given at the end of each research topic summary. More specific and detailed information is provided in the topical reports referenced in the related publications listings.

ACKNOWLEDGEMENTS

Funding for this research has been provided under U.S. Department of Energy Cooperative Agreement DE-FC21-86MC11076 and by numerous JSRP cosponsors. In addition to the efforts of the authors who prepared the topic summaries, the considerable efforts of the many researchers and support people at WRI who provided essential assistance in the design, conduct, and reporting of the work are greatly appreciated. Special thanks is due the individuals in DOE who have provided input and direction to the research studies and for their review and comments on completed studies.

EXECUTIVE SUMMARY

Numerous studies have been conducted under Cooperative Agreement DE-FC21-86MC11076 since its initiation in October 1986. Program direction at that time was broken into five principal areas: oil shale, tar sand, underground coal gasification, advanced process technology, and advanced fuels research. In subsequent years, research emphasis changed in accordance with changes in the mission of DOE. As an example, underground coal gasification was broadened to be coal research, under which several research activities were conducted that related to coal processing.

The most significant change occurred in 1989 when the agreement was redefined as a Base Program and a Jointly Sponsored Research Program (JSRP). Research topics within the Base Program continued in the same areas, with an emphasis given to exploratory research that might lead to further development under the JSRP.

Investigations were conducted under the Base Program to determine the physical and chemical properties of materials suitable for conversion to liquid and gaseous fuels, to test and evaluate processes and innovative concepts for such conversions, to monitor and determine environmental impacts related to development of commercial-sized operations, and to evaluate methods for mitigation of potential environmental impacts.

In some of the most carefully controlled experiments ever done on the thermal decomposition of oil shale to oil, gas, and residue products, it was determined that a significant fraction of the kerogen in western oil shales is converted to an intermediate bitumen, whereas only a small portion of the kerogen was converted to bitumen in eastern oil shale. The maximum amount of extractable bitumen was found to increase with temperature and heating rate. In the characterization of reference oil shales it was found that the combination of nuclear magnetic resonance (NMR) measurements with material balance Fischer Assay data provides an indication of undesired coke formation. This basic information is of importance to the development and optimization of process systems.

The most commercially viable use for shale oil in the present market is as an additive to petroleum asphalt for paving applications, for which WRI holds a patent. In a study of other such applications, western shale oil was found to provide improved physical properties when used as an asphalt recycling agent. When used for crack and joint sealant the asphalt sealant was improved, but the material was not as good as more expensive, rubber-modified sealants.

Extensive organic and inorganic characterization was done on retorted oil shale that resulted in useful information for waste management planning for disposal of spent shale. Similarly, studies on ion speciation of materials in process waters and leachates have advanced the methods for measurement of chemical species of environmental concern related to fossil fuel processes.

Because oil shale products are not competitive as transportation fuel in the present market, alternative uses were evaluated. A viable market does exist for shale oil as an additive to petroleum asphalt for paving applications. Economic evaluation of a small commercial operation indicates that the return on investment would be in the 18 to 26% range.

Process studies were conducted on several tar sand resources. One-dimensional and three-dimensional tests were run to simulate in situ combustion processes. The problem of plugging was overcome in an extremely heavy tar sand by using steam-oxygen combustion. The different results obtained for different resources indicates that accurate extrapolations of process results cannot be made between resources.

WRI has developed the Recycle Oil Pyrolysis and Extraction (ROPETM) process, for which one of the applications is to tar sand. Two long-term tests were conducted to evaluate steady-state process conditions. These conditions were reached within 2 days when the starting recycle oil was from the material being processed. Oil yields slightly greater than Fischer Assay were obtained. Also, an inclined liquid fluid-bed reactor was constructed and tested for the ROPE process. Some problems were encountered that could be resolved with modifications to the system.

Some of the oils produced in tar sand process tests were evaluated for their potential end use. Distillate from an oil from an Asphalt Ridge (Utah) tar sand that was produced by a forward combustion process was found to be potentially suitable for use as high-density or endothermic aviation fuel. The residue oil is suitable for use as an asphalt. Processed distillates of oil from a California tar sand were found to be suitable diesel fuels.

WRI participated in an underground coal gasification demonstration project that was primarily funded and directed by the Gas Research Institute and other DOE sources. Subsequent to the burn operations, WRI injected steam into the cavities to vent, flush, and cool them. This was followed by two pumping and treatment operations. The venting and flushing was effective in controlling and containing contaminants. The pumping and treatment operations were effective in restoring groundwater quality, as was observed in the groundwater monitoring that was conducted for the 5 years after the test burn.

A process called COMPCOALTM has been developed to produce a premium-quality, solid fuel from low-rank coal. Tests run with the process have shown that pitch can be deposited on char produced by drying and mild gasification of the coal, resulting in a product that is dry, contains less dust, and is less susceptible to reabsorption of moisture.

Enhancement of liquid yields from coal hydroprocessing was investigated using an integrated approach applying coal drying and coprocessing, followed by hydroprocessing. Coal was dried in an inclined fluidized-bed dryer and immediately immersed in an oil bath composed of a coal derived liquid. The resulting coal slurry was subjected to coprocessing in an inclined-screw pyrolysis reactor. The product from coprocessing was hydroprocessed in tubing bombs to determine the liquid yield. These investigations used an Illinois No. 6 coal (Herrin No. 6), a Pittsburgh No. 8 coal, and a coal-derived liquid from mild gasification of Powder River Basin coal. The drying stage had only a small effect on the fixed carbon, but the coprocessing stage significantly increased the fixed carbon in the solid product. Coprocessing of the coals decreased the yield of liquid products from hydroprocessing of the solid product as compared to coals that were only dried.

An investigation was conducted to evaluate coal pretreatment prior to hydroprocessing, characterize coke deposits on supported catalysts after coal liquefaction, and evaluate modes of hydrogen utilization during coal liquefaction. The coal pretreatment studies were based on evaluating solvent induced swelling and low-temperature hydrogenation as pretreatment methods. The effectiveness of the pretreatment was measured by changes in liquid product yield from hydroprocessing the coal with Lloydminster crude oil. A significant increase in product was observed from pretreatment of Powder River Basin coal than from Illinois No. 6 coal. Coke deposited on supported catalysts after exposure to coal liquefaction was characterized by ¹³C solid-state NMR. A linear relationship was identified between the catalyst pore volume and the size of the aromatic cluster of the coke using this technique. Solid-state and liquid-state NMR techniques were on samples from selected coal liquefaction tests to evaluate hydrogen utilization. Results from these measurements on one of the test materials indicated about 13% of the aromatic carbons in Illinois No. 6 coal was hydrogenated, and gas production accounted for 90% of the hydrogen consumption during the test.

In advanced exploratory research, the technical and economic feasibility of using oil shale as a sulfur sorbent in power plant coal combustion was studied. Oil shale does adequately reduce sulfur in coal combustion emissions and also provides energy from the kerogen. Depending on the mining and delivery costs for oil shale and the type of coal used, oil shale can be more economical to use than limestone.

Studies on the mathematical modeling of petroleum reservoirs (1) developed an improved method for determining well-block pressure and (2) extended the capabilities of WRI's mathematical thermal reservoir simulator to field-scale applications.

The Contained Recovery of Oily Wastes (CROWTM) process developed by WRI promises to be applicable to a number of environmental mitigation problems (see Volume II for descriptions of field demonstrations.) A study was conducted to evaluate the effectiveness of using chemicals, primarily surfactants, to enhance the removal of organic materials from soils. The addition of chemicals was found to be effective, especially in sandy soils.

An examination and evaluation of possible chemical additives for steamflooding applications to petroleum reservoirs found that a surfactant was more effective than selected polymers. Three-dimensional testing of the surfactant indicated that sufficient velocity of the steam and water volume in the steam are essential to the additive's effectiveness.

A problem related to the economical removal of nitrogen from natural gas by pressure swing adsorption is the regeneration of the adsorbent. A study was done to determine if microwave energy could be used to regenerate a zeolite adsorbent and improve the desorption phase of the process. It was determined that it is possible to do the regeneration, but there is excessive heating of the adsorbent. Using microwave energy for desorption may prove useful where minimal dilution is necessary.

The purpose of the advanced fuels research was to determine the feasibility of producing intermediates in the production of high-density aviation turbine fuel from western and eastern shale oil and a coal-derived liquid. The processes evaluated included acid-base extraction, solvent dewaxing, Attapulugus clay treatment, coking, and hydrogenation. Only Attapulugus clay treatment and hydrogenation of the middle distillate from western shale oil produced intermediates that were evaluated for the production of high-density turbine fuel. However, the intermediates from both processes contained excessive amounts of alkanes. It was concluded that because of the paraffinic nature of western shale oil, it would be quite difficult or expensive to use it as a feedstock for the production of a high-density aviation turbine fuel. None of the five processes investigated produced intermediates from the eastern shale oil and coal-derived liquid that were suitable for further evaluation as a high-density turbine fuel. Single-stage hydrogenation of the distillates resulted in process intermediates that still contained significant amounts of aromatics and olefins. It was determined that the aromatics were composed of high concentrations of indanes/tetralins. However, hydrogenation of these species to dicyclic alkanes results in a class of compounds that are necessary for the production of high-density turbine fuel. Consequently, it is believed that a process that includes two-stage hydrogenation can be employed to produce a high-density turbine fuel from these two fossil fuels that would meet the requirements of the U.S. Air Force.

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OIL SHALE

KEROGEN DECOMPOSITION

Francis P. Miknis

Background

The kerogen in oil shales exists in a variety of structural assemblages, so that understanding the chemistry of kerogen decomposition requires investigations of the thermal decomposition of several different types of kerogens. Eastern U.S. oil shales have a more aromatic kerogen structure than western U.S. oil shales and produce about half as much liquid product during pyrolysis compared to western oil shales. Therefore, understanding the chemistry of pyrolysis of these aromatic shales is an important factor for the development of general chemical kinetics models of kerogen decomposition.

A common feature of oil shale decomposition models is the bitumen intermediate. Although bitumen is usually considered an important intermediate in kerogen decomposition, its chemical and physical properties have not been thoroughly investigated. Therefore, the role of a bitumen intermediate in oil shale decomposition is not satisfactorily understood. Eastern Devonian and Mississippian shales have a more aromatic kerogen structure than do the Tertiary oil shales from the Green River Formation. Little attention has been paid to whether the bitumen is a significant reaction intermediate in the pyrolysis of these more aromatic shales.

Objective

The objective of this research effort was to explore the chemistry of kerogen thermal decomposition in relationship to kerogen structure. Since the kerogen in oil shales exists in a variety of structural assemblages, understanding the chemistry of kerogen pyrolysis requires investigations of the pyrolysis kinetics of several different types of kerogens. Knowing the chemistry of the pyrolysis of shales having different aromatic and aliphatic carbon distributions is necessary for the development of a

general chemical kinetics model of kerogen decomposition. Also, by understanding these relationships it may be possible to improve the efficiency of the conversion processes or to develop novel approaches for greater conversion of kerogen to oil.

Procedures

The oil shales investigated in this study were a New Albany oil shale (Clegg Creek Member) from Bullitt County, Kentucky, a Mahogany zone (Parachute Creek Member) Green River Formation shale from the Exxon Colony mine in Colorado, and a Tipton Member, Green River Formation oil shale from an outcrop near Rock Springs, Wyoming. These shales have been designated as reference shales in the U.S. Department of Energy (DOE) oil shale research program.

The shales were crushed to pass a 20-mesh (841 μ) screen and the 20-45-mesh (841 μ -354 μ) fraction was separated for decomposition studies. An initial 1500-g fraction of each shale was thoroughly mixed and was then split eight ways in two stages to yield 64 samples each weighing about 22 g. Twenty-gram samples were weighed from these for kinetic measurements.

A heated sand-bath reactor system was used for the isothermal decomposition experiments. This system gave rapid heat-up and reliable temperature control. Typically, 20-g samples were used so that sufficient products were generated for other analyses such as nuclear magnetic resonance (NMR), elemental analysis, and molecular weights. The isothermal experiments were conducted in the temperature range of 375 to 425°C (707 to 797°F).

Quenched nonisothermal pyrolysis experiments were conducted at heating rates of 2 and 10°C/min to 500°C (932°F) on a Cahn 131 thermogravimetric analyzer.

Results

The temperature dependence of the bitumen is shown in Figure 1. The data show that in the temperature range of 375 to 425°C (707 to 797°F), the maximum amount of extractable bitumen from the Kentucky New Albany shale is about 14% of the original kerogen (425°C [797°F] data). However, the Colorado and Wyoming oil shales show greater amounts of extractable bitumen, reaching maximum values between 40 and 60% at 425°C (797°F). The lower maximum value at 440°C (824°F) for the Exxon-Colony is probably due to experimental constraints that prevent rapid heating and quenching of the shale in a time sufficiently short to observe the maximum value at this temperature. The differences in carbon structure and conversion to oil between the shales suggest that bitumen formation may be a function of the original kerogen structure (i.e., the more aliphatic the oil shale, the

more bitumen that is formed during pyrolysis). The maximum value of the bitumen increases with temperature. The implication of this observation is that the activation energy of kerogen decomposition is greater than the activation energy of bitumen decomposition.

A reasonable explanation for the low bitumen yields of the New Albany shale is that direct kerogen conversion to residue, oil, and gas competes with bitumen formation. Because the overall carbon conversion of the New Albany shale is about 35 and 56% to oil and residue, respectively, during Fischer assay, direct residue formation appears to be a major pathway for kerogen decomposition in this shale. It is also possible that for the New Albany shale, given the high aromatic carbon content, a certain portion of the original kerogen resembles a residue product.

Figure 1. Time and Temperature Dependence of Bitumen

A significant finding from the 425°C (797°F) liquid product data for the western oil shales is that maxima in the oil plus bitumen curves are obtained. By quenching the reaction at the time of the maximum (~30 minutes), 85 to 95% of the carbon in the kerogen is recoverable as soluble products. For longer times, lesser amounts of soluble products are recoverable due to coking of the bitumen. Ultimately, the liquid yields will be that of the oil only, since the bitumen will have decomposed to form oil, gas, and residue products.

The behavior of the bitumen and kerogen under nonisothermal heating supported the notion that the activation energy of kerogen decomposition is greater than the activation energy of bitumen decomposition.

Hydrogen-to-carbon (H/C) ratios and molecular weights were determined for the oils and bitumens produced from isothermal decomposition of the Colorado Exxon and Kentucky New Albany oil shales. For the shale oils, the H/C ratios and molecular weights were remarkably constant at all times and temperatures for each type of shale oil.

Chemical property measurements of the bitumen were limited by the small amounts of bitumen extracted from the 20-g samples of shale. This was especially true for the Kentucky oil shale in which little bitumen was extracted throughout the decomposition, and for the Colorado oil shale at longer reaction times where little bitumen remained. In general, the composition and properties of the bitumen changed during the course of the reaction. This was most evident from the molecular weight data which showed that the bitumen molecular weight passed through a maximum during the decomposition.

Conclusions

Isothermal pyrolysis studies found that the maximum amount of extractable bitumen in the New Albany shale was 14% or less of the original kerogen at any given temperature, indicating that direct

conversion of kerogen to oil, gas, and residue products was a major pathway of conversion of this shale during pyrolysis. In contrast, significant fractions of the Colorado and Wyoming oil shale kerogens were converted to the intermediate bitumen during pyrolysis. The bitumen data indicate that the formation of soluble intermediates may depend on original kerogen structure and may be necessary for producing high yields by pyrolysis.

The H/C ratios and molecular weights of the produced oils from both shales were constant at all times and temperatures. However, the bitumen showed decreasing H/C ratios and exhibited variable molecular weights with time and temperature, demonstrating the variable composition of this material during pyrolysis.

Quenched nonisothermal pyrolysis studies were conducted on two western reference oil shales. The conversion of kerogen to bitumen and volatiles (oil and gas) was obtained for heating rates of 2 and 10 °C/min in the range of 300 to 500°C (572 to 932 °F) using a modified thermogravimetric analyzer. Particular attention was paid to the formation of the intermediate bitumen during decomposition of the shale.

The maximum amount of extractable bitumen increases with temperature and with heating rate. These observations are consistent with an oil shale decomposition model in which the activation energy for kerogen decomposition is greater than the activation energy of bitumen decomposition.

Related Publications and Presentations

Publications

Chong, S.-L., F.P. Miknis, X. Zhao, and S.A. Holmes, 1989, Characteristics of Pyrobitumen and Oil Obtained from the Pyrolysis of Tipton Member, Green River Oil Shale. ACS Div. of Petrol. Chemistry Preprints, 34(1): 71-75.

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S.-L. Chong, F.P. Miknis, X. Zhao and S.A. Holmes, 1989, Characteristics of Pyrobitumen and Oil Obtained from the Pyrolysis of Tipton Member Green River Formation Oil Shale. ACS Symposium on Comparative Studies of Various Oil Shales, Dallas, TX.

F.P. Miknis, 1988, Thermal Decomposition of DOE Reference Shale. Third Annual Oil Shale, Tar Sand, and Mild Gasification Contractor's Review Meeting, Morgantown, WV.

F.P. Miknis, 1991, Solid State ^{13}C NMR in Oil Shale and Coal Research. Government Industrial Development Laboratory, Sapporo, Japan, and National Chemical Laboratory for Industry, Tsukuba, Japan, (invited lectures).

F.P. Miknis, T.F. Turner, and L.W. Ennen, 1987, Thermal Behavior of Bitumen Produced from Isothermal Decomposition of Colorado and Kentucky Oil Shale. 1987 Eastern Oil Shale Symposium, Lexington, KY.

F.P. Miknis, T.F. Turner and R.R. Glaser, 1989, Thermal Decomposition of DOE Reference Oil Shales. ACS Symposium on Comparative Studies of Various Oil Shales, Dallas, TX.

T.F. Turner, F.P. Miknis, G.L. Berdan, and P.J. Conn, 1987, A Comparison of the Thermal Decomposition of Colorado and Kentucky Oil Shale. ACS National Meeting, Symposium on Advances in Oil Shale Chemistry, Denver, CO.

CHARACTERIZATION OF REFERENCE OIL SHALES

Francis P. Miknis

Background

In 1984, DOE made an assessment of its oil shale program based on information from industry, the Fossil Energy Research Working Group, a National Research Council review of safety issues related to synthetic fuels development, a review of available oil shale data, and an examination of the existing DOE oil shale program. This led to a restructuring of the DOE oil shale program. An integral part of the restructured program involved the measurement of fundamental chemical and physical properties of reference oil shales.

Under the DOE reference shale program, two oil shales per year were to have been acquired and characterized over a 5-year period. A total of ten oil shales were to have been acquired; five from the western United States deposits, and five from deposits in the eastern United States. The shales selected were to be as representative as possible of what may likely be used in future oil shale development.

Fundamental chemical and physical properties were acquired on two western and one eastern reference oil shale during the period of this Cooperative Agreement. The reference shale program was discontinued in 1990.

Objectives

The objectives of this research activity were to define the fundamental characteristics of oil shales selected by DOE for research conducted within the oil shale program. The reference shales were to be analyzed to provide data on the chemical and physical properties of oil shales and their products. This information could then be used to better understand the reaction chemistry and transport processes in retorting and environmental systems.

Procedures

The two western reference shales that were studied included a Mahogany zone, Parachute Creek Member, Green River Formation oil shale obtained from the Exxon Colony mine located near Parachute, Colorado and a Tipton Member, Green River Formation oil shale obtained from an outcrop near Rock Springs, Wyoming. The eastern reference shale was a Clegg Creek Member, New Albany shale obtained from the Knieriem quarry, which is located approximately 16 miles south of the Ohio River at Louisville, Kentucky.

The measurements that were made on the reference shales are listed in Table 1. The procedures are described in detail in the report by Miknis and Robertson (1987).

Results

Material Balance Fischer Assay (MBFA) results for the reference shales are presented in Table 2. The conversion of organic carbon to oil, gas, and residue carbon is given in Table 3. The greater conversion of organic carbon to oil for the western reference shale is clearly evident from the data in Table 3. The differences in conversion of organic carbon to oil, gas, and residue products are related to the carbon structure of the original organic material.

Solid-state ^{13}C nuclear magnetic resonance (NMR) measurements were made on the reference shale and liquid-state ^{13}C NMR measurement were made on the MBFA shale oils (Table 4). The carbon aromaticity values of the shales are compatible with the conversion data in Table 3.

Gross heating values were determined on the reference shales using a standard ASTM procedure (D 3286). The results are

reported in Table 4. Measurements were made on the raw shales and the spent shales from the MBFA tests. The heating value of the spent shale is greater for the eastern shale because of the greater residue carbon on the spent shale.

Eastern reference shales are dominated by silicate minerals, especially clay minerals and quartz; while western reference shales contain both carbonate and silicate minerals in moderate abundances. In the western reference shales, clay minerals constitute only a minor fraction of the total mineral assemblage, whereas clay minerals contained in the eastern reference shales are abundant and diverse in type.

The trace element data reaffirmed previous observations that all the elements of interest remain in the spent shale. Differences in the major trace element data between the shales reflected their differences in mineralogy.

ASTM D 86, D 1160, and D 2892 distillations were performed on the eastern and western shale oils. The distillation mid-point data for each cut of the ASTM D 2892 (True Boiling Point) distillations were observed to correlate quite well with the D 86 distillation end-point data over the temperature range where both the D 2892 and D 86 distillations proceeded. However, the eastern shale oil distilled at approximately 24°C (100°F) lower by the D-86 Method than by the D-2892 Method.

Table 1. Chemical and Physical Property Measurements on Reference Shales and Products

	Raw Shale	Retorted Shale	Shale Oil	Kerogen Concentrates
Material balance Fischer assay	X			
Carbon, hydrogen, nitrogen, sulfur	X	X	X	X
Pyritic sulfur	X			X
Mineral carbon	X	X		
Carbon aromaticity	X		X	X
Hydrogen aromaticity			X	
Oxygen	X	X	X	X
Trace metals	X	X	X	
Compound class separation			X	
Bulk mineralogy	X	X		
Clay content	X	X		
Molecular weight (average)			X	
Heat capacity	X	X	X	
Heat of retorting	X			
Heat of mineral dehydration	X			
ASTM D 86 distillation			X	
ASTM D 1160 distillation			X	
True boiling point distillation			X	
Specific gravity			X	
Viscosity			X	
Pour point			X	

Table 2. Material Balance Fischer Assay Results for Reference Shales

Product	wt %	Gal/ton	% Ash	Mineral Carbon wt %	C wt %	H wt %	N wt %	S wt %
<u>Colorado Reference Oil Shale</u>								
Oil	10.24	27.50	—	—	83.2	12.2	1.7	0.7
Gas	4.60	—	—	—	41.4	7.0	—	4.8
Spent shale	83.50	—	78.63	4.9	8.8	0.2	0.5	1.1
Water	1.62	3.88	—	—	—	11.1	—	—
Raw shale	100.00	—	66.90	4.2	18.0	1.9	0.6	1.3
% Recovery	99.96	—	98.14	97.42	98.8	101.4	89.7	94.1
<u>Kentucky Reference Oil Shale</u>								
Oil	5.67	14.38	—	—	84.5	10.6	1.2	1.6
Gas	3.16	—	—	—	39.5	12.4	—	40.5
Spent shale	89.54	—	87.12	0.22	8.7	0.4	0.9	4.5
Water	1.20	2.87	—	—	—	11.1	—	—
Raw shale	100.00	—	78.38	0.25	13.9	1.4	0.4	5.8
% Recovery	99.57	—	99.52	78.8	99.7	104.9	114.1	92.6
<u>Wyoming Reference Oil Shale</u>								
Oil	8.84	22.03	—	—	81.6	10.9	2.1	0.5
Gas	2.09	—	—	—	42.9	9.1	—	0.1
Spent shale	85.96	—	81.33	3.7	7.7	0.3	0.5	0.4
Water	3.15	7.56	—	—	—	11.1	—	—
Raw shale	100.00	—	71.23	3.4	14.97	1.4	0.6	0.4
% Recovery	100.04	—	98.15	93.50	98.40	129.0	102.60	97.5

Table 3. Organic Carbon Conversion in Reference Shales

Product	% Conversion		
	Colorado	Wyoming	Kentucky
Oil	61.7	62.4	35.1
Gas	13.8	7.8	9.1
Residue	23.7	29.8	55.8

Table 4. Other Properties of Oil Shale and Shale Oil

Property	Colorado	Wyoming	Kentucky
<u>Heating Value, Btu/lb</u>			
Raw shale	2,607	1,730	2,859
Spent shale	370	140	1,587
Shale oil	18,650	17,630	18,100
Molecular weight - Shale oil	295	290	275
Carbon aromaticity			
Raw shale	0.259	0.330	0.450
Shale oil	0.236	0.259	0.420
Proton aromaticity			
Shale oil	0.043	0.062	0.110

The conversion behavior of 10 oil shales from seven foreign and three domestic deposits was also studied by combining solid- and liquid-state NMR measurements with MBFA conversion data. The extent of aromatization of aliphatic carbons was determined. Between zero and 42% of the raw shale aliphatic carbon formed aromatic carbon during Fischer assay. For three of the shales, there was more aromatic carbon in the residue after Fischer assay than in the raw shale. Between 10 and 20% of the raw shale aliphatic carbons ended up as aliphatic carbons on the spent shale. Good correlations were found between the raw shale aliphatic carbon and carbon in the oil and between the raw shale aromatic carbon and aromatic carbon on the spent shale. Simulated distillations and molecular weight determinations were performed on the shale oils. Greater than 50% of the oil consisted of the atmospheric and vacuum gas oil boiling fractions.

Conclusions

The properties of the reference shales are comparable to the properties of other

western and eastern oil shales. Western oil shales from the Green River Formation typically have high conversions to oil because of their low carbon aromaticities and hydrogen richness. Eastern oil shales have low conversion to oil because of their higher carbon aromaticity and low hydrogen content.

Carbon-containing minerals dominate the mineralogy of the western oil shale, while silicates and clay minerals are predominant in the eastern reference shale. These minerals are indicative of the lacustrine and near shore to shallow marine depositional environments of the western and eastern shales, respectively.

Standard API and other published correlations do not appear to be adequate for predicting properties of shale oils. Poor agreement was obtained between calculated and measured molecular weights. Consequently, calculated properties that make use of molecular weight data, such as solubility parameters, would be expected to be in disagreement with measured results.

The combination of NMR measurements with MBFA data provides a method whereby the extent of aromatization reactions can be determined. Because these reactions are precursors to coke formation, this information can be important for process optimization. Aromatization reactions were shown to be most important in those oil shales having the lowest Fischer assay conversions to oil.

Related Publications and Presentations

Publications

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SHALE OIL RESIDUA FOR PAVING APPLICATIONS

P. Michael Harnsberger

Background

Shale oil has been used in road surfacing applications for several decades. Originally, these materials were probably used for dust control on mine roads as a way to dispose of the heavier, less-desirable fractions of shale oil similar to the way cut-back asphalts were used during the same time period. However, there has not been a great interest in using shale oil materials in paving applications (Plancher and Petersen 1984) until the last decade. During the early 1980s the work in this area resulted in a DOE patent by Plancher and Petersen (1982), licensed to Western Research Institute (WRI), using shale oil residua materials in asphalt paving applications to reduce moisture damage.

The several studies reported here investigated other uses and materials derived from shale oil residua, both eastern and western, that may be useful in the asphalt and asphalt paving industry. The studies examined using eastern and western shale oil residua as recycling agents for used pavements, the use of western shale bitumen as an additive to petroleum asphalt to reduce moisture damage susceptibility, the use of western shale oil residue as an additive to petroleum asphalt for use as a pavement crack and joint sealant material, and the energies of interaction and rheological properties of petroleum asphalt modified with western shale oil residue.

Objectives

The objectives of these studies were to explore additional uses of western shale oil residua and to explore potential uses for eastern shale oil residua in nonfuel related areas. By focusing on nonfuel uses for these residual materials, they can be easily and inexpensively prepared for uses that are generally high-dollar specialty markets. As larger amounts of the shale oil barrel are marketed in products with relatively high

prices, the economics for producing shale oil improve.

Procedures

The New Albany (eastern) and Green River Formation (western) shale oils used in the recycling study were produced by the WRI inclined fluidized-bed process (Merriam and Cha 1987). The petroleum asphalts and the recycled mixtures were aged using the thin-film accelerated aging test (Petersen 1989) to simulate asphalt aging with time in a pavement. Asphalt properties were measured using ASTM D 3381 tests to grade asphalt cements. Aged asphalts and recycled mixtures were analyzed using dynamic rheology and infrared spectroscopy (Petersen 1975; Petersen and Plancher 1981). Moisture damage susceptibility was assessed using the water susceptibility test (WST) (Plancher et al. 1980) using two aggregates of different mineral types. Low-temperature properties of recycled mixtures were analyzed using a tensile-elongation test to measure the stiffness modulus and the percent elongation.

The western shale bitumen used in the shale bitumen additive study was obtained by supercritical fluid extraction of oil shale using methanol and water at about 400°C (752°F). The products were recovered by extraction with organic solvent. Solvent was subsequently removed *in vacuo* (McKay et al. 1983; McKay and Chong 1983). The unrefined shale bitumen was added to a petroleum asphalt at levels of 15 and 20%. The effects of moisture damage were assessed using the WST on two aggregates of different mineral types.

The western shale oil residue used as an additive to petroleum asphalt for the crack and joint sealant evaluation, and also for the energy of interaction study was prepared by The New Paraho Corporation using a +371°C (+700°F) shale oil residue

that was further processed to produce a specification grade AC-20 asphalt. The evaluation of the shale oil-modified asphalts for use as crack and joint sealant material was accomplished using ASTM D 3407 extension testing, rheological testing of portland cement concrete-asphalt briquettes, dynamic rheological analysis of unaged and aged asphalts, and bonding energy measurements between the asphalt materials and four aggregates (including crushed concrete) using microcalorimetry (Ensley and Scholz 1972).

Results

The recycling study showed that the western shale oil residue could function as an asphalt recycling agent; whereas, the eastern shale oil residue had vastly different properties. The western shale oil residue-asphalt blends had good properties with respect to moisture damage resistance, but somewhat inferior properties with respect to further aging compared with a commercial recycling agent. The results also showed that the effectiveness and the properties of petroleum asphalts recycled with western shale oil residue are dependent upon the composition of the petroleum crude source of the asphalt.

The eastern shale oil residue prepared for the recycling study had a viscosity substantially too high for use as a recycling agent; therefore, it was studied as an asphalt stiffening agent with very soft asphalts. It appeared that the chemistry of the eastern shale oil residue was appropriate for asphalt recycling because of its dispersant nature, but that its initial viscosity, and/or perhaps its average molecular weight distribution, were too high to be useful.

The results from the use of unrefined western shale bitumen as an additive to petroleum asphalt to reduce moisture damage showed that there is some advantage to using this material, but substantially less than has been shown with other shale-derived materials. Some refinement of the bitumen is needed to improve its effect on reducing moisture

damage susceptibility, perhaps because of the significant amounts of carboxylic acids present in the unrefined bitumen.

The results from the addition of western shale oil residue to petroleum asphalt for use as a crack and joint sealant material showed that some improvement was obtained with the addition of the shale oil residue compared with conventional petroleum asphalt. However, the performance of the modified materials in the ASTM extension test was substantially inferior to commercially available, but more expensive, rubber-modified sealant materials. The shale oil-modified asphalts did show better adhesive properties in the extension test. The shale oil-modified asphalts also showed improved relaxation times and larger amounts of recovery in a stress-relaxation type of test using portland cement concrete-asphalt briquettes. The dynamic rheological analysis of the shale oil-modified asphalts showed some improvement in the viscosity-temperature susceptibility properties compared with the petroleum asphalt. The shale oil-modified asphalts also showed higher energies of interaction (bonding energies) with the aggregates tested compared with the petroleum asphalt, supporting previous data that indicated shale oil-modified asphalts improve the resistance to water damage in pavements.

Conclusions

The addition of western shale oil residue to petroleum asphalts showed some improved properties compared with conventional materials when used as a recycling agent and also as an additive in crack and joint sealant material. The improved properties were better resistance to moisture damage, better temperature susceptibility properties, and better bonding properties to aggregate surfaces, including crushed portland cement concrete. The addition of unrefined western oil shale bitumen only showed slight improvement in the resistance to moisture damage, indicating that some refinement is necessary.

The eastern shale oil residue did not have the necessary physical properties to be used as an asphalt recycling agent, but the material did have some dispersant characteristics that would be necessary for an asphalt recycling agent.

In summary, these studies did show that both eastern and western shale oil residua have potential for use in the asphalt and asphalt paving industry.

Related Publications and Presentations

Publications

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INORGANIC GEOCHEMICAL CHARACTERIZATION OF RETORTED OIL SHALE

Susan S. Sorini

Background

Commercial production of shale oil would result in the generation of large volumes of solid oil shale processing wastes, creating a significant disposal problem. A major concern associated with disposal of spent oil shale wastes is solubilization and mobilization of environmentally harmful chemical constituents from the spent shale by ground and surface waters. As a result, methods to predict water quality from spent oil shale disposal sites are needed. To predict the fate and behavior of the elemental constituents in spent oil shale and assess the effectiveness of proposed mitigation techniques, it is important to understand the processes controlling partitioning of the elements between solid and solution phases. This requires evaluation of the mineralogy and corresponding solution chemistry of spent shale/water systems. The information obtained by studying elemental aqueous- and solid-phase distribution will provide a basis for decisions concerning disposal of spent oil shale in an environmentally sound manner.

Objectives

Several studies were conducted on spent oil shale mineralogy and chemical and physical interactions that occur in spent oil shale/water systems to obtain a better understanding of the processes that influence the partitioning of elements between spent oil shale solid and solution phases. The objectives of this research were to (1) characterize spent oil shale and spent oil shale aqueous extracts and evaluate experimental and geochemical modeling techniques that can be used to identify processes controlling the chemical composition of oil shale leachates; (2) determine the mineralogy and leachate chemistry of spent reference oil shales, provide a preliminary assessment of spent oil shale weathering reactions, and

determine the solid and solution speciation of potentially toxic constituents in spent shale/leachate systems; (3) study processes controlling molybdenum aqueous- and solid-phase distribution in spent oil shale; (4) assess the solubility relationships of fluorine and molybdenum in spent oil shale, examine the mineralogy and leachate chemistry of combusted oil shales in laboratory weathering experiments, and examine literature on the characterization of spent oil shale; (5) examine the solution chemistry and mineralogy of spent oil shale as a function of time to determine the extent to which weathering reactions occur; (6) provide a detailed characterization of the chemistry of lysimeter leachates by subjecting the leachate concentration data to chemical equilibria model analysis; (7) evaluate trace elements in sulfide minerals from a Chattanooga shale core from central Tennessee and establish mineral residence and stratigraphic distribution of selected trace elements; (8) characterize the sulfur-bearing minerals present in raw and processed eastern and western oil shale; (9) examine the mineralogy and solubility of ettringite, a complex hydrated calcium aluminum sulfate hydroxide, in weathered spent oil shales and reexamine the ettringite equilibrium solubility characterizations of spent oil shales; (10) evaluate the applicability of existing geochemical models to predict water quality from an oil shale solid waste environment; and (11) determine the mineral phases responsible for cementation of Lurgi spent oil shale.

Procedures

Four spent western reference oil shales, one combusted, one Paraho indirectly retorted, and two Paraho directly retorted, were subjected to detailed physical, chemical, and mineralogical characterizations. Total elemental content, calcium carbonate equivalent, specific surface area, cation

exchange capacity, clay mineralogy, exchangeable cations, and soluble cations and anions were determined in each of the spent shales. Mineralogy was determined using X-ray diffraction (XRD) following nondestructive preconcentration of mineral phases into density separates using a float-sink density fractionation technique. Selective sequential dissolution analysis was performed to partition trace and minor elements into carbonate and exchangeable, organic and manganese oxide, iron oxide, and residual combusted oil shale fractions. The influence of spent oil shale solids on leachate chemistry was examined in a batch equilibrium study. The data from this study were used as input to a geochemical model to predict elemental speciation.

In a study conducted in 1988, the solubility of calcium molybdate (CaMoO_4) was determined, and the results were used to evaluate the occurrence of CaMoO_4 in the spent western oil shale samples used in the previous study. The influence of the oil extraction process, solid-solution contact time, and recarbonation on spent oil shale leachate chemical composition was examined, along with the chemical characteristics of short-term spent western, recarbonated spent western, and spent eastern reference oil shale leachates. The mineralogy of the spent eastern and western oil shale samples was determined, along with the mineralogy of hydrated and recarbonated spent oil shale samples. The use of geochemical models to predict leachate composition was also illustrated.

A study to provide information to help in understanding the processes controlling molybdenum aqueous- and solid-phase distribution was conducted in 1990. This involved measuring the ion association constants for the formation of calcium and magnesium molybdate ion pairs by potentiometric titration at pH 7 and 25°C (77°F) in NaNO_3 ionic media. The measured values were then used to examine the equilibrium solubility of powellite (CaMoO_4) in KNO_3 solutions and spent oil shale systems.

In a 1991 study, the solubility of fluorine and molybdenum in spent oil shale was examined. Combusted Green River Formation oil shale and combusted New Albany shale, both produced in a fluidized-bed reactor, and a second Green River Formation oil shale, produced by the Lurgi-Ruhrgas process (Rammler 1982) were used in the study. The spent oil shales were subjected to nonequilibrium weathering using a humidity cell technique (Caruccio 1968; Sullivan et al. 1987) involving a 7-day weathering cycle, which continued for 18 weeks. Leachates from the weathering experiments were generated weekly and were analyzed for their chemical constituents. Subsamples of the weathered spent oil shale from the humidity cells were analyzed using XRD. Fluorine and molybdenum relationships were evaluated using a modified batch leaching technique involving a solid-to-liquid ratio of 1:2 and a 28-day equilibration period. After the first equilibration period, the slurries were filtered, and a second 28-day equilibration period was started. At the completion of the second equilibration period, leachates were once again collected. The spent oil shale samples were weathered for a total of six equilibration cycles; and the resulting leachates were submitted for chemical analysis. Geochemical model analysis was performed using the model GEOCHEM (Sposito and Mattigod 1980).

In a fifth study, the changes in solution chemistry and mineralogy of spent oil shale were examined as a function of time to determine the extent of weathering reactions. The oil shale studied was a byproduct of the Lurgi-Ruhrgas processing method (Mehta et al. 1980). One hundred grams of spent shale were mixed with 50 mL of high-purity water. The mixtures were allowed to sit at room temperature for times ranging from 1 minute to 24 hours (16 time periods). After the appropriate time had elapsed, the water/spent shale mixtures were filtered, and the resulting filtrates were analyzed for pH and various cations, anions, and chemical compounds. The chemical data from analysis of the filtrates were evaluated using the chemical

equilibrium model GEOCHEM. Mineralogy of the oil shale solid waste samples was determined by XRD using an automated, computerized Scintag PAD V diffractometer.

In another study, leachates from field lysimeters containing an eastern oil shale, a retorted eastern oil shale, and an oil shale fines/retorted oil shale mixture were subjected to chemical equilibria analysis using a geochemical model. Leachates from three lysimeters were collected from sampling ports at a depth of 10 ft, and data from analysis of these leachates were studied with the chemical equilibria model GEOCHEM.

A study involving Chattanooga shale was performed to examine selected trace elements contained in sulfide minerals of the shale and to determine mineralogical residencies and stratigraphic distribution. Gravity concentration and digestion procedures were used to isolate the sulfide mineral fraction from the bulk shale. Both the bulk oil shale and the sulfide mineral fraction were analyzed for trace elements. XRD, scanning electron microscopy/energy dispersive X-ray (SEM/EDX), and analytical chemical techniques were used to evaluate the mineralogy, morphology, and elemental composition of the sulfide mineral concentrates.

In a second study to investigate sulfur-containing minerals in oil shale, raw Chattanooga shale, oil shale samples from the DOE reference shale program, and spent samples from Western Research Institute's TREE program (Mason 1984; Mones and Glaser 1986) were studied. Gravity concentration was used to concentrate the sulfide minerals; XRD analysis was used to study the mineralogy of the concentrated samples; and SEM/EDX analysis was used to study the crystal morphology, chemistry, and grain relationships to the surrounding oil shale.

In a study to investigate the composition and solubility of ettringite, a combusted oil shale, produced in a fluidized-bed reactor using air as the process gas (Merriam et al. 1987), was mixed with high-purity water in

a 1:1 solid-to-liquid ratio. The suspension was allowed to stand, with periodic shaking to precipitate ettringite from the combusted oil shale suspension. Centrifugation was used to separate a white precipitate from the other solids and liquid in the suspension. The precipitate was then washed with absolute ethanol and stored under absolute ethanol for characterization and solubility analysis. The precipitate was characterized by XRD analysis. Morphology and chemistry of the precipitate were analyzed by SEM/EDX. The precipitate was also dissolved using HNO_3 -HF-HCl (Bernas 1968), and the resulting solution was analyzed for metals by inductively coupled plasma analysis. Total sulfur content of the solution was also determined.

A stability diagram was constructed to determine the solution conditions under which ettringite has greater stability than gypsum and gibbsite. In equilibrium tests, the precipitate was subjected to 0.1-M and 0.05-M NaOH solutions for 7 days. After the equilibration period, the solids were analyzed by XRD. Based on this preliminary evaluation, equilibrium solubility was determined under two different ionic strength conditions. In these tests, 2-g samples of the precipitate were mixed with 150 mL of either 0.01-M or 0.005-M CO_2 -free NaOH for a period of 14 to 72 days. After equilibration, the solids were analyzed using XRD and SEM/EDX; and the solutions were analyzed for pH, metals, and total sulfate. Aqueous leachate data from the spent oil shale used in this study had previously been treated using the geochemical model GEOCHEM (Essington et al. 1987; Essington and Spackman 1988). As a result, information from that characterization was available for review.

Geochemical modeling research related to oil shale solid waste has involved evaluation of geochemical models and critical evaluation of thermodynamic data. To evaluate the applicability of existing geochemical codes for oil shale solid waste, the following codes were examined in detail: EQ3/EQ6 (Worley 1979), GEOCHEM (Sposito and Mattigod 1980), MINTEQ (Felmy et al. 1983), PHREEQE (Parkhurst

et al. 1980), SOLMNEQ (Kharaka and Barnes 1973), and WATEQFC (Runnells and Lindberg 1981). Based on evaluation of these models, it was decided that selection of any one of the models for application to oil shale solid waste would require the development of a more reliable thermodynamic database. This requires critical evaluation of thermodynamic data, reviewing available literature, and selecting the most reliable thermodynamic data for minerals and solution complexes that are important for oil shale solid waste studies. Critical evaluations of thermodynamic data were completed for strontium, molybdenum, fluorine, selenium, calcium, magnesium, sodium, and potassium.

A study to identify the mineral phases responsible for cementation in the byproduct resulting from the Lurgi-Ruhr gas processing of oil shale, involved preparing compacted columns of the processed oil shale and water. The columns were made using either a 20 or 30% water content, and were allowed to cure for the following periods of time: 1 day, 20% water; 1 day, 30% water; 17 days, 20% water; 14 days, 30% water; and 56 days, 30% water. The following analyses were performed: XRD analysis of unhydrated and hydrated spent shale; SEM/EDX analysis of the samples cured for 14 and 56 days; and differential thermal analysis and thermogravimetric analysis to correlate compressive strength gain with thermal alterations.

Results

A study involving extensive characterization of four spent western reference oil shales showed that with the exception of carbon content, the elemental compositions of the spent shales examined were similar. The indirectly retorted oil shale had significantly higher concentrations of total, organic, and inorganic carbon than the directly retorted and combusted oil shales. The properties of the spent shale solids that influence the mobility of elements in a leaching environment (i.e., specific surface area and cation exchange capacity) were greatly influenced by spent oil shale type. The combusted oil shale had the greatest

specific surface area and cation exchange capacity, followed by the indirectly and directly retorted oil shale samples. The spent oil shale water extracts were highly saline, sodic, and alkaline. The major mineralogy of the spent oil shales was consistent with predictions based on process temperatures. Selective dissolution of mineral phases from the combusted oil shale indicated the following mineralogical residences: strontium-carbonates; barium-carbonates, organics, silicates, and aluminosilicates; manganese-carbonates and iron sulfides; vanadium, chromium, cobalt, molybdenum, and nickel-iron sulfides and oxides; copper-iron sulfides and oxides, and carbonates; zinc-iron sulfides and carbonates; and lead-iron sulfides, carbonates, and iron oxides. The concentrations of elements, pH, and redox potential of aqueous extracts were influenced by spent oil shale type. Leachates were dominated by sodium, potassium, sulfate, reduced sulfur species, and alkaline conditions. Adsorption isotherms showed the combusted oil shale to have the highest affinity for arsenate and selenite.

Data from the 1988 study to evaluate the occurrence of CaMoO_4 in the spent western reference oil shales described above suggested that CaMoO_4 does not control molybdenum concentrations in the spent oil shale equilibrium solutions and may not even occur in the spent oil shales. The chemical characteristics of short-term spent western, recarbonated spent western, and spent eastern reference oil shale leachates show that solid-solution contact times, recarbonation, oil extraction process, and oil shale resource all affect leachate chemical composition. The mineralogical study of spent eastern and western oil shales shows that spent shale mineralogy is consistent with that predicted from the process temperature history of the samples. With the exception of the combusted oil shale samples, no mineralogical differences between anhydrous and hydrated samples were observed. Gypsum and ettringite occur in hydrated-retorted and hydrated-combusted oil shale samples.

Recarbonation resulted in the precipitation of calcite. Although geochemical models have a number of shortcomings, a geochemical model was used in this study to predict the concentrations of fluoride in spent oil shale leachates.

The results of a 1990 study to help in understanding the processes controlling molybdenum aqueous- and solid-phase distribution showed that calcium and magnesium have a significant influence on the aqueous chemistry of molybdenum. Data evaluation suggested that $\text{Ca}(\text{MoO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{NaMoO}_4 \cdot 2\text{H}_2\text{O}$ may significantly contribute to total soluble molybdenum. It was found that ion association model examination of spent oil shale solutions must include all species known to occur. However, for many important species, ion association constants are either unavailable, estimated, or not critically evaluated. In previous studies, the occurrence of powellite in spent oil shale and its control of molybdenum solubility were reported based on solubility data and ion association model analysis. However, soluble molybdenum species were not considered in the data analysis. As a result, it was believed that additional analyses were required to determine if powellite is present in spent oil shale.

During initial cycles of the equilibrium weathering study conducted in 1991 to evaluate fluorine and molybdenum in combusted oil shale, the solubility relationships for fluorine and molybdenum were similar to those found in the literature. However, as weathering progressed, the spent oil shale leachates became supersaturated with respect to fluorite (CaF_2) and saturated with respect to powellite (CaMoO_4), which was found to exist in the spent oil shale. These results indicate that in a weathering environment, subject to slow infiltration of water, the behavior of molybdenum in spent oil shale may be predicted on the basis of powellite solubility. However, fluorine behavior cannot be predicted due to the fact that the system becomes supersaturated over time as a result of an unknown factor. The leachate should not be supersaturated with

fluorine if CaF_2 is present and equilibrium exists.

In an evaluation of spent oil shale samples subjected to weathering tests, the GEOCHEM model (Sposito and Mattigod 1980) and XRD data were used to examine changes in solution chemistry and mineralogy relative to time and weathering. Modeling results showed that gypsum is near levels of saturation in solution and may control calcium and sulfate solubilities. The modeling results also suggested that diopside ($\text{CaMgSi}_2\text{O}_6$) has the potential to precipitate after 16 hours of weathering. A comparison of the 56-day hydrated sample and the 24-hour sample showed significant changes in mineral dissolutions and formations caused by hydration over time. XRD data were difficult to interpret because of the amount of amorphous material present in the samples. XRD data did show that calcite (CaCO_3) is a major component of the system. This may be responsible for cementation characteristics of the spent oil shales.

The study involving chemical equilibria model analysis of lysimeter leachate data showed that the aqueous chemistry of the oil shales used in the field lysimeters is dominated by free ionic metal species and metal sulfate ion pairs. Leachates were predicted by GEOCHEM to approach equilibrium with respect to gypsum, goethite, melanterite, Fe-jurbanite, franklinite, molybdite, and molybdic acid.

A study examining sulfide minerals in Chattanooga shale identified pyrite (isometric FeS_2) and marcasite (orthorhombic FeS_2), arsenopyrite (FeAsS), sphalerite (ZnS), millerite (NiS), and galena (PbS) to be present in the shale. Sulfide mineral abundance was found to be directly proportional to the abundance of organic matter, and trace element concentrations increased with sulfide mineral content. The phosphatic zone at the Maury Formation-Chattanooga shale contact was determined to contain significantly higher concentrations of some trace elements.

Three general trends in trace element abundances between bulk shale and sulfide mineral concentrates were identified: a large increase in arsenic, copper, and zinc levels; a moderate increase in cadmium, lead, and nickel concentrations; and a slight increase in the concentration of molybdenum. In all cases, the sulfide mineral concentrates had higher concentrations of trace elements than the bulk shale samples.

In a second study to investigate sulfur-containing minerals in oil shale samples, sulfur-bearing minerals determined in the raw oil shale samples included pyrite (FeS_2) and marcasite (FeS_2), pyrrhotite (Fe_{1-x}S), sphalerite (ZnS), and galena (PbS). Sulfur-bearing alteration minerals identified were gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and copiapite ($\text{Fe}_{14}\text{O}_3(\text{SO}_4)_{18} \cdot 63\text{H}_2\text{O}$). Sulfur-bearing minerals identified in the processed oil shale included pyrite, hexagonal pyrrhotite, oldhamite, and the alteration product, gypsum. The temperature of thermal processing was found to be an important factor in determining the sulfur-bearing minerals that result. Other important factors include the chemical composition of the source material, pressure, and the activities of iron and sulfur.

In the study to investigate the composition and solubility of ettringite, hydration of the spent oil shale did not result in a pure, stoichiometric ettringite solid. The chemical formula of the solid that precipitated, which was calculated from energy dispersive X-ray data, was $\text{Ca}_{6.32}\text{Al}_{1.05}(\text{SO}_4)_{2.27}(\text{SiO}_4)_{0.36}(\text{OH})_{9.83} \cdot 26\text{H}_2\text{O}$. A calculated pK_{sp} for dissolution of this solid was -57.01; and assuming that the precipitate was homogeneous, a ΔG_f° of $-10116.7 \pm 8.1 \text{ kJ mol}^{-1}$ was calculated. The pK_{sp} was compared to ion activity product values, calculated by applying the geochemical model GEOCHEM to the spent oil shale leachate data. The pK_{sp} and ion activity product values were comparable for leachate contact times of 28 days and less. However, at longer contact times, the spent oil shale leachates were predicted to be undersaturated with respect to ettringite, which was directly identified in the solid

matrix. These conflicting results may be due to the incongruent dissolution of ettringite. Supersaturation of the spent oil shale leachates with respect to calcite supports this and suggests that calcium released through ettringite dissolution was precipitated as calcite.

In a separate study, the geochemical models EQ3/EQ6, GEOCHEM, MINTEQA, PHREEQE, SOLMNEQ, and WATEQFC were evaluated for their applicability to oil shale solid waste. The applicability of the geochemical codes to spent oil shale was evaluated by examining the thermodynamic database and comparing ion activities in retorted shale-distilled water extracts predicted by the codes. Large differences were found in the equilibrium constants used by the models to make similar calculations. All of the models lacked data for certain relevant minerals, such as akermanite, monticellite, and rankinite, and solution species. As a result, it was concluded that selection of any one of the models for application to oil shale solid waste requires development of a reliable thermodynamic database, which in turn requires critical evaluation and compilation of thermodynamic data. This involves reviewing available literature and selecting the most reliable thermodynamic data for minerals and solution complexes that are important for oil shale solid waste studies. A compilation of thermodynamic data for calcium, magnesium, sodium, and potassium were prepared as part of this study; and in a second similar study, thermodynamic data were compiled for fluorine, molybdenum, strontium, and selenium.

Results of the study to identify the mineral phases responsible for cementation of Lurgi oil shale showed that changes occurred in the chemical properties of the hydrated spent shale that were dependent on water content and curing time. Data from XRD analysis indicated that the dissolution products of periclase, calcite, and gypsum contribute to the formation of cementitious material. SEM analysis showed that with an increase in compressive strength, there was also an increase in crystalline bridging

between particles of spent shale. EDX analysis identified magnesium, aluminum, silicon, potassium, calcium, and iron as the major elements present in all of the samples; and calcium was the major element identified in the bridging material. The initial incorporation of water into the structure of the spent shale was completed during the first 14 days of curing. Significant changes in the thermal curves of the 14- and 56-day samples were observed. This evidence suggests that a hydrated, clay-like mineral formed in the 56-day sample.

Conclusions

Results of these studies provide a variety of information that is important to waste management planning for disposal of spent oil shale. Conclusions from these studies can be summarized as follows:

1. Trace elements predominantly reside in iron sulfide phases of spent western oil shale. As a result, oxidation of the reduced sulfur may solubilize these trace elements. Equilibrium solubility evaluations suggest mineral phases for strontium, barium, fluoride, molybdenum, and arsenate in spent western oil shale.
2. Environmental influences may greatly affect basic chemical, physical, and mineralogical characteristics of spent oil shale. Hydration and recarbonation of retorted oil shale significantly influence mineralogical residences of trace and major elements.
3. In a weathering environment involving slow infiltration of water, the fate and behavior of molybdenum in spent oil shale may be predicted on the basis of powellite (CaMoO_4) solubility.
4. Fluorine chemistry in spent oil shale leachates does not appear to be controlled by fluorite (CaF_2) solubility.
5. Solid-solution contact times, recarbonation, oil extraction process, and oil shale resource affect spent oil shale leachate chemical composition.
6. Spent eastern and western oil shale mineralogy is predictable based on process temperature.
7. Geochemical evaluation of Lurgi-Ruhrgas processed oil shale relative to time and weathering suggests that gypsum is near levels of saturation in solution and may control the solubilities of calcium and sulfate. Significant changes occur in mineral dissolutions and formations caused by hydration reactions of the spent shale.
8. Leachates from field lysimeters containing eastern raw and spent oil shale are dominated by free ionic metal species and metal sulfate ion pairs.
9. Temperature of processing, chemical composition of the source material, pressure, and the activities of iron and sulfur are important factors in determining the sulfide minerals in spent oil shale.
10. Conclusions concerning sulfur-containing minerals in raw Chattanooga shale are that:
 - Sulfide-containing minerals in the Chattanooga shale include pyrite (isometric FeS_2), marcasite (orthorhombic FeS_2), arsenopyrite (FeAsS), sphalerite (ZnS), millerite (NiS), and galena (PbS).
 - Sulfide mineral abundance is directly related to organic matter abundance.
 - Trace element concentrations increase with sulfide mineral content.
11. In complex chemical systems, such as aqueous spent oil shale systems, solids can undergo incongruent dissolution, where dissolution reaction products are solid species or a mixture

of aqueous and solid species. For ettringite, the solution phase is influenced by the dissolution of ettringite and precipitation of such minerals as gypsum, portlandite, and gibbsite. This type of reaction cannot be predicted using a geochemical model; and model computed ionic activities cannot be used to substantiate the presence of ettringite.

12. Conclusions concerning evaluation of the applicability of geochemical models to oil shale solid waste are that:

- There are large differences between models in the equilibrium constants used to make identical calculations.
- Geochemical models lack data for high-temperature minerals, such as silicates and both inorganic and organic solution complexes, which are important for oil shale solid waste environmental studies.
- There is a great need to develop a reliable thermodynamic database for oil shale solid waste geochemical models.

13. Identification of the cementing material in hydrated spent oil shale requires additional analyses, possibly using electron-probe microanalysis, nuclear magnetic resonance, and transmission electron microscopy.

Related Publications

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ORGANIC CHARACTERIZATION OF RETORTED OIL SHALE AND PRODUCT WATER

Susan S. Sorini

Background

Commercial production of shale oil would result in the generation of large volumes of solid and liquid wastes. As much as 150,000 tons of spent oil shale might be produced daily by a typical oil shale facility producing 100,000 barrels of crude oil per day (Gerhart and Holtz 1981). Generation of large amounts of solid and liquid wastes would create a significant and costly disposal problem.

The solid and liquid waste products resulting from production of synthetic crude oil from oil shale contain a wide variety of organic compounds (Pellizzari et al. 1979; Stuermer et al. 1980; Leenheer et al. 1982; Poulson et al. 1985; Lane et al. 1986). Information on the nature and behavior of the organic compounds present in spent oil shale and retort water is important for assessing the environmental impact of disposal of these materials.

The potential for spent oil shale to reduce the chemical concentrations in retort waters during co-disposal has been suggested (Fox et al. 1980; George and Jackson 1985; Boardman et al. 1985). Another possible disposal option for spent oil shale may be mixing it with hazardous waste to stabilize the hazardous constituents in the waste. The high alkalinity of spent oil shale may reduce the mobility of the hazardous constituents; or the spent oil shale may sorb inorganic and/or organic constituents from the hazardous wastes and prevent their release to the environment. To develop environmentally sound and cost effective disposal techniques for spent oil shale and oil shale process waters, an understanding of the nature and behavior of organic compounds present in these wastes and their interactions with various mineral phases is needed.

Objectives

Several studies were conducted on the nature, fate, and behavior of organic compounds associated with solid and liquid oil shale production wastes. The objectives of this research were to (1) test a sampling and analysis procedure for characterizing volatile organic components (VOCs) in spent oil shale generated by both pyrolysis and combustion processes, (2) identify volatile and semivolatile organic compounds present in water extracts of spent oil shale, (3) assess the ability of clay liner material to restrict the mobility of aromatic amines commonly found in solid and liquid oil shale production wastes, (4) investigate the sorption interactions between mineral phases and model organic compounds that either have properties similar to organic compounds present in raw or spent oil shale leachates or are actually found in raw or spent oil shale, and (5) evaluate the ability of spent oil shale to stabilize organic and inorganic constituents of hazardous waste.

Procedures

In a study to test a sampling and analysis procedure for characterizing VOCs in spent oil shale, two spent shale samples were obtained from a two-stage, pyrolysis and combustion, process. In each stage, the oil shale was exposed to retorting temperatures of 480-510°C (900-950°F) for approximately 5 minutes. Retort recycle gas was used in the pyrolysis step and air was used in the combustion step. The retorting was performed in inclined fluidized-bed reactors built by Western Research Institute (Merriam and Cha 1987).

The spent shale sampling apparatus consisted of a Pyrex 500-mL, three-necked flask, connected through one neck to four Tenax traps in series. The second neck of

the flask was used as an inlet for the helium carrier gas; and the third neck was fitted with a thermometer for temperature monitoring. VOCs in the spent shale were sampled by heating a spent shale sample while sweeping the sample with helium. VOCs in the helium stream were collected on the Tenax traps and subsequently analyzed by gas chromatography/mass spectrometry (GC/MS).

In a second study, ten samples of spent oil shale resulting from retorting in a Paraho directly-fired retort at an average maximum bed temperature of 1022°C (1872°F) were extracted using high-purity water. A 1:4 solid-to-liquid extraction ratio was used (250 g of spent shale and 1000 mL of water). The solid and water were added to 2-L precleaned, high-density polyethylene bottles, and the bottles were placed in a temperature controlled (25°C [77°F]) shaker water bath for 28 days. At the end of 28 days, the extraction slurries were filtered using 0.6-0.8- μ m borosilicate glass fiber filters according to the Toxicity Characteristic Leaching Procedure (TCLP) (U.S. EPA 1986). Following filtration, the resulting filtrates were composited for analysis of volatile and semivolatile organic compounds.

The leachate was analyzed directly for volatile organic compounds using a purge and trap method combined with mass spectral analysis. Semivolatile organic compounds were analyzed using GC/MS. Base-neutral, acid-neutral, and acid fractions were generated for semivolatile analysis. All GC/MS analyses were performed using U.S. Environmental Protection Agency (EPA) contract laboratory protocol.

In a third study, calcium- and potassium-saturated bentonite suspensions were prepared by blending Wyoming bentonite and $\text{Ca}(\text{C}_2\text{H}_3\text{O}_3)_2$ and Wyoming bentonite and KCl, respectively. Aniline, o-toluidine, m-toluidine, and p-toluidine adsorption experiments were conducted in both the Ca^{+2} - and K^{+} -saturated bentonite systems at varying pH values. These were performed by placing 20 mL of the clay

suspension and 25 mL of an aniline or toluidine solution in 50-mL centrifuge tubes, along with a pH adjusting solution. The centrifuge tubes were placed on a wrist-action shaker for 24 hours at ambient temperatures (20-25°C, 68-77°F). After 24 hours, the adsorption systems were centrifuged. A 10-mL aliquot of the clear supernatant was then added to a 100-mL volumetric flask and brought to volume using the appropriate background electrolyte solution. The resulting solutions were analyzed for aniline or toluidines by ultraviolet (UV) spectrophotometry (Shimadzu UV-265 spectrophotometer) at a wavelength of approximately 280 nm.

In another study, adsorption of organic compounds found in spent oil shale by minerals comprising the bulk of the mineral composition of spent shale was studied. The organic compounds used were pyridine, p-cresol, phenol, and acetone; and the minerals involved were quartz, dolomite, and calcite. Three experimental procedures for contacting the chemicals and mineral phases were used: (1) vapor deposition, which involved contacting the mineral phase with the vapor of the organic compound, (2) directly adding the organic compound to the mineral samples, and (3) mixing the mineral and organic compound in an aqueous solution of pH 12 and evaporating the samples to dryness. The samples were analyzed using Fourier transform infrared (FTIR) spectroscopy. The infrared spectrometer used was a Digilab FTS-45 FTIR spectrometer. Three methods of detection were investigated for the study: FTIR/PAS (photo-acoustics), DRIFT (diffuse reflectance), and transmission through KBr pellet. The use of KBr pellets involves sintering the sample with intimately mixed KBr (the supporting substrate) under high pressure; DRIFT involves simply mixing the samples with KBr, and PAS involves running the samples without KBr.

A review of other studies performed at WRI to investigate the interactions between mineral phases in spent oil shale and model organic compounds was also conducted. Sorption mechanisms between the organic

compounds and mineral phases have been studied using FTIR, high-performance liquid chromatography, Raman spectroscopy, differential scanning calorimetry and thermogravimetric analysis techniques.

To evaluate the ability of spent oil shale to stabilize organic and inorganic constituents of hazardous waste, mixtures containing varying amounts of spent oil shale and hazardous waste were prepared, allowed to equilibrate, and then leached with deionized, distilled water. The spent shales used in this study resulted from retorting a western oil shale in an inclined fluidized-bed reactor. Two runs were performed, one at 843°C (1550°F) and one at 882°C (1620°F), resulting in two spent shales for testing. The hazardous wastes used in the study were an API separator sludge, creosote-contaminated soil, mixed metal oxide/hydroxide waste, metal-plating sludge, and smelter dust. The spent shales and hazardous wastes were mixed and allowed to equilibrate for 7 days. At the end of the equilibration period, deionized, distilled water was added to each mixture to give a 1:1 solid-to-liquid ratio, and the slurries were allowed to equilibrate for an additional day. After the second equilibration period, the mixtures were filtered, and the resulting filtrates were analyzed for the hazardous chemical constituent(s) of interest.

Results

Results of the study to test a sampling and analysis procedure for characterizing VOCs in spent oil shale show that collecting the organic components on Tenax traps concentrates the organic constituents and increases the sensitivity of the analytical procedure. Problems associated with an extraction procedure were eliminated. However, other problems, such as irreversible adsorption on Tenax or sample degradation, may occur. Spent shale from a combustion process was determined to contain fewer VOCs than the spent shale from a pyrolysis process. The spent shale resulting from the pyrolysis process was determined to contain low-molecular weight

hydrocarbon compounds, aliphatic and aromatic, as well as sulfur-containing species, and some tentatively identified nitrogen- and oxygen-containing species. Benzene, toluene, and xylenes were identified. These compounds are EPA priority pollutants. In the spent oil shale resulting from the combustion process, only two alkanes in the C₆-C₇ range were detected, and several alkenes or cyclic alkenes in the C₆-C₈ range were identified. Benzene was the only major compound detected. A C₂-substituted benzene and several possible nitrogen- or oxygen-containing compounds were also identified.

Results from the study to identify volatile and semivolatile organic compounds present in water extracts of Paraho spent oil shale show that organic acids are the predominant semivolatile compounds present in aqueous extracts of the spent shale. Basic semivolatile organic compounds are present in much lower concentrations, which approach or are below analytical detection limits. The semivolatile organic compounds tentatively identified and quantified in the base-neutral, acid, and acid-neutral fractions of the Paraho spent oil shale/water leachate are listed in Table 1. Methylene chloride and acetone were the only volatile organic compounds detected in the leachate of the Paraho spent shale. Because these are common solvents used in the laboratory, it is suggested that they are not indigenous to the leachate, but were contaminants from the laboratory atmosphere.

Results from the study to assess the ability of clay liner material to restrict the mobility of organic chemicals commonly found in oil shale processing wastes showed that the maximum amount of aniline and toluidines adsorbed on bentonite is pH dependent. Above pH 7, adsorption of the organic compounds was not detected, and as pH decreased from a value of 7, aniline and toluidine adsorption increased to a maximum when solution pH was approximately equal to the pK_a of the anilinium ion deprotonation reaction: $R-NH_3^+ = R-NH_2^0 + H^+$ (pH = 4.5 to 5.1).

Table 1. Organic Compounds Tentatively Identified in Paraho Spent Shale Aqueous Leachate

Compound	Concentration, $\mu\text{g/L}$
Base-Neutral Fraction	
Toluene (Methylbenzene)	2
C_8H_{16} Alkane	1
One additional compound was observed but not identified.	
Acid fraction	
Elemental sulfur	ND ^a
Benzoic acid	290
Butanoic acid or isomer	3
2,2-Dimethylpropanoic acid or isomer	0.7
Possible $\text{C}_6\text{H}_6\text{O}_3$ isomer	0.4
Possible $\text{C}_5\text{H}_{10}\text{O}_2$ carboxylic acid	2
2-Methylbenzoic acid or isomer	0.5
3-Methylbenzoic acid or isomer	0.9
$\text{C}_8\text{H}_8\text{O}_2$ Isomer	0.3
Eight additional compounds were observed but not identified.	
Acid-Neutral fraction	
Toluene	0.6
Butanoic acid or isomer	3
2,2-Dimethylpropanoic acid or isomer	0.6
Possible 2-Cyclohexen-1-one or isomer	0.4
Possible C_9H_{20} alkane	0.6
Possible $\text{C}_6\text{H}_6\text{O}_3$ isomer	0.6
Tetrahydro-2,4-dimethylfuran or isomer	0.4
Possible $\text{C}_5\text{H}_{10}\text{O}_2$ carboxylic acid	2
Benzoic acid	18 ^b
The four compounds listed below were tentatively identified to be present below the detection limit of the instrument.	
2-Methylbenzoic acid or isomer	0.1
3-Methylbenzoic acid or isomer	0.2
4-Methylbenzoic acid or isomer	0.1
Possible $\text{C}_{12}\text{H}_{10}\text{O}$ phenol	0.2

^a ND = Not Determined

^b Determined as an inorganic salt, response factor not known.

Maximum adsorption increased with decreasing ionic strength. Adsorption of the organic compounds was inhibited in the presence of sulfate and was greater in the Ca^{+2} systems than in the K^{+} systems, regardless of ionic strength. Spectroscopic data showed that the aniline compounds are adsorbed on bentonite through direct bonding of an amine hydrogen to a surface silica oxygen.

Results from the study to investigate adsorption of organic compounds by spent oil shale mineral phases suggest that minerals in spent oil shales do not significantly contribute to the retention of spent oil shale leachate organic compounds. Very little observable sorption was detected. In most cases, no interaction was observed within the detection limits of the FTIR instrument. Indications of sorption interactions between p-cresol and calcite and dolomite, and also between phenol and quartz were detected. Physisorption, in the form of hydrogen bonding between phenolic hydroxyl hydrogen and the oxygens of calcite was the only readily identifiable sorption interaction in the study.

Preliminary investigations in this study showed DRIFT to be the best sample preparation method in terms of detection limits, sample preparation, and speed of analysis. For this study, DRIFT gave higher sensitivity and less sample preparation time than KBr pellets and had a better signal-to-noise ratio than PAS.

As with the study described above, similar studies conducted at WRI have shown little sorption of organic compounds by oil shale mineral phases. However, information on application of various analytical methods to these systems has been obtained. The newer instrumental methods of photoacoustics and diffuse reflectance have been shown to be well suited for examining organic-mineral interactions; high-performance liquid chromatography was found to be a difficult method to apply, and requires further development for this type of application; Raman spectroscopy was found to be better suited for remote, in-situ

monitoring of organic compounds in subsurface environments; and thermogravimetric and differential scanning calorimetry were determined to be too insensitive for this application.

The study to evaluate the ability of spent oil shale to stabilize hazardous constituents in wastes showed that spent oil shale can stabilize a hazardous waste by reducing the mobility of metals that precipitate as solid phases from alkaline solutions. Mixing spent shales with a smelter dust and mixed metal oxide/hydroxide waste reduced the amount of cadmium released from these wastes (on a per gram basis) during water extraction. However, mixing spent shales with a metal-plating waste, high in chromium, did not reduce the leachability of chromium from the waste. As the amount of spent shale in the metal-plating waste/spent shale mixtures was increased, which in turn increased the solution pH, the solubility of chromium also increased.

Little information on stabilization of organic compounds in the API separator sludge and creosote-contaminated soil was obtained. These wastes are complex organic wastes containing several organic compounds, and difficulties in homogenizing the materials were encountered.

Conclusions

The conclusions that can be made from these studies are:

- A Tenax-trap sampling technique, combined with GC/MS analysis, was successful in trapping and identifying VOCs emitted from retorted oil shales.
- Volatile organic compounds are not present in concentrations above instrumental detection limits in aqueous leachate of Paraho spent oil shale.
- Organic acids are the predominant class of semivolatile compounds present in the aqueous leachate of Paraho spent shale. They are present in the parts-per-billion range.

- Aniline and toluidine adsorption by bentonite is minimal in high ionic strength saline systems and is not detected in systems having a pH greater than 7. Because spent oil shale leachates and retort waters have high alkalinity and salinity, bentonite liners will not be effective in reducing the mobility of anilines through sorption processes.
- Minerals in spent oil shales do not significantly contribute to the retention of spent oil shale leachate organic compounds.
- FTIR appears to be a useful technique for examining organic-mineral interactions.
- Spent oil shale can stabilize a hazardous waste by reducing the mobility of metals that precipitate as solid phases from alkaline solutions; however, evaluation of the long-term ability of spent oil shale to stabilize hazardous constituents based on alkalinity is needed.

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ION SPECIATION OF PROCESS WATERS AND FOSSIL FUEL LEACHATES

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Background

The chemical form of an element in an aqueous environment greatly influences its solubility and mobility as well as its potential environmental impact. The leaching and transport of many organic and inorganic contaminants from fossil fuel leachates and retort waters is an area of environmental concern. Geochemical models are increasingly being used to predict the distribution of contaminants in leachates. These models must be validated by comparing laboratory data to model predictions before the models can be applied to a real environment. Because model validation depends on quality laboratory data, accurate and reliable methods are needed to separate and quantify the components of interest.

Hydrophilic organic solutes in oil shale retort waters are of interest because they may be indicators of aqueous contamination from retorting operations. Many inorganic species in fossil fuel-water systems are also an area of environmental concern in predicting water quality and characterizing the partitioning behavior between solid and solution phases.

In some environments, Cr(III) may be oxidized to Cr(VI), significantly increasing its toxicity. The speciation of iron in different environments is of great interest because of its importance in controlling redox and pH conditions in aqueous and solid environments.

The behavior of many inorganic sulfur, selenium, and arsenic species are of concern because many fossil fuel combustion byproducts are being considered for use in roadbed stabilization, construction materials, and other applications. Volatile sulfur species such as sulfide or sulfite may behave very differently than more stable species such as

sulfate or thiosulfate. Selenium and arsenic species are present and may be enriched in many fossil fuel byproducts. Minerals produced during the retorting of oil shales buffer the pH of spent oil shale leachates to pH 11 or higher. Under these conditions, selenium and arsenic species are anionic in nature, and hence, soluble and mobile.

Objectives

The objectives of this research were to develop methods involving sample preparation and analysis of varied inorganic and organic species found in fossil fuel extracts. The laboratory measurements of some of these species in leachates were compared to ion speciation predictions from geochemical models.

Procedures

To characterize hydrophilic organic species in retort waters, samples from the Western Research Institute 150-ton simulated in situ retort run 17 (R-17) were selected for study. Waters from several locations in the Rio Blanco Oil Shale Company's retort 1 on federal prototype lease tract C-a, Rio Blanco County, Colorado were also studied. In the first phase of the study, the waters were separated into total hydrophilic fractions and analyzed using total organic carbon analysis, high-resolution mass spectrometry (HRMS), reversed-phase high-performance liquid chromatography with diode array detection (RPLC/DAD), gas chromatography followed by mass spectrometry (GC/MS), gas chromatography followed by thermionic ionization detection in the nitrogen-phosphorus mode, gas chromatography followed by electron-capture detection (GC/ECD), and derivatization followed by gas chromatography with electron-capture detection. In the second phase, various hydrophilic standards were derivatized and then analyzed using gas chromatography

followed by flame ionization detection (FID) and electron-capture detection (ECD). The retort waters were then derivatized and compared to the standards.

Chromium and iron redox systems were characterized using various techniques to see if laboratory speciation data compared with predictions from geochemical models. Solutions of Cr(III), Cr(VI), Fe(II), and Fe(III) were prepared over a concentration range of 0.1 μ M to 1 mM. Solutions were then prepared with Cr(VI)/Cr(III) and Fe(III)/Fe(II) ratios ranging from 1 to 10^{-4} . The solutions were analyzed using ion chromatography to determine the concentration of each ionic specie in solution. Electrode potential measurements were also made on various solutions of the metals with the oxidized and reduced forms in different ratios. The laboratory data obtained through these analyses were then compared to speciation predictions made by the geochemical model GEOCHEM and the Nernst equation.

The presence of various sulfur anions was studied in leachates from reference eastern, reference western, and Rio Blanco spent oil shales. The anions of interest were separated and quantified using a variety of ion chromatographic approaches that resulted in two sets of operating conditions. The lower sulfur anions (SO_3^{2-} , SO_4^{2-} , SCN^- , and $\text{S}_2\text{O}_3^{2-}$) were separated using an HPIC AG5 guard column and an AS5 high-capacity anion exchange column. Tetrathionate was chromatographed using an Ionpac NG1 guard column and NS1 separator column. Oxidation of the reduced sulfur species was inhibited by the addition of 10 vol % isopropanol to the standard solutions and eluant.

The spent oil leachates were prepared by placing them in containers and passing humidified air over them continuously. Every 7 days, deionized-distilled water was added to the container to establish a 1:1 solid-to-solution ratio. After 1 hour, the spent oil shale-water mixture was filtered through Whatman #42 filter paper. The shales were then allowed to air dry, and the 7-day cycle was repeated. The filtrates were

preserved with isopropanol and stored at 4°C (39°F) until they were analyzed for sulfur-containing anions.

The characterization of selenium and arsenic species in leachates from spent oil shales and coal fly ash involved developing techniques for the extraction of the ions from solid matrices without changing their chemical form, developing a method to extract total selenium from solid matrices with reliable results, and developing ion chromatography techniques to separate and quantify selenium and arsenic species in solution.

A NIST 1633a fly ash standard reference material (SRM) from the National Institute for Standards and Technology (NIST) in Gaithersburg, Maryland was used to develop an extraction technique for selenium and arsenic species prior to analysis by ion chromatography. Experiments were performed using an ultrasonic bath and 0.5-M, 2-M, and 4-M sodium hydroxide solutions and distilled/deionized water to extract selenite, selenate, and arsenate. Arsenite was extracted using a 1-M hydrochloric acid solution. The fly ash was extracted with each solution for different periods of time ranging from 4 to 24 hours to find the optimum extraction conditions. The fly ash samples were also spiked with selenite, selenate, arsenite, and arsenate prior to extraction to ensure that no speciation change took place during the extraction.

To develop a digestion procedure for the extraction of total selenium from solid matrices, the NIST 1633a SRM fly ash and a sodium bicarbonate blown fly ash were subjected to a number of different procedures. Both fly ash samples were digested using EPA Method 3050, followed by analysis for total selenium by atomic absorption spectroscopy (AA). The fly ash samples were extracted next using a highly alkaline solid:water (2:1) paste extract. The NIST 1633a SRM ash was also extracted using an ultrasonic alkaline paste extract procedure. Sodium peroxide fusion was tested on both ash samples to determine total selenium, with and without the

addition of sodium hydroxide to lower the fusion temperature. All results were then compared to determine an optimum digestion procedure for total selenium.

To develop methods to separate and quantify selenium and arsenic species in the presence of common anions using ion chromatography, several approaches were utilized. In the first phase of the study, an HPIC AG4A anion guard column was used in combination with an HPIC AS4A high-capacity anion exchange column. An anion eluant consisting of 1 mM CO_3 /0.9 mM HCO_3 was used to separate selenite and selenate. This eluant did not work because of interferences from nitrate, sulfate, and phosphate ions. In the next experiment, a 1-mM carbonate eluant was used, adjusted to pH 12 with 10 M sodium hydroxide. The elevated pH of the carbonate system was designed to eliminate interference problems from the phosphate ion. At a high pH, the phosphate ion is present in the trivalent form, and more strongly retained on the column than the selenite and selenate ions.

In the second phase of the selenium and arsenic species study, different combinations of columns and eluants were used to try and eliminate more interference problems with the selenium and arsenic species. An HPIC AG5 anion guard column was used in conjunction with an HPIC AS4A separator column. An eluant consisting of 2.0 mM Na_2CO_3 and 1.0 mM NaOH at a flow rate of 2.0 mL/min was used to separate the selenium species in the presence of other common anions. All anions were detected using suppressed conductivity at 1 micro Siemen full scale. The arsenic anions were separated using the same column combination and an eluant consisting of 2.0 mM sodium carbonate and 1.5 mM sodium bicarbonate. Arsenite was detected using electrochemical detection with a platinum working electrode at a potential of 0.5 V. The electrochemical detector was installed between the column and the suppressor device. Arsenate and other common anions were detected using conductivity detection set as 1 microsiemen full-scale.

Results

The high-resolution mass spectrometry profile of the R-17 total hydrophilic (THP) fraction showed a series of hydroxypyridines or pyridones. The presence of these compounds was confirmed with RPLC/DAD profiles. The GC/MS analysis was performed on a methylene chloride extract of the R-17 THP fraction. Benzoic acid, a compound on the U.S. Environmental Protection Agency's (EPA) Hazardous Substance List was identified at a concentration of 11 ppb. The R-17 THP fraction was derivatized with trifluoroacetic anhydride (TFAA), heptafluorobutyric anhydride (HFBA), and heptafluorobutyrylimidazole (HFBI) prior to analysis by GC/ECD. When the fraction was treated with TFAA and HFBA, no unique peaks were discovered in the GC/ECD profiles. Reaction with HFBI produced one unique peak in methanol and several unique peaks with toluene as the solvent, but none were positively identified.

The study of chromium and iron redox systems yielded valuable techniques for the separation and detection of chromium and iron species using ion chromatography. The chromium and iron species were derivatized and detected photometrically. The redox systems for chromium and iron were studied separately as they relate to the Nernst equation or GEOCHEM. The comparison of laboratory speciation data with geochemical ion speciation models showed regions of reasonable agreement for E_H for iron species above an activity ratio of $\text{Fe(III)}/\text{Fe(II)} = 0.1$ over the concentration region studied. A similar study for the chromium redox system showed no agreement with E_H over the concentration region studied.

To develop techniques to separate and detect sulfur ions, mobile phase ion chromatography was used initially to try and separate sulfite, sulfate, thiocyanate, and tetrathionate in one run. Different combinations of ion-pairing reagents, organic modifiers, and inorganic modifiers were tried to achieve this goal. In this study, tetrabutylammonium hydroxide was

chosen first as the ion-pairing reagent. Sodium carbonate was added as an inorganic modifier, and acetonitrile was added as an organic modifier. This eluant eluted tetrathionate in a reasonable period of time, but did not separate sulfate and thiosulfate. The ion-pairing reagent was changed to tetrapropylammonium hydroxide (TPAOH) to improve the resolution between sulfate and thiosulfate. Different combinations of TPAOH, sodium carbonate, and acetonitrile were tried, but none affected the resolution between sulfate and thiosulfate.

Since the NS1 column did not separate sulfate and thiosulfate, the lower sulfur-containing anions were separated with the HPIC AS5 column. A standard bicarbonate/carbonate eluant was used with p-cyanophenol added to improve the peak shapes of strongly adsorbed ions. Tetrathionate was chromatographed with the NS1 column using a TPAOH/Na₂CO₃/acetonitrile eluant. The precision of the two methods was tested by ten repeat injections of standards. The standard deviations of measured concentrations using a 50-μL sample loop ranged from 0.15 to 0.51 with the AS5 column and 0.15 to 0.29 with the NS1 column. The detection limit calculations were based on a threefold signal-to-noise ratio of the baseline. Table 1 lists the detection limits for each anion.

The leachates were analyzed using each method. The main constituent of all the leachates was sulfate with minor amounts of thiocyanate and thiosulfate. None of the leachates analyzed contained sulfite or tetrathionate.

Selecting the optimum digestion method for the determination of total selenium in fly ash samples seems to be dependent on sample type and source. When the sodium carbonate blown fly ash was digested using

EPA Method 3050 (acid digestion), the total selenium value obtained was 3.18 mg/kg. When the same sample was extracted using an alkaline paste extraction procedure, the total selenium value obtained was 6.88 mg/kg. This result confirms earlier work showing higher total selenium values from base extracts than from acid extracts.

The 3050 Method was used on the NIST 1633a SRM fly ash, and an average total selenium value of 11.6 mg/kg was obtained. An alkaline paste extraction of the NIST sample yielded a selenium value of 3.18 mg/kg, while an ultrasonic alkaline extraction procedure gave a total selenium value of 10.8 mg/kg. The certified selenium value of the NIST fly ash is 10.3 mg/kg. Sodium peroxide fusion was also tested to determine total selenium with and without the addition of sodium hydroxide to lower the fusion temperature. Fusion of the carbonate blown fly ash yielded a total selenium value of 5.54 mg/kg with sodium hydroxide, and 4.34 mg/kg without sodium hydroxide. The fusion of the NIST fly ash yielded total selenium values of 7.07 and 5.86 mg/kg with and without the sodium hydroxide, respectively.

To extract selenium and arsenic species from solid matrices without changing their chemical forms, a 0.5-M sodium hydroxide solution was added to the samples, and they were placed in an ultrasonic bath for 4 hours. This procedure effectively extracted selenite, selenate, and arsenate. A 1-M hydrochloric acid solution was used to extract arsenite. Longer extraction times did not result in any increase in the levels of selenium or arsenic detected in the leachates. The use of stronger sodium hydroxide solutions led to baseline interruption problems during chromatographic analysis. Deionized-distilled water did not extract detectable levels of the anions, even after 24 hours.

Table 1. Detection Limits for Sulfur Anions, mg/L

Injection Volume	SO ₃ ²⁻	SO ₄ ²⁻	SCN ⁻	S ₂ O ₃ ²⁻	S ₄ O ₆ ²⁻
50 μL loop	0.10	0.01	0.02	0.02	0.09

Spiking experiments performed to see if there was any speciation change during extraction all showed quantitative recoveries of the anions of interest.

Preliminary attempts to separate and detect selenium species in spent oil shale leachates using ion chromatography with a bicarbonate/carbonate eluant and an anion exchange column were not successful because of interference problems from chloride, nitrate, sulfate, and phosphate. Separations using a 1-mM carbonate eluant adjusted to pH 12 with sodium hydroxide also had problems. The higher pH solved interference problems from sulfate and phosphate, but retention times and peak areas were not repeatable for selenite and selenate.

In the second phase of the study, an AG5 anion exchange guard column was used

with the AS4A analytical separation column instead of the customary AG4 guard column. This combination of columns effectively separates nitrate and sulfate from selenite and selenate due to the differences in the hydrophobicity of the functional groups in the column packings. A sodium carbonate/sodium hydroxide eluant eliminates interferences from phosphate because at an elevated pH, phosphate is present in the trivalent form, and hence retained longer on the column. Arsenite and arsenate were also separated using this column combination, using a carbonate/bicarbonate eluant. A flow rate of 1 mL/min was necessary when separating the arsenic anions because higher flow rates cause an unstable baseline with the electrochemical detector used to detect arsenite. Figure 1 shows a chromatogram of selenite and selenate with other common anions in reagent water.

Figure 1. Ion Chromatogram of Selenite and Selenate in the Presence of Common Anions. Column, Dionex AG5 + AS4A; Eluant, 2.0 mM Na_2CO_3 , 1.0 mM NaOH ; Conductivity Detection.

Figure 2 shows chromatograms of arsenite and arsenate with other anions in reagent water. Table 2 shows the method detection limits for the selenium and arsenic species.

Method detection limit calculations were based on a threefold signal-to-noise ratio of the baseline ($S/N = 3$).

Figure 2. Ion Chromatogram of Arsenite and Arsenate in the Presence of Common Anions. Column, Dionex AG5 + AS4A; Eluant, 2.0 mM Na_2CO_3 , 1.5 mM NaHCO_3 ; Conductivity Detection with Electrochemical Detection for Arsenite.

Table 2. Detection Limits for Selenium and Arsenic Anions, mg/L

Injection Volume	$\text{SeO}_3\text{-Se}$	$\text{SeO}_4\text{-Se}$	$\text{AsO}_2\text{-As}$	$\text{HAsO}_4\text{-As}$
50 μL	0.01	0.01	0.002	0.10

The NIST 1633a fly ash was extracted ultrasonically and analyzed for selenite and selenate using the ion chromatography techniques described above. The only specie detected was selenite. The value obtained for selenite as selenium was 11.2 mg/kg, which was close to the total selenium value of 10.8 mg/kg obtained by AA analysis. Three other fly ash samples were extracted and analyzed by ion chromatography. Two of the ashes contained only selenite, and one contained only selenate. The values obtained by ion chromatography compared well with the total selenium values obtained by AA analysis.

The four fly ash extracts were also analyzed for arsenic species. The NIST 1633a fly ash contained 130 mg/kg arsenate as arsenic, compared with a total arsenic value of 135 mg/kg obtained by AA analysis. Arsenic species were not detected by ion chromatography in the other extracts, although low levels were detected by AA analysis.

In general, the concentrations of selenium and arsenic species detected using ion chromatography agreed with the total selenium and arsenic values obtained by AA analysis. The alkaline ultrasonic extraction is the best sample preparation method for the determination of selenite, selenate, and arsenate by ion chromatography. The ultrasonic hydrochloric acid extraction is required for the determination of arsenite. The determination of total selenium in solid matrices may require both the ultrasonic alkaline extraction and the acid EPA Method 3050 digestion. Only the EPA 3050 digestion technique is required for total arsenic determination. Additional work is needed to establish optimized and practical analytical approaches for the determination of other species, such as selenide or organically-bound arsenic and selenium species.

Conclusions

Characterization of the R-17 retort water for hydrophilic organic species resulted in the

detection of hydroxypyridines by HRMS and RPLC/DAD analyses. The R-17 THP fraction was analyzed by GC/MS, and contained benzoic acid at a concentration of 11 ppb. The R-17 fraction was subsequently treated with several different derivatizing agents prior to analysis by GC/ECD. Derivatization with HFBI produced one unique peak in methanol and several unique peaks with toluene as the solvent, but none were positively identified.

Chromium and iron species were derivatized and subsequently analyzed using ion chromatography. The speciation data obtained from these analyses, along with electrode potential data, was compared with geochemical ion speciation model predictions. The model predictions for iron species showed regions of agreement for E_H above an activity ratio of $Fe(III)/Fe(II) = 0.1$ for the concentrations studied. Model predictions for the chromium redox system did not correlate to laboratory data over any concentration regions studied. Further work is needed to understand speciation behavior and improve model predictions.

Various sulfur-containing anions of interest in fossil fuel leachates were separated using two different methods. The more reduced sulfur anions were separated with an HPIC AS5 column and a bicarbonate/carbonate eluant. Tetrathionate was strongly adsorbed using this method, and did not elute in a reasonable period of time; so it was chromatographed using an HPIC NS1 column with a $TPAOH/Na_2CO_3$ /acetonitrile eluant. The leachates analyzed using these methods contained sulfate with minor amounts of thiocyanate and thiosulfate.

Four methods for extraction of total selenium were studied with two coal fly ash samples. Acid digestion and sodium peroxide fusion yielded the highest recoveries for the NIST 1633a SRM, while ultrasonic extraction gave the highest recovery for the other fly ash.

Selenium and arsenic species were successfully separated using ion chromatography in the presence of other

common anions. Comparison of arsenic and selenium concentrations obtained by ion chromatography with total concentrations obtained by atomic absorption spectroscopy showed good agreement. Further work in this area could be done to develop techniques to extract and separate organically-bound arsenic and selenium species in fossil fuel materials.

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STUDIES ON DEVELOPMENT OF WESTERN OIL SHALE

Verne E. Smith

Background

Interest in oil shale development has waxed and waned a number of times in the past 150 years. The greatest level of oil shale research and development activity in the United States was precipitated by the energy crises of the 1970s. Subsequent stability of petroleum prices in the \$17-25 range and the perceived reliability of reserves have gradually curtailed most oil shale activities in the United States. It is generally considered that shale oil is not economically competitive with conventional petroleum for transportation fuel. However, alternative uses and markets for oil shale should not be precluded from consideration for this immense resource. Higher value products from oil shale and related byproducts may be economically viable in a smaller market arena.

Objectives

Studies were undertaken to (1) evaluate the market potential for different products that can be derived from oil shale, (2) assess the economic feasibility of a small-scale production operation, (3) evaluate conventional and innovative mining techniques, (4) study the performance of propellants to enhance fracturing of oil shale, (5) study methods for economic enhancement of shale oil upgrading, (6) analyze the economics of a combined underground and surface processing system, and (7) provide technology transfer information on oil shale.

Procedures

An extensive number of products and byproducts from oil shale were evaluated for their market potential in a study by Sinor (1989). The study examined specialty chemicals, asphalt blends, petrochemicals, special fuels, sulfur sorbent, cement, and construction materials produced from oil shale as to their value, marketability, quantities of materials present, and cost of production and delivery.

An analysis of costs of several oil shale mining alternatives, an estimate of spent shale disposal costs, and an examination of some unconventional uses for oil shale were made by McCarthy and Clayson (1989). Mining approaches considered were room and pillar, open pit, and chamber and pillar. Cost estimates were prepared based on the capital equipment and operating requirements of each mining configuration. Using oil shale with coal for cogeneration of electricity, for sulfur removal in coal-fired power plants, and for roadbed stabilization were also examined.

Innovative mining concepts were evaluated in a study done at the Colorado School of Mines (Hieta and Hustrulid 1991). Buffer blasting was studied in small field tests as a technique for improving fragmentation. A paper study was also done comparing mining features and costs of large-hole stoping, continuous loading and hauling, and mechanical miners to conventional room and pillar mining operations.

Plant construction and operating costs were estimated in a process engineering study made by Ford, Bacon and Davis Inc. (Walker et al. 1989). Capital and operating costs were developed for a 2,000 bbl/day shale oil processing system at a plus or minus 30% design level. The retorting system selected was a Paraho process combined with an inclined-fluid-bed retort to process the shale fines. The option of replacing the inclined-fluid-bed retort with a power-generation system was also evaluated.

Drawing on the results of several of these studies, an economic evaluation was made of a small-scale shale oil production facility (Smith et al. 1989). The study considered all costs from environmental compliance and permitting through plant retirement and included a sensitivity analysis of capital costs, operating costs, and production variation.

A small laboratory study was conducted by Netzel (1991) to examine increasing the amount of asphalt blending material produced from shale oil by polymerization of shale oil distillates to higher molecular weight materials. Three distillates were tested with anhydrous aluminum chloride and with sulfuric acid.

The performance of propellants to enhance fracturing of oil shale was studied in the field by Lekas et al. (1989, 1991). Propellant charges were placed in shallow oil shale deposits, detonated, and the resulting fracturing was evaluated by air injection tests and visual observation of cracks.

Methods for economic enhancement of shale oil upgrading were investigated by Bunker et al. (1989, 1992). The process system consisted of distillation of topped shale oil to three distillate fractions and residue, cracking the residue by hydropyrolysis, and selective hydrotreating of the fractions and residue.

The economics of larger-scale commercial production of shale oil, combining modified in situ and surface retorting with power cogeneration was evaluated in a feasibility study conducted by Bechtel (1989). Commercial, demonstration, and pilot-scale cases were considered.

To provide information on oil shale resources and their potential for development, a video tape entitled "Oil Shale: A New Light," was prepared by the Associated Governments of Northwest Colorado, and a brochure, "Oil Shale," was produced by the Department of Natural Resources of the State of Utah.

Results

Sinor (1989) found that it is technically feasible to produce a wide spectrum of products from oil shale. However, the concentrations of many individual compounds are too small for separation and purification to be practical. In addition, the relationship of price to produced volume of many organic

chemicals is such that if production were significantly increased, the price would drop greatly, resulting in an uneconomic production situation. The one potentially viable market for shale oil appears to be an asphalt blending material. Laboratory and field tests indicate that the heavy fraction of shale oil mixed with petroleum asphalt results in a superior road pavement. The economic benefits derived from longer pavement life make the shale oil material worth considerably more than conventional asphalts.

Oil shale itself can serve a regional market for such things as sulfur sorber for fluidized-bed coal combustors, cement (Sinor 1989), and soil stabilization (McCarthy and Clayson 1989). The limiting factor for these uses is transportation cost. About 500 to 700 miles appears to be the economic shipping distance.

Mining constitutes a major portion of the cost of a shale oil facility. So methods to reduce mining costs significantly will improve the economics for shale oil production. Larger-scale mining operations result in lower per-ton mining costs (McCarthy and Clayson 1989), and the development of better mining techniques would also decrease mining costs (Hieta and Hustrulid 1991).

The capital and operating costs for a 2,000 bbl/day shale oil plant using a Paraho process combined with an inclined-fluid-bed retort to process the shale fines are \$82,097,600 and \$11,091,000/yr, respectively, in mid-1989 dollars (Walker et al. 1989). If the inclined-fluid-bed retort is replaced with a power-generation system, the capital cost changes to \$96,240,000 and the operating cost changes to \$9,233,000/yr, indicating that the inclined-fluid-bed retort is the more economical method for processing the raw shale fines.

An economic evaluation of a 2,000-bbl/day shale oil facility (Smith et al. 1989) indicated that the operation is potentially viable, if the price obtained for the shale oil residue is in the top range of prices projected for this product. At \$700 to

\$1,000 per ton of shale oil residue, the estimated discounted cash flow-return on investment is in the range of 18 to 26%. This return on investment results in about a 4- to 5-year return of capital. Variation in plant production capacity has a potentially greater relative impact on the economic return than does variation in the capital or operating costs. Just a 5% increase or decrease in plant throughput will increase or decrease the rate of return by over 12%.

In the study by Netzel (1991) on polymerization of shale oil distillates to heavier materials, little change in hydrocarbon composition was found using anhydrous aluminum chloride in reactions at low temperatures. However, the reaction of 85% sulfuric acid at room temperature with three distillates produced oils with higher saturate hydrogen contents and no olefins.

The initial study on using propellants for fracturing in shallow oil shale deposits determined that (1) permeability was significantly increased at distances of 5 ft from propellant charges, with increases in permeability estimated to extend up to 12 ft, (2) both horizontal and vertical fractures were created, (3) sequentially firing two propellant charges in the same hole significantly increased permeability compared to a single charge, and (4) induced fractures were more permeable in the direction of the dominant regional fracture pattern (Lekas et al. 1989). In follow-on work (Lekas et al. 1991), a propellant tool was developed that did not use blasting caps and created horizontal fractures that extended at least 20 ft.

The shale oil upgrading study by Bunger et al. (1989, 1992) found that hydropyrolysis of the residue portion reduced the average molecular weight from 495 to 359 at moderate severities, but high hydrotreating severities were required to remove sufficient nitrogen from the residue. Tests on the distillate cuts of molecular weight effects determined that geometric hindrance accounted for the inhibition to denitrification, indicating that molecular

weight reduction is important to improved catalytic hydroprocessing.

The feasibility study of combined modified in situ and surface processing of oil shale by Bechtel (1991) determined that a commercial plant (24,300 bbl/day) with an investment of 1.2 billion dollars and a 20% return on equity would require a syncrude price of \$23.35/bbl. A pre-commercialization program, with pilot-scale and demonstration tests that would confirm the process concepts, was estimated to require an expenditure of 213.4 million dollars over a period of 10 years.

Conclusions

There are a number of products and byproducts that can be processed from oil shale. However, the one that appears to have the greatest potential for commercial development in today's marketplace is an additive to conventional asphalt used in pavement applications. A small-scale plant with shale oil additive as its primary product could provide an acceptable return on investment.

Methods to improve processing efficiencies, from mining through upgrading, need to be developed to make the vast oil shale resources of the United States a viable and competitive alternative to other resources that may become more costly or unavailable in the future.

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TAR SAND

IN SITU COMBUSTION SIMULATION TESTING OF TAR SAND

Lyle A. Johnson, Jr.

Background

Previous laboratory studies conducted by WRI have evaluated the potential of steamflood, hot-gas pyrolysis, reverse combustion, and dry- and wet-forward combustion for the in situ production of bitumen from Utah tar sands (Romanowski and Thomas 1985a-d; Johnson and Thomas 1988; Johnson et al. 1980, 1982). These studies have shown that all of the processes are effective to varying degrees for producing oil from Asphalt Ridge and Tar Sand Triangle tar sands. Based on the results of these studies, forward combustion using steam-oxygen injection was selected as the process for further study, for the following reasons: (1) the product oil quality is improved relative to steamflood produced oils, (2) the coke formed from pyrolysis of the oil exceeds fuel requirements for the process, (3) frontal velocities with steam-oxygen injection are faster than those with air injection, and (4) the plugging problems experienced with air-only combustion simulations are reduced when steam-oxygen injection is used. More detailed studies (Romanowski and Thomas 1986a, b) of the process parameters which affect the application of forward combustion to Utah tar sands showed that:

- Ignition temperature for tar sand was 343-399°C (650-750°F).
- Coke produced from the pyrolysis of tar sand was sufficient (even for the leaner Tar Sand Triangle material) to provide thermal energy for the process.
- Using steam-oxygen injection gave higher oil yields than using straight-air injection.
- Reduced fuel consumption and oxygen requirements were found in the steam-oxygen tests versus the air-combustion tests.

- The combustion-front velocity was increased in the steam-oxygen tests because of improved process efficiency.
- The product oil quality was improved with respect to the bitumen for in situ combustion. The air-combustion process produced better quality oil than the steam-oxygen process because the steam-produced oil in the steam-oxygen process diluted the pyrolysis-produced oil.
- The steam-oxygen tests in the richer tar sands did not experience the severe plugging problems that were characteristic of the air-combustion process.

Objectives

Based on the review of the results of the initial one-dimensional tests of Sunnyside tar sand, it was decided that the plugging problem needed to be further studied so that it might be prevented in future testing. Objectives of this study were thus to run simulations to evaluate steam-oxygen combustion as a production process for selected deposits and to identify the mechanisms that caused reactor plugging in simulations using Sunnyside tar sand. A three-dimensional simulation was also conducted to further evaluate the process for the Asphalt Ridge deposit.

Procedures

Two Utah and one California tar sands were used. The Asphalt Ridge tar sand deposit, located in the Uinta Basin of Utah, is a low-sulfur (<0.5%), 10° API bitumen with a viscosity in excess of 1,000,000 centipoise (cP). The second Utah tar sand is from the Sunnyside tar sand deposit located in east-central Utah. The Sunnyside bitumen has an API gravity of 8°, a sulfur content of 0.7 wt % and a viscosity of 1,000,000 cP at reservoir temperature. The third tar sand was from the Arroyo Grande deposit in

California. The bitumen has a 2.6° API gravity with 3.5 wt % sulfur and a viscosity in excess of 1,000,000 cP at reservoir temperature. Simulations using Arroyo Grande tar sand contribute to the development of evaluation criteria for in situ combustion of tar sand by providing data on a geologically diverse deposit that has characteristics similar to Utah deposits.

Three reactor systems were used to perform the tests. The physical simulations to investigate the steam-oxygen combustion process performance were conducted in WRI's tube and block reactors. The investigation of the plugging problem in the Sunnyside tar sand simulations was conducted in both a slim tube system called a laboratory reference reactor (LRR) and the tube reactor system.

The LRR is a 3/4-inch i.d. by 12-inch long retort constructed of stainless steel into which 130 g samples were placed. The injected gases (N_2 , N_2/O_2 , or N_2/O_2 /steam) were monitored with rotameters. Steam was produced with a metering pump and heat exchanger. Product gas was passed through a series of condensers and knockouts to remove liquid products and then analyzed by an on-line gas chromatograph. All liquid samples were collected and weighed for material balance calculations.

The tube reactor is capable of simulating the thermal recovery process of forward combustion, in addition to the processes of steam displacement, hot-gas pyrolysis, and reverse combustion. The reactor tube (3 5/16-inch i.d x 32-inch long) is uniformly packed with approximately 18 lb of tar sand and is vertically oriented within a series of insulated shield heaters. Auxiliary equipment includes inlet gas injection and product gas metering devices, a steam generator, a gas heater, product separation equipment, a continuous oxygen analyzer, and a gas chromatograph. The entire system is instrumented and interfaced to a data acquisition computer which records temperatures, pressures, and flow rates every 5 minutes.

The block reactor, a three-dimensional experimental apparatus, is a unique and versatile, microprocessor-controlled, high-pressure reactor. The main component of the system is a large pressure vessel into which an encapsulated sample as large as 2 x 2 x 7 ft is placed. The 1000 psig pressure vessel is a thick-walled, horizontal, cylindrical unit 9-ft long and 6 ft in diameter. The vessel is sealed using 6-ft and 2-ft diameter screw-on domed ends.

The fluid handling system consists of an injection system, a product collection and sampling system, and a product gas flaring system. Injection capabilities include independent or co-injection of gases (air, N_2 , CO_2 , and steam) at rates up to 35 scfm (85 lb/hr steam) at 1000 psig and 482°C (900°F). Fluid production during the test can exit from up to seven production ports, depending on the injection-production scheme desired. At any one time, gas and liquid products from up to four of the production ports can be simultaneously monitored by passing the individual product streams through one of four parallel knockout pots where liquids are collected and measured. The gas then enters a gas cleanup system where the cleaned gas is measured for volume and analyzed by an on-line gas chromatograph.

For this simulation, a 2 x 2 x 1-ft block was reconstructed from crushed tar sand material. To produce the block, a bulk density equal to that of the one-dimensional simulations was maintained during packing. The block was completed with a production and injection well and 18 temperature monitoring wells.

Results

One-Dimensional Asphalt Ridge Simulations

Three one-dimensional simulations were conducted using Asphalt Ridge tar sand at steam-to-oxygen ratios of 3.1:1, 4.3:1, and 6.0:1, and oxygen fluxes of 10.8, 8.6, and 8.0 scfh/ft². Ignition was established between 343 and 399°C (650 and 750°F) in all simulations, and the combustion front

was successfully propagated through the tar sand bed. The peak combustion temperatures for the tests ranged from 649 to 871°C (1200 to 1600°F). The shape of the temperature profiles as the combustion front moved down the tubes is similar to those given by several other investigators. Similar combustion temperatures have been reported by other investigators burning similar reservoir materials at the same oxygen flux.

As the combustion fronts advanced, the injection pressure rapidly increased to the maximum pressure, ranging from 630 psig for the lowest steam-to-oxygen ratio to 400 psig for the highest steam-to-oxygen ratio. The injection pressures remained high for a period of time, then decreased sharply before starting a slow pressure increase throughout the remainder of the tests. During the high pressure period for all three tests, 25 and 40% of the total product oil was produced.

The fuel deposition during the simulations ranged from 10.9 wt % of the initial bitumen to 9.2 wt % based on the nonpyrolysis-produced carbon monoxide, carbon dioxide, and hydrogen in the produced gas, the excess product water, and the residual coke on the spent sand. Fuel laydown decreased as the steam-to-oxygen ratio, and therefore the steam concentration, increased. The higher steam concentration (1) improved the displacement efficiency of the process by removing a larger portion of the bitumen from the reaction tube before it pyrolyzed to produce coke and (2) increased suppression of coking by the steam.

The overall material balances for the one-dimensional tests averaged 98.4%, while the carbon balance had a slightly lower average of 97.7%. Oxygen and hydrogen balances averaged 93.6 and 97.8%, respectively. The high average closure of all balances gave confidence in the simulation results.

Oil yield for the simulations was consistently high, ranging from 80.1 to 80.3 wt % of initial bitumen. The anticipated

trend of increasing oil yield with increasing steam-to-oxygen ratio was observed. The volumetric oil yields were slightly higher (82.2 to 93.0% original oil in place) than the weight percentage of oil recovery because of the upgrade condition of the product oil. The product oils from the three one-dimensional simulations were all upgraded compared with the initial bitumen with lower molecular weights, percentage residual compounds (compounds with >538°C [1000°F] boiling point), and viscosities. The initial bitumen API gravity for the product oils ranged from 14.1 to 15.0°, compared with 10.2° for the original bitumen.

Three-Dimensional Asphalt Ridge Simulation

The three-dimensional simulation test was preheated for 6 hours by electrical wellbore preheat with a low sweep of nitrogen gas. Ignition was accomplished by switching from nitrogen to air with the wellbore heater activated. When ignition was determined, oxygen was added to the air stream. During the ignition cycle, the injection pressure increased from 30 psig to approximately 400 psig, at which point air injection was terminated and steam injection initiated. The injection pressure steadily increased to a maximum of 670 psig as the total injection was increased to maintain an approximate flux of 40 scfh/ft² at the 482°C (900°F) isotherm. The steam-to-oxygen ratio during this period averaged 3.0:1.

The peak combustion temperatures for the thermocouple locations nearest the injection well were approximately 538°C (1000°F) and were used as the indicators for successful ignition. The vertical combustion front then moved rapidly between the injection and production wells to produce a heated channel between the process wells. Peak temperatures during the enriched air period, with its rapidly advancing combustion front, ranged from 538 to 927°C (1000 to 1700°F).

Following the start of steam injection, the combustion front stagnated between the process wells. It is postulated that the

steam began to move bitumen from the edges of and into the heated channel. This movement of steam-displaced oil into the combusted region was indicated by observed secondary and tertiary combustion peaks.

The volumetric sweep of the combustion simulation was 26.1% for the combusted zone, with an additional 6.0% for the pyrolysis zone. This 32.1% total sweep is well below the theoretical 50% sweep of an unconfined five-spot pattern. The lower sweep was caused by the rapid growth of a channel between the injection well and the production well, which limited the areal extent of the sweep zone.

Fuel deposition, as determined from the nonpyrolysis-produced gas composition and residual coke, was 56.9 wt % of the initial bitumen within the sweep area. This value is five times higher than the 10.9 wt % fuel deposition of the one-dimensional test operated at nearly identical pressure and steam-to-oxygen ratio. This result tends to support the hypothesis that additional bitumen and/or product oils were swept into the existing heated channel and were directly combusted, pyrolyzed, or cracked to produce additional fuel that had to be consumed before the front could advance.

The oil yield for the three-dimensional simulation was 41.3 wt % of the original bitumen from the sweep zone, compared with an average of 83.5% for the one-dimensional simulations. The overall material balance was 96.2%, slightly less than the 98.4% average for the one-dimensional simulations. However, the carbon balance was 100.3%, higher than the average for the one-dimensional tests. The oxygen and hydrogen balances were 96.2 and 84.7%, respectively.

Product oil from this test was significantly upgraded compared with the original bitumen and even the one-dimensional product oils. Production of an upgraded oil indicates that a large portion of the heavier components of the product oil was either pyrolyzed or cracked to produce lighter fractions.

One-Dimensional Simulations with Sunnyside Tar Sand

Five simulations of the in situ forward-combustion process and one one-dimensional simulation of hot-gas injection (HGI) were conducted on a Sunnyside tar sand containing 11.6 wt % bitumen. The combustion simulations used steam-oxygen, air-oxygen, or air as the injectant. The HGI simulation used nitrogen, carbon dioxide, and steam. Vigorous combustion was established in all combustion simulations as indicated by the complete utilization of the injected oxygen and the production of carbon monoxide and carbon dioxide. Ignition temperatures were in the range of 343 to 371°C (650 to 700°F) for all tests.

The three simulations with steam-oxygen experienced severe plugging of the reactor tube within hours of establishing oxygen injection. Attempts to resolve the plugging problem, including venting the production system to relieve the high pressure and increasing the guard heater temperature in the plugged region, were unsuccessful.

To evaluate the plugging problem three additional one-dimensional simulations were conducted. The three simulations were an enriched-air dry-combustion, an air-only dry combustion, and a HGI simulation. Enriched air was selected to minimize the effect that steam or its condensation may have on the plugging problem. Within 5 hours of establishing oxidant injection, the same plugging problem experienced in steam-oxygen tests was again occurring. Neither pressure venting of the injection end of the reactor tube nor increasing the temperature of the entire tube overcame the plugging problem.

A sample of the residual oil in the zone ahead of the pyrolysis zone was extracted from the spent sand. The oil saturation had increased from the original 11.6 wt % to 14.6 wt %. The viscosity of this residual oil at 91°C (195°F) was 207,000 cP, a 150-fold increase over the original bitumen viscosity of 1,300 cP at the same temperature.

The dry forward-combustion test with air as the only injectant also plugged within 4 hours of ignition. The injection pressure began to mirror that of the previous two simulations, however, increasing the temperature with the guard heaters in the zone immediately ahead of the combustion and pyrolysis zones reduced the plugging problem to a point where the test could be conducted at a constant injection rate and pressure. This test produced 46% of the bitumen as a highly upgraded oil by establishing and maintaining a sharp combustion front throughout the tube. However, even though the yield and the product oil quality are good, extrapolating this type of process to a field test is not practical.

The HGI test was conducted with a nonoxidative atmosphere consisting of carbon dioxide and steam which approximated the gas typical to the pyrolysis zone in the steam-oxygen tests. The tube was preheated in an identical manner as the combustion tubes so that initial bitumen mobilization and displacement would be the same. The temperature of the guard heaters was increased from the top of the tube to the bottom in such a manner as to simulate the advance of the combustion front. Within 5 hours the injection pressure had increased to greater than 950 psig. This pressure profile was very similar to those for the previous combustion tests. One pressure venting and repressurization cycle was conducted in an attempt to displace the plug, but it was not successful. The test was terminated at this point and the sample material was removed for analysis.

During the test, 8.8 wt % of the initial bitumen was produced. This product oil was very similar in quantity and appearance to the oil produced in the combustion simulations. Analysis of the HGI tube material extracted from the plug region showed a viscosity three to four times greater than the original material, indicating that the oil bank was being formed by the heavier components of the bitumen. Functional group analysis of the material indicated the viscosity increase

was caused by devolatilization in the top of the plug, with condensation in the bottom of the tube.

The performance of the HGI simulation compared to that of the Sunnyside combustion tests indicates that the oxygen flux in the injected gas is not the controlling factor in the plugging experienced in the Sunnyside simulations. What appears to be the cause of the plugging in the combustion simulations is the formation of a highly viscous, highly saturated region produced by conventional fluid flow, with the alteration of the flowing material by a combination of devolatilization and oxygen incorporation.

To further evaluate the Sunnyside plugging problem, twenty LRR experiments were conducted. Nitrogen, oxygen, and steam were injected into the tar sand at 149°C (300°F) or 204°C (400°F). Organic material was extracted from the top half, bottom half, or the entire tube based on the amount of material remaining after each test. For those runs when steam was used, it was found that not enough bitumen could be extracted from only half of the bed material, so the entire bed of spent tar sand was extracted for analysis. Infrared functional group analyses, compound type analysis, viscosities (at three temperatures), and specific gravities (at two temperatures) were conducted.

The LRR experiments indicated that two mechanisms contribute to an increase in bitumen viscosity and, therefore, the plugging of the reactor during simulations. These two mechanisms are devolatilization in the upper portions of the tube and the apparent production of more viscous, polar materials in the oxidative environment. The ketone, a polar material, concentration in the reacted bitumens generally increases with the material's viscosity. The material from the top of the tubes is generally more viscous than the material from the bottom of the tube. This indicates devolatilization of the top material and dilution of the bottom material with condensed material from the top. The effect of the reactor temperature on the resultant viscosity is

that, as the initial reactor temperature was increased, the viscosity of mobile (extractable) material decreased. This may be due to coking of some of the heavier material and production of lighter products that concentrate in the lower section of the tube.

Arroyo Grande One-Dimensional Simulations

The two Arroyo Grande, one-dimensional simulations were conducted at steam-to-oxygen ratios of 4.3:1 and 6.4:1, both with an oxygen flux of 8.0 scfh/ft². Ignition of both tests occurred in the range of 343-399°C (650-750°F) and the combustion front propagated through the tube without any problems. The peak combustion temperatures were 737 and 684°C (1359 and 1264°F). These temperatures are comparable to those of previous steam-oxygen tests using Asphalt Ridge tar sand. The maximum injection pressure for both simulations was 17.5 psig. This low injection pressure is in drastic contrast to the high pressures (400-630 psig) observed in simulations using Asphalt Ridge tar sand and the total plugging of the tubes in the Sunnyside simulations. The one operational condition that may have caused this reduction in injection pressure was the slightly higher preheat temperature used in these simulations than in the majority of the other simulations.

The fuel (coke) deposition during the simulations was 15.8 and 15.2 wt % of the initial bitumen. Fuel deposition is calculated from the nonpyrolysis-produced carbon dioxide, carbon monoxide, and hydrogen in the product gas, the excess product water, and the residual coke on the spent sand. This fuel deposition is higher than the 9 to 13 wt % for the comparable Asphalt Ridge tests, but is not unexpected based on the heavy original nature of the Arroyo Grande bitumen compared to the Asphalt Ridge bitumen.

The overall material balances for the simulations averaged 98.7%. Carbon, oxygen, and hydrogen balances averaged 92.7, 103.3, and 98.7%, respectively.

The high average closure of all balances, typical of similar simulations, gave confidence in the simulation results.

Oil yield for the simulations were 55.7 and 69.3 wt % of initial bitumen, with an increasing oil yield trend with increasing steam-to-oxygen ratio. The observed oil yields were lower than the yields obtained for simulations with similar saturations using the lighter Asphalt Ridge tar sand. The product oils from the two Arroyo Grande simulations were highly upgraded compared with the initial bitumen.

Conclusions

The three one-dimensional and one three-dimensional simulations of steam-oxygen forward combustion using Asphalt Ridge tar sand showed that as the steam-to-oxygen ratio increases, the fuel deposition decreases, yielding a higher recovery rate and combustion front velocity. The three-dimensional tests showed that channeling of the combustion front increases fuel consumption and oxygen demand while reducing oil yield. All tests showed significant increases in produced oil quality.

One-dimensional simulations using Sunnyside tar sand did not perform as expected. The tar sand can be ignited at a temperature of 343 to 371°C (650 to 700°F). However combustion could not be maintained because of plugging of the reactor. The plugging is undoubtedly caused by an increase in the viscosity of the oil bank material. Two mechanisms have been identified which contribute to this increase in viscosity: (1) devolatilization of the bitumen by the flow of hot gas ahead of the combustion zone, leaving behind a more viscous material and (2) oxygenation of the bitumen-yielding materials that are more polar, and hence, more viscous. Plugging during forward combustion will be a problem in Sunnyside tar sand. However, development of an ignition and operational procedure that produces a sharp combustion front may eliminate the plugging problem.

Arroyo Grande simulations showed that an extremely heavy tar sand can be successfully produced by steam-oxygen combustion without the plugging problem experienced with the similar Sunnyside resource. The simulations also validated the trends of decreasing fuel deposition and oxygen demand with increasing steam-to-oxygen ratio, and the increase of product oil yield and frontal velocity with increasing steam-to-oxygen ratio that were noted in previous simulations using Asphalt Ridge tar sand. The product oil quality was also significantly improved compared to the original bitumen.

The difference between the results of the Asphalt Ridge and Arroyo Grande simulations show that extrapolations from one tar sand resource to another is not accurate enough to base predictions upon. Laboratory simulations must be conducted prior to the field application of any process to a given resource.

Related Publications

Johnson, L.A., Jr., and J.J. Duvall, 1988, Physical Simulations of In Situ Forward Combustion Using Sunnyside and Arroyo Grande Tar Sand. Laramie, WY, DOE/MC/11076-2652.

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VALIDATION OF STEADY-STATE OPERATING CONDITIONS FOR THE RECYCLE OIL PYROLYSIS AND EXTRACTION (ROPETM) PROCESS

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R. William Grimes

Background

Major obstacles to the commercialization of tar sand are the high costs associated with mining, processing, and upgrading of the raw tar sand oil and refining the upgraded tar sand oil to produce salable products. To promote tar sand commercialization at a reduced financial risk, new processing technologies are required. WRI has developed the Recycle Oil Pyrolysis and Extraction (ROPETM) process. The process consists of four major steps: (1) preheating and extracting the hydrocarbonaceous material with recycled product oil, (2) pyrolyzing the extracted material at a low temperature ($\leq 399^{\circ}\text{C}$ [750°F]) in the presence of recycled product oil, (3) completing the pyrolysis of the residue at a higher temperature ($>399^{\circ}\text{C}$ [750°F]) in the absence of product oil, and (4) combusting the solid residue and pyrolysis gas to produce process heat. To simulate the process, WRI has developed 2-inch and 6-inch diameter screw pyrolysis reactor (SPR) systems. Numerous tests on three different tar sand resources had encouraging results (Cha et al. 1986, 1987, 1988, 1990; King 1989; Thomas et al. 1989; and Guffey and Holper 1990).

Objective

The objective of this task was to conduct long-term tests to prove process efficiency and to provide steady-state process evaluation criteria on the ROPE process.

Procedures

The 6-inch diameter SPR used for this study was significantly modified compared to SPR systems used in previous tests. These modifications, the operation of the modified reactor system, and the feed materials are discussed by Johnson and Grimes (1992). In summary, the system consisted of the following subsystems:

- Slurry preparation
- Slurry pumping to provide a constant reactor feed rate
- Preheat-screw reactor for water removal and bitumen solubilization
- Pyrolysis screw for the production of selected products
- A drying reactor composed of two intermeshing screws to prevent coke buildup in the segment
- Heavy product oil recycle with a calibrated metering tank
- Heat exchangers and knockouts on individual reactor segments for product oil segregation
- Sweep gas injection to remove the vaporized products from the reactor segments
- Product gas cleanup
- Spent solids collection tank

Two experiments were conducted in the modified 6-inch SPR using Asphalt Ridge tar sand. For the first test, BSPR-8, SAE-50 weight oil was used to fill the transition sections and the heavy oil metering tank and to produce the initial tar sand slurry. After the initial charge of SAE-50 weight oil, no further additions of the SAE-50 weight oil were required since sufficient quantities of heavy and product oil were being produced. The second test, BSPR-9, was initiated with heavy oil and product oil produced during BSPR-8. After the initial oil charge, no further BSPR-8 oils were required. All operating conditions were maintained as steady as possible for the tests. The average operating conditions are given in Table 1.

Table 1. Average Operating Conditions

	BSPR-8	BSPR-9
Tar sand composition, wt %		
Bitumen	9.6	10.0
Water	6.0	2.4
Sand	83.9	86.9
Insolubles	0.5	0.7
Operating time, hr	194	197
Tar sand, lb/hr	70.0	81.6
Recycle oil, lb/hr	70	80
Average reactor temperatures, °F		
Preheat screw	395	447
Pyrolysis screw	728	746
Drying screw	939	957
Average residence time, min ^a		
Preheat screw	15	15
Pyrolysis screw	40	35
Drying screw	50	50

^a Residence time for the individual screws is based on pretest calibrations using varying rpm settings.

The products consisted of oils obtained from the three knockouts and from the heavy oil recycle tank, spent sand, and produced gas. As appropriate, these products were analyzed for the following: viscosity, specific gravity, hydrocarbon-group types, and elemental composition (oil); residual carbon (spent sand); and CO₂, CO, H₂, CH₄, C₂H₆, C₂H₄, C₃H₈, C₃H₆, C4's, and C4+ hydrocarbons (produced gas).

Results

Operational times for the two extended tests, BSPR-8 and BSPR-9, were 194 and 197 hours, respectively. The feed rate and temperatures for the three reactor sections were stabilized after 36 hours for BSPR-8 and 4 hours for BSPR-9. The 36-hour time to stabilize BSPR-8 was caused by

problems with the slurry feed pump. The pump problem resulted in a 20-hour shutdown period to modify the slurry system. Following this modification, stability was quickly re-established.

Overall material balances were essentially the same, with 99.91% closure for BSPR-8 and 99.95% closure for BSPR-9. The total closure for the two tests was 99.93%. The approximate 100% closure for the overall and total organic balances show a high degree of accuracy for the testing protocol. These closures are acceptable for determining the steady-state operation of the ROPE process.

The normalized oil yields for BSPR-8 and BSPR-9 were 76.0 and 80.4 wt % of the bitumen, respectively. Normalized oil yield was determined by (1) reducing the

quantity of heavy oil produced in each test by the quantity of recycle oil used to initiate each test, (2) determining the percent of initial bitumen each product represented, and (3) normalizing the total percentage of products to 100%. The total overall oil yield for the two tests, 78.7 wt %, was approximately the same as the total oil yield from Fischer Assay of the same material, 78.0 wt %. The amounts of normalized coke produced for the two tests were 18.6 and 15.6 wt % of the bitumen for BSPR-8 and BSPR-9, respectively. The distributions of the products for the individual and combined tests are given in Table 2.

From the specific gravity and viscosity data for product oils from the BSPR-8 and BSPR-9 tests it was estimated that the effect of the SAE-50 weight oil used to initiate BSPR-8 on the properties of the heavy recycle oil had essentially been eliminated after 120 hours. The SAE-50 weight oil has a specific gravity of 0.90 and a viscosity of approximately 300 cP at 38°C (100°F). Therefore, steady-state conditions were projected to exist for the final 74

hours of BSPR-8. The change in the feed rate and the preheat and pyrolysis temperatures between BSPR-8 and BSPR-9 caused a minor change in the properties of the produced fluids. However, the upset of the system lasted less than 48 hours, as indicated by the properties of the produced oils. Therefore, steady-state operation was reestablished and maintained for over 149 hours at the conditions used in BSPR-9. The determination of the amounts of carbon on the spent sand further confirms the time required for the system to return to steady-state operation.

The elemental analyses of the produced oils obtained from four sources show generally constant values after the establishment of steady-state conditions, as did the specific gravity and viscosity data. A decrease in the hydrogen content in the heavy recycle oil, from 11.8 wt % down to less than 11 wt %, supports the hypothesis that the effect of the initial SAE-50 weight oil is eliminated after 120 hours of BSPR-8 operation. The original bitumen had a hydrogen content of 10.9 wt %.

Table 2. Oil Yield for Steady-State Tests, Normalized to 100 wt % of Bitumen

	Fischer Assay	BSPR-6 ^a	BSPR-8	BSPR-9	Combined Tests
Pyrolysis temperature, °F	932	750	728	746	--
Oil					
Light	--	--	37.8	33.2	35.0
Heavy	--	--	<u>38.2</u>	<u>47.2</u>	<u>43.7</u>
Total	78.0	83.3	76.0	80.4	78.7
Gas	4.0	6.7	5.4	4.0	4.5
Coke	18.0	10.0	18.6	15.6	16.8

^a Cha et al. 1988

Conclusions

The following conclusions can be made from the two extended-time (approximately 200 hours) Asphalt Ridge tests of the ROPE process:

- Tar sand can be processed using the ROPE process without major operational problems.
- Oil yields slightly greater than Fischer Assay were obtained when the Asphalt Ridge tar sand was pyrolyzed in the presence of recycled product oil composed of heavy oil produced from the bitumen.
- If a recycle oil other than a product of the material being processed is used to initiate the process, the effect of the oil can be eliminated within approximately 120 hours and steady-state conditions can be expected. If a heavy product oil derived from the material being processed is used as the starting recycle oil, then steady-state operations can be established and maintained within 1 to 2 days.
- The oils produced by the ROPE process are highly upgraded compared to the bitumen and can be used as a refinery feedstock for the production of diesel fuel.

Related Publications

Cha, C.Y., F.D. Guffey, and L.J. Romanowski, 1987, Tar Sand Pyrolysis with Product Oil Recycling-Progress Report. Laramie, WY, DOE/MC/11076-2642.

Cha, C.Y., L.A. Johnson Jr., and F.D. Guffey, 1990, Investigation of the ROPETM Process Performance on Sunnyside Tar Sand. Laramie, WY, DOE/MC/11076-2912.

Guffey, F.D., and P.A. Holper, 1990, Laboratory Simulation Studies of Steady State and Potential Catalytic Effect in the ROPETM Process. Laramie, WY, DOE/MC/11076-3032.

Johnson, L.A. Jr., and R.W. Grimes, 1992, Recycle Oil Pyrolysis and Extraction (ROPETM) Process, Validation of Steady-State Operation Conditions, Laramie, WY, WRI-92-R059.

King, S.B., 1989, Processing of Arroyo Grande Tar Sand Using the Recycle Oil Pyrolysis and Extraction (ROPETM) Process. Laramie, WY, DOE/MC/11076-2991.

Thomas, K.P., P.M. Harnsberger, and F.D. Guffey, 1989, Evaluation of the Potential End Use of Oils Produced by the ROPETM Process from California Tar Sand. Laramie, WY, DOE/MC/11076-2950.

DEVELOPMENT OF AN INCLINED LIQUID FLUID-BED REACTOR SYSTEM FOR PROCESSING TAR SAND

Lyle A. Johnson, Jr.

Background

A new processing technique and reactor system for the surface processing of tar sand has been investigated by WRI. The process is referred to as ROPETM (recycle oil pyrolysis and extraction) and consists of two pyrolysis steps for recovering products that require minimal upgrading. The initial step is low-temperature (<427°C [800°F]) retorting of the tar sand in the presence of recycled product oil. Then the retorted sand is further pyrolyzed at a higher temperature (>482°C [900°F]) in the absence of recycled product oil. One reactor system being developed, based on the ROPE process, is an inclined liquid fluid-bed reactor (ILFBR).

The advantages of an inclined fluid-bed reactor are high heat transfer rates, high solids throughput, and the flexibility of the system to operate with a wide range of residence times. This latter item can be addressed by changing the bed angle and/or the fluidizing velocities of the system. Also, a nearly horizontal, inclined bed provides plug flow for solids at more uniform residence times and permits a wider range of particle sizes to be used. Uniform residence time is attained by the vertical flow of gas through the nearly horizontally flowing solid and liquid bed. An added advantage of the fluid bed is the absence of internal moving parts.

An ILFBR system was designed and constructed based on data obtained during WRI development of the screw pyrolysis reactor (SPR) systems (Cha et al. 1987, 1988) and on cold-flow model studies (Johnson and Cha 1987). The shakedown tests using this reactor system showed that most of the bitumen could be recovered from Asphalt Ridge tar sand.

Objective

The objective of this investigation was to evaluate an ILFBR system when modified to improve operability.

Procedures

The original ILFBR system is described in the report by Merriam and Cha (1987). Modifications to an existing ILFBR system consisted of changes in the product collection, the product oil recycle, and the tar sand feed components of the reactor system. Knockout pots on the product collection system were enlarged to permit additional settling time for entrained liquids, and a vertical baffle was added so the gas must traverse a larger portion of the vessel before exiting. Also, a cyclone separator was added to the composite gas line to remove any entrained liquids and solids that may pass the condensers and knockouts. The slurry feed system was changed so that the feed did not drop vertically onto the disperser plate, but entered the unit horizontally with an increased amount of recycle oil.

A test was conducted with the modified ILFBR to determine the operability of the system. The test used Asphalt Ridge tar sand and product oil from a previous Asphalt Ridge 6-inch SPR ROPE test as the initial recycle oil. The test used the operational parameters identified in 2-inch-diameter SPR tests as producing the best oil yield-oil quality combination. The slurry feed for this test was approximately 20 lb/hr (9.0 kg/hr) of a 1:1 tar sand/product oil mixture. The three fluidization sections had operating temperatures of 316, 371, and 399°C (600, 700, and 750°F). The recycle oil reflux zone and the residual bitumen pyrolysis (high-temperature) zone were operated at 399 and 524°C (750 and 975°F), respectively.

The test was conducted for 11 hours, with occasional interruptions for equipment adjustments and repairs. At the end of 11 hours, the test was terminated because there was still excessive liquid carryover into the gas cleanup system and there was no indication of solids return from the high-temperature region of the pyrolysis screw.

Results

The liquid collected from the gas cleanup system during the test amounted to more than 45 wt % of the total recycle oil and bitumen fed to the fluidized bed. From simulated distillation tests, about 27 wt % of the total recycle oil and bitumen is distillable up to 399°C (750°F). Therefore, at least 40% of the collected liquid was from entrainment of liquid droplets in the fluidizing gas stream or from extensive pyrolysis of the material in the plugged region because of the extended time it remained in the 399°C (750°F) zone. The amount of entrained or pyrolysis-produced liquid may have been higher than 40% of the collected liquid because a considerable amount of liquid carryover past the cyclone was evident during cleanup of the system. The amount of entrained and pyrolysis-produced liquid may be approximated by simulated distillation analysis.

Following the test, the fluidized bed was opened for inspection. A blockage had developed beginning in the second fluidizing zone and continuing through most of the third. The material removed from this blockage was fairly cohesive and closely resembled raw tar sand. Only a small amount of sand was removed from the pyrolysis screw. It was also noted that the seals on the three discharger sections, especially in the second and third zones, had failed during the test from heatup and cooldown cycles. This had gone unnoticed because of their location within the insulating blanket.

The failure of the test to operate satisfactorily may be attributed to (1) excessive entrainment of liquid in the

fluidizing gas and/or (2) failure to maintain sufficient fluidizing gas velocities in the three zones because of external leakage of the gas.

In the first case, liquid entrainment would increase the density of the slurry phase as it progressed down the fluid bed. As the density increased, so must the minimum fluidizing velocity. But since the fluidizing gas rate and, therefore, the fluidization velocity were constant in the test, at some point the required minimum fluidization velocity for the increasingly dense slurry would be greater than the fluidizing velocity in the zone. The bed, especially solids, would cease to move, causing a buildup within that area.

In the second case, the fluidizing velocity within a zone would decrease proportionally to the amount of gas escaping from the discharger outside of the bed. When the fluidizing gas velocity became less than the required minimum fluidization velocity, the slurry would not continue to move as a single uniform mass. It would separate into solid and liquid dominant phases, and the solid dominant phase would settle out. If entrainment was occurring at the same time, then plugging would occur more rapidly than with either cause alone.

Two approaches are proposed to overcome the problems identified in this test. To prevent leakage of the fluidizing fluid before it passes through the discharger, the seal between the discharger and the fluidizing fluid supply system should be changed to a positive (i.e., welded) seal. As for the liquid entrainment problem, many possible solutions exist. Areas to be considered for solving this problem are: (1) maintaining fluidization velocities closer to the minimum fluidization velocity for the slurry, (2) adding a spray system within the disengaging space of the fluid bed to increase coalescence of the entrained liquid and to replenish the liquid content within the fluid bed, and (3) modifying the system to a liquid-solid system rather than the present gas-liquid-solid system.

Conclusions

Although several problems occurred during the development of the ILFBR system, the development of such a system will be valuable for the processing of variable feed resources that require different operating parameters. To progress with development, two different approaches should be investigated. These are (1) adding a spray system to induce coalescence and to replenish the liquid content within the fluid bed and (2) changing the system so the feed slurry is fluidized by liquid, thereby eliminating the injected gas phase. In either case, simulated distillation analysis should be conducted on the produced oils to determine what percentage of the excess produced oil is from entrainment or pyrolysis.

Related Publication

Johnson, L.A., Jr., 1987, Development of an Inclined Liquid Fluid-Bed Reactor System for Processing Tar Sand. Laramie, WY, DOE/MC/11076-2951.

AN EVALUATION OF OIL PRODUCED FROM ASPHALT RIDGE (UTAH) TAR SAND AS A FEEDSTOCK FOR THE PRODUCTION OF ASPHALT AND TURBINE FUELS

**Kenneth P. Thomas
P. Michael Harnsberger
Frank D. Guffey**

Background

The potential end use of the bitumen from the Asphalt Ridge (Northwest) tar sand deposit in Utah was previously evaluated by Thomas et al. (1986). In that investigation, it was determined that the bitumen and a vacuum distillation residue met ASTM specifications as viscosity-graded asphalts, AC-5 and AC-30, respectively. In addition, the materials possessed unusual properties regarding performance. Wenger et al. (1952) and Bunger (1979) also investigated the potential of producing asphalt from several tar sand bitumens and concluded that the products compared well with petroleum-derived asphalts and ASTM specifications.

The potential of producing transportation fuels, in particular aviation turbine fuels, from tar sand bitumens has also been investigated. Under contract to the U.S. Air Force, the Ashland Petroleum Company (Moore et al. 1987) and the Sun Refining and Marketing Company (Talbot et al. 1986) have produced small quantities of specification-grade JP-4 and JP-8 fuels from Big Clifty (Kentucky) and Sunnyside (Utah) tar sands. Thomas et al. (1986) have also evaluated the potential of producing aviation turbine fuels from vacuum distillates of Asphalt Ridge (Northwest) tar sand bitumen. Based on molecular composition data, they concluded that the distillates have the potential to be hydrogenation feedstocks for the production of aviation turbine fuels.

Objective

The objective of this study was to evaluate the potential end uses of Asphalt Ridge tar

sand by studying the properties of oil produced by the wet, forward combustion of a block of that material.

Procedures

The oil evaluated in this study was produced from a block of Asphalt Ridge tar sand using a wet, forward combustion process (Johnson and Romanowski 1987). A composite of the oil was subjected to vacuum distillation to produce a residue and a distillate.

Asphalt ASTM specification tests were performed on the residue in accordance with the procedures set forth in Method D 3381 (ASTM 1991) for viscosity-graded asphalts. However, viscosities were determined on a Brookfield viscometer instead of by Methods D 2170 and D 2171. Method D 3381 contains two tables that define the minimum and maximum specification values for paving asphalts. The second table contains the more restrictive set of values. The other test procedures applied to the residue included the thin-film accelerated-aging test (TFAAT) and an evaluation of briquettes to water susceptibility.

The chemical and physical properties of the distillate sample (elemental composition, molecular weight, density, viscosity, and distillation data) were obtained using standard WRI or ASTM procedures. The hydrocarbon-group-type distribution of the neutral fraction was determined using a gas chromatographic/mass spectrometric (GC/MS) method.

Results

Asphalt Potential

Vacuum distillation of the thermally-produced oil resulted in 46.6 wt % residue boiling above 412°C (775°F). The viscosity of the +412°C (+775°F) residue measured at 60°C (140°F) was 1174 P, which is within the specification limits for an AC-10 viscosity-graded asphalt.

Examination of the data from the residue analysis (Table 1) indicates that the material would pass the ASTM Method D 3381 Table 1 requirements for an AC-10 viscosity-graded asphalt. The residue also meets all of the D 3381 Table 2 requirements for an AC-10 asphalt except the requirement for the 135°C (275°F) viscosity (250 cP required). The lower viscosity (202 cP) indicates that the residue has a higher temperature susceptibility than allowed for D 3381 Table 2 asphalts. The penetration value for the residue (102) is also somewhat high compared with the

specification values, although there is not a maximum value for penetration. These findings are consistent with other data previously obtained on tar sand products derived from Asphalt Ridge (Northwest) tar sand bitumen which were evaluated with respect to asphalt specifications (Thomas et al. 1986).

Rheological analysis of the sample before and after TFAAT aging indicates that the residue had an extremely low aging index (Table 2). In most cases, a low aging index is good from the standpoint of long-term pavement embrittlement; however, the extremely low aging index may indicate that the asphalt will not harden properly, resulting in low pavement stability. It may also indicate resistance to rapid age hardening. It may be possible to offset this problem by blending the residue with a higher viscosity-graded asphalt or conducting the vacuum distillation to a higher final boiling point, thus producing a more viscous residue.

Table 1. Results of ASTM D 3381 Specification Tests on +412°C Residue

Test	Specifications for AC-10	+412°C Residue
Viscosity, 60°C, P	1000 ±200 ^a	1174
Viscosity, 135°C, cP, min	150 ^b , 250 ^c	202
Penetration, 25°C, 100 g, 5 sec, dmm, min	70 ^b , 80 ^c	102
Flash Point, Cleveland open cup, °C, min	219 ^a	263
Solubility in trichloroethylene, %, min	99.0 ^a	99.9
Tests on residue from thin-film oven test		
Viscosity, 60°C, P, max	5000 ^a	3124
Ductility, 25°C, 5 cm/min, cm, min	50 ^b , 75 ^c	105+

^a Value common to ASTM D 3381 Tables 1 and 2

^b ASTM D 3381, Table 1

^c ASTM D 3381, Table 2

Table 2. Rheological Characteristics of Unaged and TFAAT-Aged Petroleum Asphalts and +412°C Residue

Sample	Dynamic Viscosity, Poise, 60°C		Tan Delta		Aging Index
	Unaged	Aged	Unaged	Aged	
+412°C Residue	1.23×10^3	4.89×10^4	24.8	6.4	39.8
Boscan asphalt	8.11×10^2	1.79×10^5	9.1	3.0	220.7
California Coastal asphalt	1.27×10^3	1.72×10^5	9.9	4.0	135.4

Tan delta = viscous flow modulus/elastic modulus

Tan delta determined at $G^* = 2.2 \times 10^4$

Aging Index = aged viscosity/unaged viscosity

Rheological measurements were made in the dynamic mode, which facilitates obtaining the elastic and viscous flow components of viscosity. The elastic modulus and viscous flow modulus are related to viscosity by: $\eta^* = [(G')^2 + (G'')^2]^{1/2} / \omega$, where η^* = dynamic viscosity, G' = elastic modulus, G'' = viscous flow modulus, and ω = shear frequency. The elastic modulus has been related to the ability of a system to recover from deformation caused by a load. The viscous flow modulus has been related to plastic or permanent deformation of a system caused by a load. The tan delta (viscous flow modulus/elastic modulus) is a ratio used to measure the relative contribution of each component to the viscosity (Ferry 1961). A high tan delta at low temperatures has been related to the ability of a system to relieve low temperature thermal stress by a creep flow mechanism. However, at higher temperatures, such as 60°C (140°F), a high tan delta may indicate a tender asphalt (an asphalt that flows too easily under stress and, thus may be prone to rutting).

Although there are no direct correlations between tan delta values and pavement performance properties, tan delta values may indicate tendencies for certain pavement problems to occur. The tan delta values for both the unaged and aged residues are quite high compared with those for petroleum asphalts. The tan delta

values (both unaged and aged) are compared at the same G^* , or complex dynamic modulus. The G^* value can be called the stiffness value; therefore, the tan deltas are all compared at the same asphalt stiffness. Relative to petroleum asphalts, the tan delta values of both unaged and aged samples are significantly higher, indicating that the viscous flow component of viscosity has more influence on the properties of the asphalt than does the elastic component. As a result, the asphalts may be tender.

The water susceptibility test is an indirect measure of the resistance of an asphalt-aggregate mixture to moisture-induced damage. The +412°C (+775°F) residue performed quite well when compared with petroleum asphalts. The two aggregates (Hol limestone and Texas silica) used in the test are very susceptible to water stripping. The Hol limestone aggregate is essentially calcium carbonate with very few crystal imperfections. Most petroleum asphalts survive only about 5 cycles with this aggregate, the exception being the California Coastal asphalt, which survived 23 cycles. This large number of cycles is due primarily to the fact that the California Coastal asphalt contains a high concentration of carboxylic acids that interact strongly with this carbonate aggregate. The Texas silica aggregate is a highly moisture-sensitive aggregate.

Although the residue briquette only survived 2 cycles, this result represented some improvement because the commonly used Boscan asphalt only survived 1 cycle.

Aviation Turbine Fuel Feedstock Potential

In general, the chemical and physical properties of the -412°C (-775°F) distillate are improved with respect to the original bitumen and the thermally-produced oil. For example, the molecular weight is decreased from 690 amu for the bitumen (320 amu for the thermally-produced oil) to 220 amu for the distillate, and the viscosity of the distillate is only 15 cP at 16°C (60°F) (Table 3). The chromatographic separation of the distillate fraction provides quantitation of the neutral and polar fractions. The neutral fraction represents 64.7 wt % of the distillate fraction. The polar fraction represents 35.3 wt % by difference. These results indicate that a majority of the distillate fraction is composed primarily of hydrocarbon compounds, while the polar fraction contains the undesired heteroatomic compounds.

The neutral fraction was further analyzed by combined GC/MS to determine the hydrocarbon-group types present in the

distillate fraction. These results indicate that the neutral fraction is composed primarily of aromatic species that include alkylbenzenes, indanes/tetralins, naphthalenes, fluorenes, and anthracenes/phenanthrenes. These aromatic hydrocarbon types comprise 87.1 wt % of the neutral fraction. Saturated hydrocarbons account for the remaining 12.9 wt % of the neutral fraction. The tricyclic alkanes are the most predominant saturated hydrocarbon class present in this subfraction. Only a trace (1.9 wt %) of alkanes was found in the fraction.

The high aromatic content of the neutral fraction indicates that the distillate has potential use as an advanced aviation turbine fuel feedstock. Hydrogenation of the distillate fraction would be necessary to saturate the aromatic ring systems and remove the heteroatom-containing species. Depending on the degree of hydrogenation, the intermediate may satisfy feedstock requirements for the production of either a high-density fuel or an endothermic fuel (Smith et al. 1986). The degree of hydrogenation required to produce a high-density fuel (JP-8X) is severe, but current prototypic specifications for JP-8X allow for up to 30 vol % aromatic hydrocarbons to be present in the finished fuel.

Table 3. Chemical and Physical Properties of the Bitumen and Its Products

Property	Bitumen	Thermally-Produced Oil	IBP-412°C Distillate
Carbon, wt %	85.8	86.4	87.0
Hydrogen	11.5	11.6	11.8
Nitrogen	1.1	1.1	0.6
Sulfur	0.4	1.3	0.7
Oxygen (by difference)	1.2	-	-
H/C Ratio	1.61	1.60	1.62
Gravity, °API	10.1	16.0	22.8
Molecular weight	690	320	220
Viscosity, cP			
16°C	-	-	15
38°C	-	134	-
60°C	59,000	41	-

Production of a prototypic endothermic-type fuel would require more complete hydrogenation than that required for the production of a high-density fuel. The greater severity of hydrogenation is required because endothermic-type fuels are envisioned to be composed of entirely saturated ring systems that would undergo dehydrogenation reactions during hypersonic flight by adsorbing heat from aircraft surfaces.

The relatively low concentration of alkanes in the distillate fraction (1.2 wt %) is advantageous for production of both high-density and endothermic-type fuels. A low concentration of alkanes in the finished fuels should not adversely affect either the freeze point or density requirement specified for high-density fuels. In addition, a low concentration of alkanes will not have a significant impact on the relative concentration of cyclic saturated hydrocarbons required in endothermic-type fuels.

Conclusions

The +412°C (+775°F) distillation residue met all of the specification tests for Table 1 requirements of an AC-10 asphalt. In addition, the residue met all of the more stringent Table 2 requirements but one, the viscosity requirement at 135°C (275°F). This indicates the residue has a higher temperature susceptibility than allowed by Table 2 requirements. The residue also had an unusually low aging index, indicating that it may not set properly or it is resistant

to rapid age hardening. Results from successive freeze-thaw cycling indicate that the residue, when coated on appropriate aggregates, is comparable to or better than some petroleum asphalts coated on the same aggregates. This indicates the residue is resistant to moisture-induced loss of strength.

The -412°C (-775°F) distillate of the thermally-produced oil was improved in quality with respect to the bitumen and the produced oil. Significant reductions were noted in molecular weight and viscosity. Combined GC/MS analysis of the neutral fraction of the distillate indicated it is composed of primarily 3-ring saturate-type compounds and 2- and 3-ring aromatic-type compounds. It is believed that these aromatic compounds, upon hydrogenation, could serve as the basis for the production of high-density or endothermic aviation turbine fuels.

Related Publications

Thomas, K.P., P.M. Harnsberger, and F.D. Guffey, 1994, An Evaluation of Oil Produced from Asphalt Ridge (Utah) Tar Sand as a Feedstock for the Production of Asphalt and Turbine Fuels, accepted for publication in Fuel Sci. and Tech. Int.

Thomas, K.P., P.M. Harnsberger, and F.D. Guffey, 1987, Potential End Uses of Oil Produced by Wet Forward Combustion of Asphalt Ridge Tar Sand. Laramie, WY, DOE/MC/11076-2451.

EVALUATION OF THE POTENTIAL END USE OF OILS PRODUCED BY THE ROPETM PROCESS FROM CALIFORNIA TAR SAND

**Kenneth P. Thomas
P. Michael Harnsberger**

Background

The evaluation or production of transportation fuels and asphalts from tar sand has been the subject of numerous publications. Thomas et al. (1986, 1987) evaluated oil recovered by wet, forward combustion and bitumen recovered by steamflood from the Asphalt Ridge tar sand deposit in Utah. Bunker (1979) and Wenger et al. (1952) also investigated the potential of producing asphalt from several tar sand bitumens and concluded that the products compared well with petroleum-derived asphalts and met ASTM specifications.

Under contract to the U.S. Air Force, the potential for producing aviation turbine fuels from tar sand bitumens was studied. Ashland Petroleum Company and the Sun Refining and Marketing Company each produced specification-grade JP-4 and JP-8 turbine fuels from both Big Clifty (Kentucky) and Sunnyside (Utah) tar sands. Ashland concluded that high-quality aviation turbine fuels can be produced from tar sand bitumens, but that in today's market the cost is not competitive. Their processing scheme included asphalt residual treatment (ARTSM), reduced crude conversion (RCCSM), and hydrotreatment (Moore et al. 1987). Sun also produced specification-grade turbine fuels using a process that consisted of hydrovisbreaking and catalytic hydrotreating or hydrocracking (Talbot et al. 1986).

Objective

The objective of this study was to evaluate the potential end uses of two oil streams produced from California tar sand by the ROPETM process. A distillate and its

hydrogenated process intermediates were evaluated as transportation fuels. A residue prepared from the heavy product oil stream was evaluated as an AC-10 asphalt.

Procedures

The distillate and heavy product oil were obtained during process development unit (PDU) run SPR-111 (King 1989). Tar sand from the Arroyo Grande deposit near Edna, California, was processed in the reactor. The distillate was obtained from the second knockout, and the heavy product oil was obtained from the heavy oil outlet of the screw reactor.

Hydrogenation of the distillate was conducted in a bench-scale, fixed-bed system, operated in the downflow, once-through mode. Six process intermediates were collected during steady-state operation of the reactor. The chemical and physical properties (elemental composition, specific gravity, and distillation range) of the distillate and the process intermediates were obtained using ASTM (ASTM 1991) or standard procedures developed by WRI. The hydrocarbon-group-type distribution of the distillate and a process intermediate were determined using a gas chromatographic/mass spectrometric (GC/MS) procedure.

After the removal of very fine solid material from the heavy product oil, it was subjected to vacuum distillation to produce a residue suitable for evaluation as an asphalt. The asphalt ASTM specification tests were performed on the residue in accordance with the procedures set forth in Method D 3381 for viscosity-graded asphalts.

However, viscosities were determined on a Brookfield viscometer instead of by Methods D 2170 and D 2171. Method D 3381 contains two tables that define the minimum and maximum specification values for paving asphalts. The second table contains the more restrictive set of values. Other test procedures applied to the residue were the thin-film accelerated-aging test (TFAAT) and an evaluation of briquettes to water susceptibility.

Results

Transportation Fuel Potential

The chemical and physical properties of the distillate and three of the process intermediates are listed in Table 1. The sample number of the process intermediate corresponds to the test number listed by Thomas and Harnsberger (1989). In general, the trace amounts of nitrogen and sulfur decreased with increasing severity of the reactor operating conditions and were less than that contained in the original distillate. In addition, the percentage of oil

distilling above 371°C (700°F) decreased from 19.1 to 13.0 wt % with increasing severity and was less than that contained in the distillate. The distillate originally contained 26.7 wt % distilling above 371°C (700°F). The hydrogen-to-carbon atomic (H/C) ratio of Sample #6 increased from 1.70 for the distillate to 1.89, and the specific gravity decreased from 0.8972 to 0.8355.

Because Sample #6 contained part-per-million levels of heteroatoms and had the highest H/C ratio, it was analyzed by GC/MS for hydrocarbon-group types (Table 2). The data in Table 2 are divided into the approximate boiling ranges for the production of gasoline (IBP-177°C/IBP-350°F) and jet and diesel fuel (177-371°C/350-700°F). The distillate contained no material distilling in the gasoline feedstock range, whereas Sample #6 contained about 47 wt % distilling in this range. This hydrotreated product still contained some alkenes (14 wt %), which need to be hydrogenated before a stable fuel can be produced from this fraction.

Table 1. Chemical and Physical Properties of the Distillate and Selected Process Intermediates

Property	Distillate	Sample #1	Sample #2	Sample #3
Elemental composition, wt %, (ppm)				
Carbon	84.8	86.4	86.0	85.6
Hydrogen	12.1	13.2	13.4	13.6
Nitrogen	0.5	(400)	(<20)	(<20)
Sulfur	1.7	(910)	(66)	(140)
Oxygen	1.4	ND	ND	ND
Hydrogen-to-carbon atomic ratio	1.70	1.82	1.86	1.89
Specific gravity, 16°C	0.8972	ND	ND	0.8355
Distillation data, vol %, ASTM D 2887				
IBP-177°C	6.8	11.5	11.2	13.6
177-371°C	66.5	69.4	71.3	73.4
+371°C	26.7	19.1	17.5	13.0

ND = not determined

Table 2. Results of Hydrocarbon-Group-Type Analysis of the Distillate and Sample #6 Determined by GC/MS, wt %

Hydrocarbon Type	Distillate 177-371°C ^a	Sample #6 IBP-177°C	Sample #6 177-371°C
Alkanes	32.0	7.7	27.7
Alkenes	26.6	14.2	15.4
Monocyclic alkanes	0	19.0	2.2
Dicyclic alkanes	0	0	1.2
Total saturate hydrocarbons	58.6	40.9	46.5
Alkylbenzenes	0.4	5.9	2.1
Indanes/tetralins	4.7	0	3.8
Naphthalenes	1.6	0	0
Fluorenes	1.1	0	0
Anthracenes/phenanthrenes	0.3	0	0
Total aromatic hydrocarbons	8.1	5.9	5.9
Total hydrocarbons	66.7	46.8	52.4

^a 30.9 wt % of the sample was not analyzed because it was in the polar fraction

Unfortunately, this fraction, after hydrotreating to convert the alkenes to alkanes, will have too high of a concentration of alkanes to be suitable for the production of gasoline or gasoline-blending stock. Too high of a concentration of these alkanes will have a detrimental effect on the octane rating of the finished fuel. The distillate contained about 67 wt % distilling in the jet and diesel fuel feedstock range, whereas Sample #6 contained about 52 wt % distilling in this range. Again the hydrotreated product still contained some alkenes (15 wt %), which will have to be hydrogenated before a stable fuel can be produced. Upon hydrogenation, the alkenes are converted to alkanes. Consequently, the 177-371°C (350-700°F) distillate from the process intermediate is not suitable for the production of conventional or high-density aviation turbine fuels because the alkane content is too high. The limit for this class of compounds in a high-density turbine fuel is 10 vol %. High concentrations of alkanes in aviation turbine fuels can have an adverse effect on the freeze point of the fuel.

However, because of the high alkane content of this distillate range, this fraction is valuable as a diesel fuel blending stock. In diesel fuels, alkanes are valuable because they have a positive effect on the cetane number.

Asphalt Potential

After vacuum distillation of the filtered heavy product oil to an equivalent temperature of 416°C (780°F), the viscosity of the residue was 1381 poise (P) at 60°C (140°F), slightly high for an AC-10 asphalt. Therefore, 6.06 g of the 385 to 416°C (725 to 780°F) distillate (0.9% of the total material, 11.5% of the 385 to 416°C/725 to 780°F distillate, or 4.4% of the total distillate) were added back to the residue. Using the data from simulated distillation analysis, 80.7 wt % residue is reached at 410°C (770°F). This resulted in a residue with a viscosity of 1060 P at 60°C (140°F).

Examination of the data listed in Table 3 for the residue shows that it did not pass one of the ASTM Method D 3381 requirements for an AC-10 viscosity-graded asphalt.

Table 3. Results of ASTM D 3381 Specification Tests on +410°C Residue

Test	Specifications for AC-10	+410°C Residue
Viscosity, 60°C, P	1000 ± 200 ^a	1060
Viscosity, 135°C, cP, min	150 ^b , 250 ^c	200
Penetration, 25°C, 100 g, 5 s, dmm, min	70 ^b , 80 ^c	97
Flash point, Cleveland open cup, °C, min	219 ^a	290
Solubility in trichloroethylene, %, min	99.0 ^a	98.1
Tests on residue from thin-film oven test		
Viscosity, 60°C, P, max	5000 ^a	3153
Ductility, 25°C, 5 cm/min, cm, min	50 ^b , 75 ^c	80

^a Value common to ASTM D 3381 Tables 1 and 2

^b ASTM D 3381, Table 1

^c ASTM D 3381, Table 2

The requirement not met was the trichloroethylene solubility test. This is an indication of the difficulty in removing solids to a level of 99+% solubility of the residue and the extreme fineness of the solids in the original heavy oil. All other values obtained in the testing show that the residue meets the requirements in D 3381 Table 1, but not the more stringent requirements in D 3381 Table 2. With the exception of the solubility value, these results are quite similar to findings previously reported on other tar sand asphalts (Thomas et al. 1986, 1987).

The data from rheological analysis of the sample before and after TFAAT aging are listed in Table 4. These data suggest that the residue had an extremely high aging index. An asphalt with such a high aging index will be very susceptible to cracking and embrittlement, even in the most favorable climates. The extremely high aging index may be the result of the fine solid material in the residue catalyzing an oxidation process, or perhaps the solid material promotes molecular structuring after aging resulting in the large observed viscosity increase.

Table 4. Rheological Characteristics of Unaged and TFAAT-Aged Petroleum Asphalts and +410°C Residue

Sample	Dynamic Viscosity, Poise, 60°C		Tan Delta		Aging Index
	Unaged	Aged	Unaged ^a	Aged ^b	
+410°C Residue	1.06 x 10 ³	1.66 x 10 ⁷	13.8	1.08	15,660
Wyoming Sour	1.50 x 10 ³	3.04 x 10 ⁵	17.8	1.52	202.6
Boscan asphalt	8.11 x 10 ²	1.79 x 10 ⁵	8.5	1.19	327.3
California Coastal asphalt	1.27 x 10 ³	1.72 x 10 ⁵	10.4	1.21	557.3

Tan delta = viscous flow modulus/elastic modulus

Aging Index = aged viscosity/unaged viscosity

^a Tan delta determined at G* = 1.9 x 10⁴

^b Tan delta determined at G* = 2.1 x 10⁶

Rheological measurements were made in the dynamic mode, which facilitates obtaining the elastic and viscous flow components of viscosity. Definitions of the rheological parameters are provided in the preceding article of this report.

The tan delta value for the unaged residue falls in the range typical of petroleum asphalts; however, the tan delta value for the aged residue is significantly lower than the aged petroleum asphalts. This is another indication that the residue will be subject to cracking and embrittlement. The tan delta values are compared at the same G^* , or complex dynamic modulus. The G^* value can be called the stiffness value; therefore, the tan deltas are all compared at the same asphalt stiffness. In effect, the extremely high viscosity of the aged residue is factored out in this comparison.

The water susceptibility test is an indirect measure of the resistance of an asphalt-aggregate mixture to moisture-induced damage. The residue performed adequately when compared with petroleum asphalts. The Teton aggregate used in the test is very susceptible to water stripping, whereas the Wyoming limestone shows moderate resistance to water stripping. Although the sample prepared with the Teton aggregate broke on the first cycle as did the petroleum asphalts, other binders that have been tested on this aggregate have virtually disintegrated on the first cycle. The sample prepared with the +410°C (+770°F) residue on the Wyoming limestone aggregate showed improvement over the petroleum asphalt. The petroleum asphalt briquette broke after 14 cycles, whereas the briquette prepared with the +410°C (+770°F) residue survived more than 30 cycles without breaking. Wyoming Sour petroleum asphalt is a common asphalt used in the region where both aggregates are obtained. The California Coastal petroleum asphalt is another common asphalt that was chosen for comparison. These two petroleum asphalts were chosen for comparison purposes only and do not necessarily represent the results of all petroleum asphalts coated on these two selected aggregates.

Conclusions

A series of hydrotreating experiments was conducted on the distillate obtained from PDU run SPR-111. In general, the amounts of heteroatoms decreased with increasing severity of the reactor operating conditions. A process intermediate (Sample #6) was selected and analyzed for hydrocarbon-group types, and the subsequent data were arranged according to gasoline and jet and diesel fuel production. The data show that the fraction of Sample #6 distilling in the gasoline feedstock range is inappropriate for the production of either gasoline or gasoline-blending stock because it is too high in alkanes. The fraction of material distilling in the jet and diesel fuel feedstock range is also inappropriate for the production of aviation turbine fuels because it is too high in alkanes. However, the presence of alkanes makes this fraction valuable for the production of diesel fuel.

After filtration and distillation of the heavy product oil, a +410°C (+770°F) residue met all of the ASTM specification tests for viscosity-graded asphalts except the solubility specification. This specification was not met because the residue still contained a small amount of fine solid material. The residue had a very high aging index, which suggests that it is quite susceptible to rapid age hardening or molecular structuring and that a pavement constructed with this material will be subject to excessive embrittlement. Results from successive freeze-thaw cycling show that the residue is comparable to petroleum asphalts when it is coated on the same, appropriate aggregates.

Related Publication

Thomas, K.P., and P.M. Harnsberger, 1989, Evaluation of the Potential End Use of Oils Produced by the ROPETM Process from California Tar Sand. Laramie, WY, DOE/MC/11076-2950.

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COAL RESEARCH

GROUNDWATER REMEDIATION ACTIVITIES AT THE ROCKY MOUNTAIN 1 UNDERGROUND COAL GASIFICATION TEST SITE

Steven R. Lindblom

Background

The Rocky Mountain 1 (RM1) underground coal gasification (UCG) test was the most extensive UCG experiment to be conducted outside the former Soviet Union. The RM1 test was designed to simultaneously test two UCG process configurations: elongated linked well (ELW) and controlled retracting injection point (CRIP). The test was conducted from November 16, 1987 through February 26, 1988 near Hanna, Wyoming. Testing of the ELW process lasted approximately 57 days, ending on January 16, 1988. A total of 4,430 tons of coal was gasified using the ELW process and the average higher heating value (HHV) of the product gas was 261 Btu/scf on a dry gas basis. The CRIP experiment lasted 93 days, ending on February 26, 1988. A total of 11,280 tons of coal was gasified. The average dry gas HHV was 287 Btu/scf. Restoration of groundwater at the site was required by the Wyoming Department of Environmental Quality.

Objectives

The objectives of groundwater remediation at the RM1 site were to minimize postburn contaminant generation from pyrolysis products by accelerating the cooling of the ELW and CRIP cavities, to maximize the removal of potential organic and inorganic groundwater contaminants from the subsurface, and to prevent transport of contaminants away from the UCG cavities.

Procedures

Two restoration activities were carried out: venting, flushing, and cooling of the cavities shortly after completion of the test burns, and groundwater pumping and treatment operations.

Procedures for the first activity were based on the results of laboratory research and

numerical modeling that indicated that postburn operation was critical to reducing the impact of UCG on groundwater quality. The key concept of the postburn operation was steam stripping, which allowed potential organic and inorganic groundwater contaminants to be mobilized in the UCG cavity. Steam for stripping the cavities was provided by injecting steam through the process wells immediately after gasification and by influxing groundwater that flashed to steam in the hot cavities. Sustained venting of the postburn UCG cavity was critical because the venting promoted groundwater influx into the postburn UCG cavities and because the venting provided the means to transport the mobilized contaminants to the surface. This transport prevented contaminant introduction into the underground strata surrounding the UCG cavities.

The second activity was designed to maintain the flow of UCG affected groundwater into the two cavities in the Hanna coal seam where it could be pumped to the surface and treated for removal of contaminants. The groundwater pumping and treatment restoration operations were carried out in the summers of 1988 and 1989. A pump was placed near the bottom of each UCG cavity. The volume of water pumped from the cavities was based on the calculated cavity void volume or on indications that water levels in the cavities were dropping below the level of the pump intakes. The treatment system used in the first restoration was designed to remove oils, dissolved nitrogen and sulfur species, dissolved metals, and organic compounds. The treatment system consisted of six steps:

- Gravitational separation and air flotation were used to separate oil and water.

- In a flocculation chamber, a chlorine solution was added to oxidize cyanide and ammonia. This was followed by the addition of a 50% sodium hydroxide solution to raise the pH and react with heavy metals to form and precipitate metal hydroxides.
- A tube settler allowed precipitates to settle out. The precipitated solids were removed and incinerated on-site.
- A two-stage pressure filter was used to remove suspended solids. The filter consisted of an anthracite coal stage to remove the coarser particles, followed by a silica sand stage for the finer solids.
- In a clearwell compartment, 93 to 98% sulfuric acid was added to reduce the high pH resulting from the addition of sodium hydroxide in the flocculation chamber.
- Two carbon adsorber units, each containing 100 ft³ of activated charcoal, were used to remove organic compounds.

The treated water was stored in a holding tank and then applied to the land surface using an atomizing spray system.

The treatment system for the second restoration operation was modified based on the effectiveness of the first treatment system and consisted of two steps:

- A two-stage pressure filter consisting of anthracite coal and silica sand was used to remove suspended solids.
- Two carbon adsorber units were used to remove organic compounds. The same activated carbon used in the first treatment system was reused for the second system.

Treated water was applied to the land surface in the same manner as was done in the first treatment. Water samples were collected from various stages of each treatment operation.

Results

Steam was injected into and produced from each of the two cavities for several days immediately after gasification to cool the cavities and to remove residual contaminants. The cavities were continuously vented to remove effluents and to enhance groundwater influx.

The ELW cavity was flushed with steam for approximately 10 days and remained vented for approximately 65 additional days. During venting and flushing, the following materials were brought to the surface: 207 kg of phenols, 974 kg of total organic carbon (TOC), 171 kg of sulfides, 103 kg of sulfates, 969 kg of ammonia, 14 g of arsenic, and 356 g of boron.

The CRIP cavity was flushed with steam for 10 days and remained vented for an additional 145 days. During the venting and flushing, the following materials were brought to the surface: 328 kg of phenols, 666 kg of TOC, 368 kg of sulfides, 114 kg of sulfates, 1209 kg of ammonia, 60 g of arsenic, and 186 g of boron.

For the first pumping and treatment restoration operation, approximately 2,100,000 gallons of water were pumped from the two cavities and treated. The treatment system effectively removed dissolved organics and ammonia from the groundwater. Concentrations of selected analytes in the treated water from September 15-20, 1988 included 0.3 mg/L of ammonia, 0.638 mg/L of boron, and 15 mg/L of TOC, and less than 0.020 mg/L of total phenol. Concentrations of these analytes in the untreated cavity water on September 20, 1988 were 6.4 mg/L of ammonia, 0.387 mg/L of boron, 27 mg/L of TOC, and 0.021 mg/L of phenol. The treatment system was not effective in removing boron from groundwater because boron does not easily form hydroxide compounds when mixed with sodium hydroxide and therefore did not precipitate out of the groundwater during treatment. Total dissolved solids increases of 23 to 47% were observed between the untreated and treated water. These increases resulted

from the addition of chlorides, sodium, and sulfates (i.e., chlorine, sodium hydroxide, and sulfuric acid) during the treatment.

During the second pumping and treatment restoration operation, approximately 1,570,000 gallons of groundwater were treated for the removal of dissolved organics. This treatment system did not use the addition of chemicals because in the first treatment system, these had only a small beneficial effect and resulted in a high TDS level in the treated water. The treatment system was not effective in removing dissolved organics from the cavity water because of contamination in the carbon adsorbers. Large quantities of chloroform (CF) and bromodichloromethane (BDCM) were detected in the treated water but not in the untreated cavity water. This was the same carbon used in the first treatment and it is probable that the chlorine added as part of the first treatment system partially chlorinated some organic compounds that adsorbed onto the activated carbon. Because the carbon adsorber units were sealed and stored on-site between treatments, it is possible that anaerobic bacterial reactions broke down the higher molecular weight organic compounds into lower molecular weight compounds such as CF and BDCM. These compounds could have loaded the activation sites on the activated carbon and greatly reduced the effectiveness of the carbon adsorption treatment. After treatment, the quality of cavity water was very similar to baseline conditions and generally improved during pumping. Boron was the only parameter significantly higher than baseline concentrations.

Flushing and pumping of the cavities during restoration operations resulted in water levels in the coal seam being at least 250 ft below baseline elevations in the area of the UCG cavities. These levels indicated a cone of depression in the coal seam potentiometric surface centered near the cavities. This resulted in groundwater flow from the site periphery toward the cavities. Water levels subsequently returned to baseline conditions.

Conclusions

The venting, flushing, and cooling of the RM1 UCG cavities followed by two pumping and treatment restoration operations were successful in containing and treating contaminants. Steam injection and the groundwater influx provided cooling of the cavities, reducing postburn pyrolysis, which was identified in the numerical modeling and laboratory research as a major source of groundwater contamination from UCG. Groundwater influx also stripped contaminants from the surrounding coal, char wall, and cavity, preventing transport of contaminants away from the cavities. Thus, a large quantity of the contaminants generated during gasification and most of the contaminants generated after gasification were transported to the surface.

Most UCG-induced analyte concentrations were significantly reduced after the first pumping and treatment restoration. This was particularly evident in the change in phenol concentrations in the cavity water during pumping. The first pumping and treatment operation was effective in lowering the concentrations of all analytes of concern except boron. However, the addition of chemicals increased TDS levels in the treated water. The second treatment system was not effective in removing targeted analytes because of contamination in the system itself. Even so, the results have shown that pumping and treating UCG cavity water can be an effective method for restoring groundwater quality.

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GROUNDWATER MONITORING AT THE ROCKY MOUNTAIN 1 UNDERGROUND COAL GASIFICATION TEST SITE

Steven R. Lindblom

Background

The Rocky Mountain 1 (RM1) underground coal gasification (UCG) test was conducted from November 16, 1987 through February 26, 1988, near Hanna, Wyoming, to test simultaneously two UCG process configurations and to address environmental concerns associated with UCG. The target for gasification was the Hanna No. 1 coal seam, a 30-ft seam of bituminous-rank coal lying at depths between 330 and 390 ft below the surface. The coal seam is the primary aquifer at the site and is essentially bounded by adjacent stratigraphic units of sandstone, claystone, and shale.

Contamination of groundwater may have occurred at previous UCG sites due to insufficient consideration of potential environmental impacts. However, laboratory research performed by Western Research Institute has shown that contamination may be controlled through careful site selection and the use of operational procedures developed to reduce generation, deposition, and transport of contaminants.

Objectives

A major objective of the RM1 test was to demonstrate that underground coal gasification can be successfully carried out in an environmentally safe manner. Groundwater monitoring was performed to verify the effectiveness of procedures used during the RM1 UCG test to control contaminant generation, deposition, and transport; to assess the long-term impacts of the UCG process on site hydrology; and to comply with Wyoming Department of Environmental Quality permitting and restoration requirements.

Procedures

Baseline groundwater sampling and analyses were done on a quarterly basis, beginning in August 1986. These activities continued during the UCG test and long-term groundwater monitoring began at the completion of gasification operations (February 26, 1988). The last sample collection was performed in December 1992. Twenty-two wells were designated for sampling during postburn groundwater monitoring. Of these, eight were outer ring wells completed into the Hanna No. 1 coal seam, eight were inner ring coal seam wells, four wells were completed into the overburden, and two were process wells completed into the UCG cavities.

Three different suites of samples were collected for analyses during postburn monitoring activities. The sample suites consisted of a full suite, a limited suite, and a compliance suite. An extensive quality assurance and control program was followed to ensure sample and analysis quality. Quality assurance and quality control samples included rinsates of the sampling system, duplicate samples from wells with historically higher levels of contamination, and standard samples of known concentration.

Water levels were measured in the wells across the site at the start of each sampling event. Each well was purged for a minimum of 80 minutes at approximately 1 gallon per minute. Field parameters of Eh, pH, conductivity, temperature, flow rate, and water level were measured every 20 minutes during the purging process and recorded in a laboratory notebook. Strict chain of custody procedures were followed after each sample collection.

Results

Water level measurements made since the end of groundwater restoration activities have shown that water levels in the second overburden unit and the understrata have essentially remained constant. Water levels in the adjacent overburden unit have gradually recovered to near baseline levels. Water levels in the Hanna No. 1 coal seam have essentially recovered from the effects of the UCG tests and groundwater restoration activities. Baseline water elevations in the Hanna No. 1 coal seam varied between 6880 and 6915 ft above sea level. The water level measurements of December 1992 indicated groundwater elevations of approximately 6900 ft.

With few exceptions, groundwater quality is at, or near, baseline quality. Some analytes (TOC, TDS, and ammonia) in groundwater samples from wells in the west and southwest areas of the site were consistently higher in concentration than in samples from wells in other areas of the site. This pattern was also observed during the baseline evaluation and test monitoring. These higher concentrations may have resulted from influx of water with naturally higher concentrations of these parameters from off the site. The higher transmissivity of the coal seam in this area would facilitate movement of groundwater onto the site in response to hydraulic gradients induced by UCG and restoration operations.

Low concentrations of benzene have persisted in a few wells at the site. Two coal seam wells have often yielded water containing benzene. Benzene concentrations in groundwater samples from one well have varied from less than 0.010 mg/L to 0.044 mg/L, while values in the other well have ranged from less than 0.010 mg/L to 0.019 mg/L. Concentrations have stabilized over the last 2 years at approximately 0.020 mg/L.

For some parameters, the groundwater quality in the UCG cavities is slightly worse than in the surrounding strata. Sulfate and TDS concentrations are above baseline

in one of the UCG cavities. Boron concentrations remain an order of magnitude above baseline concentrations in both cavities. Other parameters have stabilized at concentrations at or below baseline.

Conclusions

The RM1 test had significant temporary impacts on the hydrology of the primary aquifer at the site. Lesser impacts were detected in the strata above the coal seam and no impacts were observed below the coal seam. Water levels, which had decreased over 200 ft near the center of the site during the UCG tests and postburn activities, have completely recovered. The groundwater flow patterns observed during the baseline site evaluation have been reestablished. No remaining effect on groundwater elevations is apparent.

The UCG tests did affect groundwater quality at the site. However, long-term monitoring has shown that the procedures used during the test and the postburn restoration measures were effective in containing and removing most contaminants from the subsurface environment. Boron in the two UCG cavities remained an order of magnitude above baseline concentrations. This is not the case over the remainder of the site, as boron in groundwater samples from all other wells has remained below baseline concentrations for the last 2 years. Low concentrations of benzene have frequently been detected in a few inner ring coal seam wells. The benzene is probably associated with coal tars in the vicinity of these wells. The majority of wells at the site have shown no evidence of benzene. Total organic carbon and total dissolved solids concentrations have often been detected above baseline levels in peripheral wells along the western edge of the site; however, it is doubtful that these higher concentrations resulted from byproducts of the UCG tests. Except for these instances, water quality parameters at the site at the end of 1992 were at or below baseline levels.

Related Publications

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Crader, S.E., 1989, Sampling and Analyses Report for Postburn Sampling at the RM1 UCG Site, Hanna, Wyoming, March, 1989. Laramie, WY, WRI-89-R052.

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Western Research Institute, 1988, Sampling and Analyses Report, Postburn Sampling for the RM1 Site, Hanna, Wyoming, March, 1988. Laramie, WY, WRI-88-R047.

Western Research Institute, 1988, Sampling and Analyses Report, Postburn Sampling for the RM1 Site, Hanna, Wyoming, June, 1988. Laramie, WY, WRI-88-R045.

Western Research Institute, 1988, Sampling and Analyses Report, Postburn Sampling for the RM1 Site, Hanna, Wyoming, September, 1988. Laramie, WY, WRI-88-R046.

INITIAL STUDY OF COAL PRETREATMENT AND COPROCESSING

T. Fred Turner

Background

Laboratory studies suggest that coke formation during hydropyrolysis can be prevented by a prior treatment that involves immersing the coal in an inert liquid at temperatures between approximately 350 and 400°C (662 and 752°F) (Berkowitz and Speight 1973). Such treatment removes moisture in the coal and raises its calorific value by as much as 10 to 12%. After the coal is coprocessed, it is more stable than the dried coal before the coprocessing step.

It is speculated that the presence of a suitable liquid within the pore system of the coal stops the collapse of the pores that occurs at the onset of coking. The presence of the liquid can also improve the access of hydrogen to the pores. The presence of the liquid, especially a hydrogen-donor liquid, can thus enhance hydrogen transfer within the pore system, thereby reducing potential coke-forming reactions.

Finally, the heavy oil that is coprocessed with the coal will be upgraded compared with the original material. Previous testing suggests that the primary mechanism for this upgrading step is distillation, which reduces the viscosity and the gravity of the product oil.

Objective

The objective of this study was to conduct an initial evaluation of the potential for enhancing liquid yields by integrating coal pretreatment and coprocessing technologies.

Procedures

Two eastern coals were studied. The first was a Herrin seam (Illinois No. 6) low moisture bituminous coal from the Peabody Coal Company River King Mine, pit 3, near

New Athens, Illinois. The second coal was provided by Consolidation Coal Company and was a high moisture, Pittsburgh No. 8, filter cake coal. This material was a wet, pasty material that could not be processed as received and had to be air dried prior to pretreatment in an inclined fluidized-bed (IFB) reactor. The properties of these coals are shown in Table 1. The heavy oil used in the coprocessing tests was produced from mild-gasification experiments conducted on western, Powder River Basin coal in a fluidized-bed pyrolyzer (Merriam and Jha 1991). Properties of the oil are shown in Table 2.

The thermal-pretreatment stage of the experiments was performed in an IFB reactor (Boysen et al. 1990). The dried coal exiting the reactor was immediately immersed in a preheated, tared barrel of heavy oil. The dried coal-heavy oil slurry produced from the pretreatment step was fed into an inclined screw pyrolysis reactor (SPR) using a screw feeder. As the slurry mixture moved through the first two-thirds of the SPR, the coal and oil were heated, vapor products were swept from the system, and the upgraded oil was condensed in knockout pots. The remaining coal and heavy oil were exposed to higher temperatures in the last third of the screw conveyor. Here additional oil was recovered, and the coal stabilized. Depending on the temperature, residence time, and heavy oil injection rate, a dried or semidried product exited the SPR and was collected for the liquefaction tests to be conducted as a separate task. In a fully integrated operation, the IFB and the SPR reactor systems would be combined as one unit. However, to better understand the operation of the two systems each was operated independently in a semibatch mode.

Table 1. Properties of Raw Coals

	<u>Herrin</u>	<u>Pittsburgh No. 8</u>	
	as received	as received	air dried
<u>Proximate, as received wt %</u>			
Moisture	3.4	30.6	1.3
Volatile Matter	36.6	23.7	33.0
Ash	10.5	5.5	9.8
Fixed Carbon	49.5	40.2	56.0
<u>Proximate, moisture free wt %</u>			
Volatile Matter	37.9	34.1	33.4
Ash	10.9	7.9	9.9
Fixed Carbon	51.2	57.9	56.7
<u>Ultimate, moisture free wt %</u>			
Carbon	66.3	64.3	74.7
Hydrogen	4.7	5.4	4.9
Nitrogen	1.2	1.2	1.4
Sulfur	3.6	1.3	1.4
Oxygen (diff)	13.3	19.9	7.7
<u>Heating Value, Btu/lb</u>	11,771		13,343
<u>Fischer Assay, wt %</u>			
Oil	13.53		13.55
Water	10.69		4.72
Gas	6.99		5.53
Spent Coal	68.79		76.19

Results

The results of the analysis of the products resulting from the pretreatment tests indicate that, in general, higher temperatures and longer residence times result in higher fines production for both coals (11 to 27 wt %). However, the results of pretreatment had only a minor effect on the properties (proximate, ultimate, and Fischer assay) of the Herrin and Pittsburgh No. 8 coal products.

The significant result of the coprocessing tests is that the weight of the char formed during coprocessing is greater than the weight of the coal feed. This increase must result from conversion of heavy oil to char. For the Herrin pretreated coal the fraction of heavy oil forming char and the fraction of char formed from the heavy oil are reduced as the coprocessing temperature increases.

The percent of heavy oil forming char goes from 82 to 63%. Similarly, the percent of the product char that is derived from the heavy oil drops from 66 to 57%. However, the tests with unpretreated Herrin coal, show dramatically different behavior, a factor of two different than tests with the pretreated coals. Only 35% of the product char is oil derived and only 39% of the heavy oil forms char. Clearly, the pretreated coal binds the heavy oil more strongly than the unpretreated coal.

The coprocessing series with the Pittsburgh No. 8 coal were performed with a higher starting oil-to-coal ratio (~3:1). However, less heavy oil formed char (36 to 39%), and less product char was derived from heavy oil (51 to 56%) than in similar experiments with pretreated Herrin coal. The percent of heavy oil forming char in the Pittsburgh No. 8 tests is as low as that of the unpretreated Herrin coal coprocessing series.

Table 2. Properties of Coal-Derived Heavy Oil

<u>Proximate, as received wt %</u>	
Moisture	12.99
Volatile Matter	86.96
Ash	.01
Fixed Carbon	.04
<u>Proximate, moisture free wt %</u>	
Volatile Matter	99.94
Ash	0.01
Fixed Carbon	0.05
<u>Ultimate, moisture free wt %</u>	
Carbon	80.7
Hydrogen	8.1
Nitrogen	0.9
Sulfur	0.6
Oxygen (diff)	9.7
<u>Solubility Profile, wt %</u>	
Pentane Solubles	61.8
Toluene Solubles	29.2
THF Solubles	8.4
Residuum	0.6
Specific Gravity	1.0427

Proximate, ultimate, and Fischer assay analyses of the solid products were conducted. However, it was not always possible to complete the Fischer assay analysis on the spent coal material. In many cases the solid material swelled so much that the system plugged. On disassembly, the analyst discovered a solid, "foamed" material filling the reactor and outlet tubing.

The average char heating value for the solid products resulting from all tests using pretreated Herrin coal was 14,300 Btu/lb. In general, the solid products from pretreated Pittsburgh No. 8 coal also had increased heating values with respect to the original coal. In addition, a plot of the heating value of the original coals and the chars increased as the volatile content as determined by proximate analysis of the materials increased. This is attributed to increasing amounts of heavy oil coated on the chars.

Conclusions

Drying, regardless of the conditions, reduces fixed carbon (or coke) in the Herrin and Pittsburgh No. 8 coals by only a minor amount, typically 1 to 7 wt %. However, the drying conditions do have an effect on the amount of fixed carbon formed during coprocessing. Coprocessing of a Herrin coal pretreated in a CO₂ atmosphere increases fixed carbon by as much as 18 wt % over the raw coal. Coprocessing the same coal pretreated in a CO₂/steam atmosphere results in an increase in fixed carbon content of as much as 51 wt %. This obviously has a negative effect on any subsequent hydroprocessing, with fixed carbon being more difficult to convert. Unpretreated coal showed a net reduction of fixed carbon during coprocessing.

The heating values of the solid products of coprocessing show an increase over raw coal. This is presumably because of the incorporation of heavy oil components into the coal structure. This may also be the reason for the "foaming" occurring during Fischer assay analysis. Excessive swelling such as this may limit processing options.

The reactivity of the coals is increased by pretreatment. This is seen both in the increased fixed carbon production and in the binding of heavy oil to the solid. A substantial amount, up to about 80%, of the original heavy oil ends up in the solid product. The resulting solid product is typically over 50 wt % heavy oil-derived for the pretreated Herrin coal tests. When the coal is not thermally pretreated, less oil ends up in the solid product.

Related Publication

Vaillancourt, M., T.F. Turner, and L.J. Fahy, 1991, Initial Study of Coal Pretreatment and Coprocessing. Laramie, WY, WRI-92-R002.

EVALUATION OF COAL PRETREATMENT PRIOR TO COPROCESSING

Frank D. Guffey

Background

Western Research Institute (WRI) has been conducting research to develop a mild-gasification process to produce a stabilized char product for use as a fuel (Merriam et al. 1990). The process also produces a heavy liquid with limited economic value. The composition of this liquid does not make it attractive as refinery feedstock because of its high molecular weight and heteroatom content. This liquid, because of its limited economic value, may be suited as a solvent for coal-oil coprocessing.

Coal-oil coprocessing began receiving attention in the early 1970s as a potential process for simultaneously upgrading heavy oils and coal to produce liquid products more suited for introduction into refineries. Reported results have demonstrated that the coprocessing concept can be applied to a variety of feedstocks and that yields can be increased over processing the two feedstocks independently (Speight and Moschopedis 1986; McMillen et al. 1991). Applying coprocessing technology to upgrading the liquid produced from mild gasification of coal offers several technological benefits.

Swelling of coal before it undergoes liquefaction reactions has been shown to increase the liquid product yield (Joseph 1991). Coal can be made to swell by two procedures: (1) interaction with polar solvents and (2) thermally, at moderate temperatures. In addition, it has been shown that a coal swollen in a solvent will allow the solvent to penetrate the coal structure and disperse a catalyst dissolved in it (Warzinski 1990). The mild-gasification liquid is polar because of the high heteroatom content and it has the potential of inducing coal swelling. If an oil-soluble catalyst precursor is used, it can be dissolved in the liquid and be readily dispersed as the coal swells. Uniform

dispersion of the catalyst should improve liquid yield during coprocessing.

Objectives

The objectives of this study were (1) to evaluate the potential of using the coal-derived solid produced from a process development unit as a feedstock for additional coprocessing and (2) to evaluate coal pretreatment to induce coal swelling and promote dispersion of iron-based, disposable catalyst precursors, into the coal structure.

Procedures

The two coals used in this study were Herrin seam coal and a filter cake coal produced from Pittsburgh No. 8 seam coal. Properties of the coals are listed in Table 1 of the preceding summary report (page 83). Both of the coal samples were dried in an inclined fluidized-bed (IFB) dryer as discussed in the preceding summary report. The coal-derived liquid used as the coprocessing material was generated by mild gasification of coal during another project conducted by WRI (Merriam et al. 1990). Physical properties of the mild-gasification liquid are listed in Table 2 of the preceding summary report (page 84). Ferrocene and iron pentacarbonyl were the two catalyst precursors evaluated.

The coprocessing studies were conducted in 7.5-inch long by 0.75-inch o.d. stainless tubing bombs. Normally, 1.0 g of IFB dried coal and 3.0 g of the mild-gasification liquid were charged to each tubing bomb. The catalyst precursor was added at a weight to represent 1.0 wt % of the metal on the basis of the coal charge. Carbon disulfide was added as an excess to ensure sulfiding of the metal catalyst during coprocessing. After loading, each tubing bomb was frozen at -80°C (-112°F) and evacuated to remove air.

A pretreatment step under a helium atmosphere was performed as part of each coprocessing experiment to ensure good mixing of the reactants, to swell the coal, and to allow the liquid-catalyst precursor solution to enter the coal structure. The pretreatment tests were performed by pressurizing the bombs with 20 psig of helium (pressure at room temperature) and placing them in a sand bath at the pretreatment temperature for the desired time period. The pretreatment was not performed under hydrogen so the results of this study could be used to evaluate the effects of coal swelling without interference from effects of low-temperature hydroliquefaction (Derbyshire et al. 1990). Pretreatment at 90°C (194°F) for 30 minutes was selected as the base condition for this study because this condition provides sufficiently high temperature to decrease viscosity of the coprocessing liquid and allow good mixing of the reactants without thermally altering the coal structure. Pretreatment at 275°C (527°F) for 30 minutes was performed to swell the coal by both thermal and solvent interaction with the coal, and allow the liquid and dissolved catalyst access to the coal structure before coprocessing.

After venting the helium, the tubing bombs were then pressurized to 800 psig by addition of hydrogen (pressure at room temperature). The tubing bombs were heated in a sand bath set at 400°C (752°F) and shaken at a rate of 100 cycles per minute for 60 minutes. At the end of each experiment, the tubing bombs were rapidly cooled to quench the reactions.

The tubing bombs were vented into a chamber of known volume, the pressure measured, and a sample of gas taken for analysis. The tubing bombs were disassembled, the components placed in extraction thimbles, and extracted with tetrahydrofuran (THF) for 48 hours. The THF was removed from the soluble fraction with a rotary evaporator until a constant weight of the extract was achieved. The residual solid material from the extraction was dried in a vacuum oven at 80°C (176°F) for 24 hours and the weight

determined. The dried solid was ashed at 427°C (800°F) for 16 hours. The weight of residual organic material (unconverted coal) was determined by difference. The concentrations of hydrogen and other product gases were determined by gas chromatography. Coal conversion and hydrogen consumption values were determined.

The experiments to investigate coprocessing of the IFB dried coal and coal pretreated in the 2-inch process development unit were performed in a stirred-batch autoclave. The batch autoclave was charged with the mild-gasification liquid and coal at a weight ratio of 2:1. The catalyst and sufficient carbon disulfide to ensure an excess of sulfur to convert the catalyst to the sulfide form were added last. The autoclave was sealed and charged with hydrogen at 1500 psig. The autoclave was then brought to a reaction temperature of 400°C (752°F) as fast as possible and held there for 1 hour. The reactor was cooled by opening the tube furnace and blowing air through the cooling coils attached to the reactor.

An oil fraction was generated from the THF-soluble product by solubility in cyclohexane. The elemental composition of the THF-soluble product and the cyclohexane soluble oil was determined using conventional methods.

Results

Examination of the material balance closures for the tubing bomb tests shows they range from about 102 to 108 wt %. These values are typical of the reaction system and are considered to be acceptable since material balances from other studies are frequently below 90 wt % (Ceylan and Stock 1991).

Coal conversions for each coal are significantly higher when iron pentacarbonyl is used as the catalyst precursor compared to ferrocene. This confirms work by other researchers (Kamiya et al. 1988; Watanabe et al. 1984). The results indicate iron pentacarbonyl is either more easily converted to the more

active sulfided form than is ferrocene or it is better dispersed in the coal structure. In all of the experiments using iron pentacarbonyl as the catalyst precursor, higher conversion was observed for pretreatment at 275°C (527°F), as compared with pretreatment at 90°C (194°F).

Coal conversion data for the two experiments using Herrin coal performed without catalyst show the experiment conducted at 275°C (527°F) had higher conversion than the experiment conducted at 90°C (194°F). The increase in the coal conversion is caused by disruption of the weaker bonds (carboxylic acid functions and ethereal linkages) in the coal structure during the higher temperature pretreatment (Derbyshire et al. 1990).

For the conditions studied, changes in temperature and time in the presence of the catalyst precursor did not significantly affect coal conversion or hydrogen consumption. However, the differences between the experiments conducted with the catalyst as compared to those without are significant and the large differences in coal conversion and hydrogen consumption demonstrate catalyst activity is increasing coal conversion.

Comparison of the coal conversion and hydrogen consumption data for the two experiments conducted using the filter cake product from Pittsburgh No. 8 coal without the iron pentacarbonyl catalyst precursor shows the results are comparable, within experimental error. The absence of increased coal conversion with increased pretreatment temperature, which differs from the experiments using Herrin coal, is attributed to the lower reactivity of filter cake product.

Increasing the pretreatment time at 90°C (194°F) from 30 to 45 minutes increased the coal conversion from 22.2 to 50.0 wt %. This is a significant increase and shows the coal will undergo a significant degree of swelling caused by solvent interactions at the lower pretreatment temperature, if the residence time is sufficient. The coal

conversion and hydrogen consumption observed for the experiment conducted with pretreatment at 90°C (194°F) and residence time of 45 minutes are comparable to the values observed at the shorter pretreatment residence time at 275°C (527°F).

For the two experiments conducted in the batch autoclave with Herrin coal and the mild-gasification liquid, one of the experiments was conducted in the absence of the iron pentacarbonyl catalyst precursor and the second with the added catalyst precursor. The results of these experiments are listed in Table 1. The material balance closures were 101.6 and 99.4 wt %.

The results show the coal conversion in both experiments are significantly higher than was observed in the tubing bomb experiments. This is attributed to the higher hydrogen pressure as compared to the tubing bomb experiments (1500 versus 800 psig), resulting in increased coal conversion to THF-soluble product and produced gas. The length of time (35 to 40 minutes) required to heat the autoclave from 350 to 400°C (662 to 752°F) is also sufficiently long to allow the coal to undergo low-temperature hydroliquefaction. Low-temperature hydroliquefaction has been demonstrated to drastically improve coal conversion by utilizing slower reaction rates of coal dissolution to compensate for diffusion limitations of hydrogen availability (Derbyshire et al. 1986). The hydrogen consumption is lower for the batch-autoclave experiments as compared to the tubing bomb experiments and is attributed to the lower liquid to coal mass ratio which decreases the amount of hydrogen added to the mild-gasification liquid.

Three thermally-pretreated Herrin coal samples (Vaillancourt et al. 1991) were coprocessed in the batch autoclave with the mild-gasification liquid to evaluate the pretreatment approach using the process development unit. Each sample was tested with and without the iron pentacarbonyl catalyst precursor. The material balance closures ranged from 98.6 to 102.7 wt %.

Table 1. Results from Stirred-Batch Autoclave Experiments Coprocessing IFB-Dried Herrin Coal with Iron Pentacarbonyl as the Catalyst Precursor at 400°C (752°F)

	Without Iron Catalyst	With Iron Catalyst
Reactants, g		
Coal	50.04	26.25
Coal Liquid	100.70	52.00
Catalyst	---	1.75
Hydrogen	8.17	8.82
Total	158.91	88.82
Products, g		
Unconverted Coal	2.42	0.57
Mineral Matter	6.75	3.85
THF Solubles	126.34	63.45
Produced Gas	8.12	7.15
Hydrogen	6.98	8.05
Water ^a	10.91	5.23
Total	161.52	88.30
Closure, %	101.6	99.4
Coal Conversion, wt %	94.4	97.5
Hydrogen Consumption, wt % of coal	2.7	3.4

^a Water determined by oxygen balance

The presence of the iron pentacarbonyl catalyst precursor enhanced the conversion of the thermally-pretreated coals. Without the catalyst present only 85 to 87 wt % of the coal was converted to THF-soluble product. The addition of the catalyst increased the conversion to approximately 96 wt %. Similarly, the hydrogen consumption also increased with the addition of the catalyst. It is interesting to note that no differences between the three thermal-pretreatment regimes can be detected from the coprocessing results. All of the tests run without catalyst are quite comparable. The same can be said for the coal-oil coprocessing tests that included the catalyst precursor.

The thermal pretreatment of the coals adversely affected the coal-oil coprocessing under hydrogen pressure. Comparison of the results from the experiments conducted on the thermally-pretreated coals with those on the dried coal show that there was less coal conversion. Even without the catalyst added, the sample that was only dried exhibited coal conversion comparable to the pretreated samples with the catalyst present. The hydrogen consumption for the thermally-pretreated coals without the catalyst was considerably lower than the dried coal as well as all of the tests in which the catalyst was added.

Conclusions

From the results of this investigation, the following conclusions can be made:

- Iron pentacarbonyl is more effective as a catalyst precursor than is ferrocene for conversion of the Herrin coal and the filter cake coal product derived from Pittsburgh No. 8 coal.
- Induced coal swelling in the presence of the mild-gasification liquid is a viable means of dispersing the catalyst. However, the two coals studied exhibit different degrees of improved yield from the pretreatment.
- The filter cake product exhibited a higher degree of swelling and better catalyst dispersion, as defined by increased coal conversion, than did the Herrin coal. The filter cake product showed a broader range of coal conversion percentages because of the induced swelling.
- Even though the filter cake product showed a greater tendency to swell and disperse the catalyst, the Herrin coal showed higher coal conversion in the tubing bomb experiments due to its higher reactivity.
- Results from analysis of the product obtained from coprocessing the Herrin coal showed it was upgraded in terms of oxygen content and hydrogen-to-carbon (H/C) atomic ratio when compared to the mild-gasification liquid.

- The thermal pretreatment of the coals adversely affected the coal-oil coprocessing under hydrogen pressure. Thermally-pretreated coals coprocessed without catalyst present exhibited about 86 wt % conversion as compared to 96 wt % for coal that was only dried.
- The addition of the iron pentacarbonyl catalyst precursor to the thermally-pretreated coals did improve the conversion to nearly that of the dried coal.

Related Publications and Presentations

Publications

Guffey, F.D., F.A. Barbour, and R.F. Blake, 1992, Induced Coal Swelling and Co-Processing with a Mild-Gasification Produced Liquid. Fuel Sci. and Tech. Int., 10:(7) 1207-1232.

Guffey, F.D., F.A. Barbour, and R.F. Blake, 1991, Evaluation of Coal Pretreatment Prior to Co-Processing. Laramie, WY, WRI-92-R026.

Presentations

Barbour, F.A., F.D. Guffey, and R.F. Blake, 1992, Coal/Oil Co-Processing with a Mild Gasification Produced Liquid. Confab '92, Winter Park, CO.

Guffey, Frank, D., 1992, Coal Liquefaction and Catalysis. Meeting of the Denver Coal Club, Denver, CO.

INVESTIGATIONS INTO COAL COPROCESSING AND COAL LIQUEFACTION

Kenneth P. Thomas

Background

The conversion of coal to a liquid that is suitable as a feedstock to a petroleum refinery is a process that is dependent upon several different variables. These variables include temperature, pressure, coal rank, catalyst type, nature of the feed to the reactor, and type of process. Western Research Institute initiated research in the area of coal liquefaction to address the impact of some of these variables upon the yield and quality of the coal-derived liquid. The principal goal was to improve the efficiency of the coal liquefaction process. With respect to catalyst type, two different approaches have been investigated. These were (1) coprocessing a heavy liquid, such as crude oil, with coal, using a dispersed catalyst and (2) direct liquefaction of coal using a supported catalyst.

Another important consideration in coal liquefaction is hydrogen utilization. This is because the incorporation of externally-supplied hydrogen during conversion of this very aromatic fossil fuel to, for example, transportation fuels is very expensive. There are a number of ways in which hydrogen can participate in the direct liquefaction of coal (Finseth et al. 1985). These include hydrogenolysis, alkyl bond scission, and hydrogenation.

Objectives

The objectives of this study were: (1) to evaluate coal/oil pretreatment conditions that are expected to improve the liquid yield through more efficient dispersion of an oil-soluble, iron-based catalyst, (2) to characterize the coke deposits on novel, supported catalysts after coal liquefaction experiments and to correlate the carbon skeletal structure parameters of the coke deposit to catalyst performance as measured by coal liquefaction product yield, and (3) to determine the modes of

hydrogen utilization during coal liquefaction and coprocessing. The study was divided into three subtasks: coal coprocessing, ^{13}C solid-state nuclear magnetic resonance (NMR) investigation of coke deposits on catalysts used in coal liquefaction, and hydrogen utilization.

Procedures

Two coals were used in the coal coprocessing study. The Illinois No. 6 (Herrin seam) coal sample was a bituminous coal obtained from the Peabody Coal Company River King Mine, pit 3, near New Athens, Illinois. The second coal sample was a Powder River Basin, subbituminous coal obtained from the Amax Coal Company, Eagle Butte Mine near Gillette, Wyoming. Both of the coal samples were dried in an inclined fluidized-bed dryer as part of another study to evaluate coal pretreatment (Merriam et al. 1990). Lloydminster crude oil was used for coprocessing. A 500-mL sample of this oil was distilled at 130°C (266°F) and 20 inches of mercury vacuum to remove low boiling components in the oil. The resultant heavy oil was used for this study. Iron pentacarbonyl was selected as the catalyst precursor because previous research had shown that it has good catalytic activity for coprocessing (Guffey et al. 1992; Watanabe et al. 1984) and because recent analysis has shown it has good economic value for coprocessing (Anderson et al. 1993).

For the coke deposits on catalysts part of the study, catalysts of the cobalt-molybdenum (CoMo) type were prepared on four different surface-modified alumina supports. The preparation of the catalyst, the modified supports, and the evaluation of the modified supports as coal liquefaction catalysts have been described in detail by Zhang (1993). The cobalt-

molybdenum (CM) catalysts that were evaluated were TiO₂-coated alumina support via impregnation (CM/TA-I), ZrO₂-coated alumina support via impregnation (CM/ZA-I), TiO₂-coated alumina support via deposition (CM/TA-D), and carbon-coated alumina support via pyrolysis (CM/CA-P). The alumina blank support was Amocat 1A. Details of the coal liquefaction experiments in the catalytic coal liquefaction microreactor unit and the calculation of liquefaction yields have been described by Zhang (1993). Three materials were used as the coal paste feed to the unit. These were coal from Arco's Black Thunder Mine (Wyoming), deashed residue material derived from this same coal by the Wilsonville R&D Facility (S/N 99672), and Allied 24 CB raw creosote oil.

The ¹³C solid-state NMR spectra of the coke deposits on the catalysts were obtained using a Chemagnetics CMX 100/200 NMR spectrometer operating at a frequency of 25 MHz. Cross-polarization with magic angle spinning (CP/MAS) and dipolar dephasing techniques were used to determine the carbon types present in the coke. Spectra were obtained at a spinning rate between 3.5 - 3.8 kHz. A total of 10,000 acquisitions were summed using a pulse width of 5.1 μsec, a pulse delay of 1 sec, a contact time of 1 msec, and a sweep width of 16 kHz. For the dipolar dephasing experiments, an additional delay of 40 μsec after the pulse was used before data acquisition. The ¹³C spectra were externally referenced to liquid tetramethylsilane (TMS) based on the solid-state spectrum of hexamethylbenzene (HMB) as the secondary reference and assigning 17.21 ppm to the shift of the aliphatic carbons of HMB relative to liquid TMS (Hayashi and Hayamizu 1989).

The NMR structural parameters for the coke deposited on the catalyst were determined from ¹³C cross polarization and dipolar dephasing spectral data. An important structural parameter is the aromatic cluster size. This parameter is calculated from the fraction of aromatic bridgehead carbons (Solum et al. 1989).

For the hydrogen utilization subtask, solid-state ¹³C NMR measurements were made using a large-volume sample spinner (2.1 mL) and a spinning rate of ~3.8 kHz. Other instrument parameters were a pulse delay of 1 sec, a contact time of 1 msec, 6.3 μsec pulse width, sweep width of 16 kHz, 1,000 data acquisition points, and a line broadening factor of 50 kHz. These values are typical of those used in solid-state NMR measurements of coals.

Liquid-state ¹³C NMR measurements were made using a JEOL GSX-270 NMR spectrometer. Typical conditions for recording a spectrum were ~10 μsec pulse width, 0.8 sec acquisition time, 10 sec pulse delay, 32,000 time domain data points, and gated decoupling with the decoupler on during data acquisition. Chromium(III) acetylacetonate was used as a relaxation agent.

A detailed description of the treatment of the NMR data has been given by Miknis et al. (1993). Samples for evaluation were obtained from the UOP Bench-Scale Coprocessing Unit and the Wilsonville Direct Liquefaction Facility. The material processed by UOP was an Illinois No. 6 coal and Lloydminster vacuum residue. The material processed at Wilsonville was a subbituminous coal obtained from the Black Thunder Mine. Details concerning the sources of the samples and the operation of the processes are contained in the reports by Guffey et al. (1993) and Piasecki et al. (1991).

Results

Results of the coal coprocessing subtask indicated that the Lloydminster crude oil will function as a solvent for coprocessing either Illinois No. 6 or Powder River Basin coal. However, it does not appear to be as effective as the coal liquid derived from mild gasification of a Wyodak coal used in an earlier study (Guffey et al. 1992). Coal conversions of 58.5 to 61.3 wt % were obtained in this study, compared to 76.2 and 71.2 wt % obtained in the earlier study. The lower coal conversions observed in this study are attributed to solvent effects.

These effects, as they relate to the solvent capabilities for coal-derived products, are expected to be more effective using mild-gasification liquids than crude oils.

The application of low-temperature hydrogenation as part of the pretreatment approach did provide an increase in the coal conversion for coprocessing experiments with Powder River Basin coal. There was not a comparable increase in coal conversion noted for Illinois No. 6 coal.

In the coke deposits on catalysts part of the study, the impact of using modified, supported catalysts on direct coal liquefaction yield was evaluated. An Amocat alumina support was modified with TiO_2 , ZrO_2 , and carbon by means of different techniques to coat the alumina surface and consequently change its surface properties. Four CoMo catalysts were then prepared using these modified supports. These catalysts possess essentially the same pore structure as Amocat 1A catalyst but with slightly smaller pore volumes and specific surface areas. The coal liquefaction experiments indicated that the catalysts' overall performance did not significantly depart from those of the Amocat 1A catalyst. However, differences in conversion yield did exist for the catalysts as a result of the different coating materials on the alumina surface.

CM/TA-I performed as well as the Amocat 1A catalyst in terms of cyclohexane solvent conversion. CM/ZA-I performed less efficiently than the CM/TA-I catalyst particularly in terms of cyclohexane and conversion yield. The difference is explained by the strong metal-support interaction (SMSI) effect of TiO_2 (but not ZrO_2) which enhances hydrocracking and hydrogenation activities and resists deactivation due to active metal sintering. CM/TA-D gave the poorest coal conversion yield. As a result of changes in the acidic properties of the surface by vapor deposition technique, coke had deposited on CM/TA-D which led to catalyst deactivation and, thus, poor conversion yield. CM/CA-P gave a coal conversion

yield that was between the yields noted for catalysts CM/TA-I and CM/TA-D. Carbon coated on alumina overcomes the drawbacks associated with alumina and allows complete sulfiding of active metals.

The total aromatic carbons and, specifically, the amount of aromatic quaternary carbons of the coke deposited on the spent catalyst correlated with the coal conversion performance of the catalysts. Although a relationship is not necessarily a cause and effect correlation, the results indicate that the catalyst (CM/TA-D), which promotes the most coke deposition, also performs poorly in terms of coal liquefaction conversion. This relationship holds only for the catalysts that have TiO_2 and ZrO_2 deposited on the alumina support. The catalyst CM/CA-P with carbon deposited on the alumina support not only had a large amount of coke deposited on its surface after coal liquefaction service, but also performed quite well in terms of coal conversion yield.

The structural properties of the coke deposited on the spent catalysts depend on the initial pore volume of the fresh catalyst and on the percentage of surface coating of the alumina support by TiO_2 , ZrO_2 , and carbon. A linear relationship was found between the pore volume and the size of the aromatic cluster of the coke (the larger the pore volume, the greater the cluster size). Also, a linear relationship was observed between the amount of coating material and the number of aromatic carbons per aromatic cluster. When the amount of material coating the surface of the alumina support was high, the size of the aromatic cluster of the coke was small. This effect may be related to the pore volume in that a higher surface coating resulted in reduced pore volume.

For the hydrogen utilization subtask, the UOP bench-scale coprocessing of Illinois No. 6 coal with Lloydminster vacuum residue showed that only about 13% of the feed coal aromatic carbon was hydrogenated; whereas for Wilsonville two-stage catalytic/catalytic runs with a Black

Thunder subbituminous coal, almost two-thirds of the feed coal aromatic carbon was hydrogenated.

Gas production, both hydrocarbon and heteroatomic gases, accounted for most (90%) of the hydrogen consumed during UOP bench-scale coprocessing. During direct coal liquefaction at Wilsonville, most of the hydrogen consumed in the first stage for both run periods (G and J) involved heteroatom reactions. More than twice as many moles of hydrogen were consumed in the second stage during period J than during period G (46.3 versus 20.7) of Wilsonville Run 263. This was attributed to the addition of Criterion 324 support catalyst whose effect was to increase the slurry throughput during period J. For the Wilsonville overall two-stage liquefaction, Run 263, the major differences in the hydrogen consumption reactions between the two run periods involved the matrix cleavage and heteroatomic gas reactions. The greater number of moles of hydrogen consumed during period J could be accounted for mainly by the net hydrogen utilization for these reactions.

Conclusions

Conclusions from the study results are:

- The Lloydminster crude oil is a suitable solvent for coprocessing either of the coals studied. For the Illinois No. 6 coal, the coal conversion values obtained with Lloydminster crude oil were lower than those from experiments using a mild gasification-produced coal liquid.
- The application of low-temperature hydrogenation as part of the pretreatment approach provided significant increases in the liquid product yield for experiments coprocessing Powder River Basin coal.
- Higher yields of tetrahydrofuran-soluble material and oil fractions were observed from coprocessing the Powder River Basin coal as compared to coprocessing Illinois No. 6 coal.
- Amocat blank alumina support was modified with TiO_2 , ZrO_2 , and carbon by means of different techniques. Results of the coal liquefaction experiments indicated that the catalysts' overall performances did not significantly depart from those of the Amocat 1A catalyst. However, differences in conversion yield did exist for the catalysts as a result of different coating materials on the alumina surface.
- CM/TA-I performed as well as the Amocat 1A catalyst in terms of cyclohexane solvent conversion. CM/ZA-I performed less efficiently than the CM/TA-I catalyst particularly in terms of cyclohexane and conversion yield. The difference is explained by the SMSI effect of TiO_2 (but not ZrO_2) which enhances hydrocracking and hydrogenation activities and resists deactivation due to active metal sintering.
- CM/TA-D gave the poorest coal conversion yield. As a result of changes in the acidic properties of the surface by the vapor deposition technique, more carbonaceous residue (coke) had deposited on CM/TA-D leading to catalyst deactivation and, thus, poorer conversion yields.
- CM/CA-P gave a coal conversion yield that was between the yields noted for catalysts CM/TA-I and CM/TA-D. Carbon coated on alumina overcomes the drawbacks associated with alumina and allows complete sulfiding of active metals.
- The total aromatic carbons and aromatic quaternary carbons in the coke deposited on the spent catalysts correlated with coal conversion performance. This relationship holds only for catalysts that have TiO_2 and ZrO_2 deposited on the alumina support. CM/CA-P not only has a large amount of coke deposited on its surface after coal liquefaction service, but also performs quite well in terms of coal conversion yield.

- A direct linear relationship was found between the pore volume and the size of the aromatic cluster of the coke. Also, an indirect linear relationship was observed between the amount of coating material and the number of aromatic carbons per aromatic cluster.
- Only about 13% of the aromatic carbons in Illinois No. 6 coal was hydrogenated during UOP bench-scale coprocessing with Lloydminster vacuum residue. Almost two-thirds of the aromatic carbons in Black Thunder subbituminous coal was hydrogenated during Wilsonville two-stage processing.
- Gas production accounted for 90% of the hydrogen consumed during UOP bench-scale coprocessing. For Wilsonville, Run 263, most of the hydrogen consumed in the first stage for periods G and J involved heteroatom reactions. During second stage processing, 46.3 moles of

hydrogen were consumed during period J, while 20.7 were consumed during period G. This was attributed to the addition of catalyst Criterion 324 whose effect was to increase the slurry throughput during period J. For the overall process, the major differences in the hydrogen consuming reactions between the two periods involved matrix cleavage and heteroatomic gas reactions.

Related Publications

Guffey, F.D., D.A. Netzel, F.P. Miknis, and K.P. Thomas, 1993, Investigations into Coal Coprocessing and Coal Liquefaction. Laramie, WY, WRI-93-R018.

Netzel, D.A., F.P. Miknis, T. Zhang, P.D. Jacobs, H.W. Haynes, Jr., 1994, Carbon-13 Solid State NMR Structural Investigation of Coke Deposits on Spent Catalysts Used in Coal Liquefaction. Journal article in preparation.

VALUE-ADDED COAL PRODUCTS

Norman W. Merriam

Background

It is relatively easy to develop a process to drive the moisture from Powder River Basin (PRB) coal. A large number of combinations of gas flow and temperature can be used to dry minus 8-mesh PRB coal to zero or low moisture content using a fluidized-bed having a coal residence time of 3 minutes. However, the dried coal must be stabilized to maintain the characteristics of a good-quality fuel.

A premium-quality fuel process should go beyond simply removing water from coal. Much of the oxygen in PRB coal can be removed by driving carbon dioxide, and some carbon monoxide, from the coal. This partial decarboxylation not only increases the heating value of the coal, but the removal of oxygen from the coal helps to stabilize the coal and to reduce the susceptibility to self-heating. Partial decarboxylation was controlled in previous mild-gasification work to avoid generation of coal liquid in the dryer. In the reactor used, tar was driven from the coal at temperatures above 315°C (600°F).

Objectives

Western Research Institute is developing a process to produce a premium-quality, solid fuel from low-rank coal. This process is based upon past experience with development of coal-drying and mild-gasification processes and what has been learned from technical and economic evaluation of those processes. The process, called COMPCOALTM, focuses on a low-cost method to produce a premium-quality fuel that is less susceptible to formation of dust, reabsorption of moisture, and self-heating than the parent coal. The COMPCOAL product must also have a high heating value, as well as low sulfur and moisture content, and must exhibit good combustion characteristics.

Procedures

An existing bench-scale inclined fluidized-bed (IFB) reactor system was modified by adding a stabilizer into the effluent gas line. The stabilizer is a batch fluidized-bed reactor that was loaded with char or raw coal before the start of a test. Carbon dioxide was passed through the system, the IFB reactor was heated to the test temperature, and minus 16-mesh Wyodak coal was fed to the IFB reactor at a rate of 10 lb/hr for a period of either 0.25 or 0.50 hour. The high-boiling fraction of the pyrolysis liquids (pitch) was deposited on the char or coal in the stabilizer. The low-boiling fraction of the coal liquid passed through the stabilizer because the stabilizer was maintained at a temperature above the dew point of this fraction.

To evaluate the economics of the process, the cost of capital equipment items were proportioned from published costs of similar equipment designed for a 1000-ton-per-day (TPD) mild-gasification plant using PRB coal. It was assumed that the plant would be located at a PRB mine and would use existing crushing and screening equipment. The plant would operate for 300 days each year and produce 573 TPD of COMPCOAL product. The plant would use 16.6×10^9 Btu/day in coal feed in producing 14.3×10^9 Btu/day of COMPCOAL, for a conversion efficiency of 86%.

PRB coal was charged to the operating costs at a rate of \$4.25/ton. A 10-year straight-line depreciation was used to provide rapid recovery of the capital investment and to simplify the calculations. Electrical power was estimated by proportioning gas flow rates to horsepower taken from a preliminary design. Fifty percent debt financing was assumed for the project.

Results

In the process, char containing 20 to 25 wt % volatiles and having a gross heating value of 12,500 to 13,000 Btu/lb is produced. The char is then contacted by smoke, driven from the char, depositing 6 to 8 wt % pitch on the char particles. Gas and vapors not deposited on the char are burned as fuel.

The economic evaluation shows the process will be economically attractive if the product can be sold for about \$20/ton or more.

Conclusions

Preliminary tests show that pitch can be deposited on char, resulting in a product that is less dusty and less susceptible to reabsorption of moisture than raw PRB coal. Initial evaluation indicates that additional development of the COMPCOAL process is justified.

Related Publication

Merriam, N.W., and V.K. Sethi, 1992, Initial Evaluation of a Process for the Production of a Premium, Solid Fuel from Powder River Basin Coal. Laramie, WY, WRI-92-R004.

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**ADVANCED EXPLORATORY
PROCESS TECHNOLOGY**

THE USE OF OIL SHALE AS A SULFUR SORBENT IN A CIRCULATING FLUIDIZED-BED COMBUSTOR

John S. Nordin

Background

The use of limestone or dolomite as a sulfur sorbent in fluidized-bed combustion of coal was reviewed by Nordin and Cha (1989). They found that, typically, pilot circulating fluidized-bed combustors achieved a 90% reduction in sulfur emissions using a limestone calcium to coal sulfur ratio of 2.3 to 2.7, expressed as a molar ratio of Ca:S. With bubbling fluidized beds the molar ratio of Ca:S ranged from 2.9 to 3.5. When lower-sulfur coal was combusted, much higher ratios of Ca:S were required to achieve a 90% reduction in sulfur emissions. The optimal capture of sulfur on limestone was achieved at temperatures of 815 to 870°C (1500 to 1600°F), with sulfur capture significantly decreasing at temperatures above 900°C (1652°F). The Ca:S ratio required for a 90% sulfur emissions reduction was lower for dolomite than conventional limestone, especially in pressurized fluidized-bed combustors, with a Ca:S ratio of 1.4 being typical for a dolomite containing 45% MgCO₃. The magnesium carbonate was believed to be converted to magnesium oxide in the fluidized-bed combustor, resulting in a much more porous structure for sorbing sulfur gases.

Oil shale should theoretically offer a much more favorable Ca:S ratio compared to limestone when used as a sulfur sorbent in coal-fired fluidized-bed combustors. The surface area of retorted or combusted oil shale exposed to sulfur gases from coal should be large compared to limestone; not just because of the magnesium carbonate content, but also because of voids left by the kerogen. In addition, raw oil shale has a heating value, typically ranging from 1100 to 3400 Btu/lb, compared to zero for limestone. These advantages should be expected to be partially offset by the higher ash content of combusted oil shale.

This study was done in 1989 when the old Clean Air Act rules were in effect. Those rules required a 90% reduction in sulfur emissions for electric utility steam generators burning solid fuels and constructed after September 18, 1978 if the potential to emit without controls was equal to or greater than 0.60 lb of sulfur dioxide per million Btu heat input. If the potential to emit was less than 0.60 lb of sulfur per million Btu heat input, a 70% reduction was required. This meant that the utility must achieve at least an additional 70% reduction in sulfur, even when burning low-sulfur coals. The Clean Air Act of 1990 removed the restriction that another 70 or 90% reduction in sulfur emissions must be removed, regardless of the sulfur content of the coal.

Objective

The objective of this study was to perform a technical and economic assessment of using oil shale as a sulfur sorbent with three western coals in a circulating fluidized-bed combustion power plant, such as the one being tested in Nucla, Colorado.

Procedures

The study approach was to evaluate the operating experience of Colorado-Ute Electric Association's circulating fluidized-bed power plant in Nucla, Colorado, through 1989. This facility completed a series of tests using limestone as a sulfur sorbent for three western coals. The Nucla power plant conditions were then extrapolated for oil shale in place of limestone based on pilot plant tests performed by Synfuels Engineering and Development Inc. (1988), who evaluated sulfur removal using limestone, spent oil shale, and raw oil shale. Additional research work, reviewed by Cha and Fahy (1989), was incorporated into this study, as well as input from Pyropower Corporation,

which provided the Nucla power plant circulating fluidized-bed combustor. The Nucla power plant tests were funded in part by the Electric Power Research Institute, which provided results of some of the facility tests (Friedman et al. 1989).

An economic comparison was then made between limestone and three raw and one combusted oil shale as sulfur sorbents for three western coals under conditions similar to those experienced at the Nucla power plant. The three western coals evaluated were Peabody A (0.73% S, 26.1% ash, 5.8% water), Peabody B (2.5% S, 33% ash, 6.0% water), and Salt Creek (0.44% S, 15.1% ash, 9.9% water). The limestone used as a base comparison cost the Nucla power plant \$20.90 per ton, delivered, and contained approximately 90% calcium carbonate, 1.8% magnesium carbonate, and 8.2 % silica and other impurities. The hypothetical oil shales used for the economic comparison had properties as listed in Table 1. When computing limestone or oil shale sorbent requirements, the assumption was made that the Nucla power plant must meet either a 70% reduction in sulfur emissions or the Colorado emission standard of 0.4 lb sulfur dioxide per million Btu input, whichever was more stringent. These were the emission limits imposed on the power plant

in 1989. The Colorado standard was the limiting condition for the Peabody coal, but the federal 70% reduction was the limiting condition for the Salt Creek coal.

Results

An average Ca:S molar ratio was calculated for the three coals used at the Nucla power plant using limestone from plant data. If the calcium included the calcium in the limestone plus the calcium in the coal, the molar ratios required to meet emission standards were 1.76, 3.44, and 2.1 for Peabody A, Peabody B, and Salt Creek coals, respectively. These numbers compare with values of 1.61, 3.50, and 1.32 for the respective coals using limestone based on extrapolation of Synfuels Engineering and Development (1988) data. On this basis, the molar alkali to sulfur ratio for oil shale for the three respective coals should be 0.77, 2.75, and 0.5 at 871°C (1600°F). When doing the economic analysis for oil shale, an alkali to sulfur molar ratio of 1.0 rather than 0.5 was assumed for Salt Creek coal. When limestone was used with Salt Creek coal, a 1.32 molar ratio was predicted, compared to the 2.1 molar ratio actually experienced. Agreement between Nucla power plant data and extrapolated data for Peabody coal was very good.

Table 1. Oil Shale Compositions Used in Economic Analysis

	Combusted Shale	Retorted Shale	Low-Grade Shale	Medium-Grade Shale	High-Grade Shale
Fisher Assay, gpt	0	0	12	25	38
Heating Value, Btu/lb	0	800	1100	2250	3350
Moisture, %	10	2	0.24	0.25	0.3
Kerogen, %	0	0	7.17	14.46	21.75
Char, %	0.3	4	0	0	0
% Ca	14.64	13.08	12.36	11.38	10.40
% Mg	4.63	4.13	3.91	3.60	3.29
% Na	1.08	0.96	0.91	0.84	0.77
% K	2.97	2.64	2.50	2.31	2.11
% Si	17.87	15.95	15.08	13.88	12.69
Loss on Ignition, %	10.3	23	28.08	33.75	39.45

At the 110 megawatt capacity, the quantity of solid waste (fly ash plus bottom ash) using limestone as a sulfur sorbent was calculated to be 29,400, 72,850, and 17,940 lb/hr for Peabody A, Peabody B, and Salt Creek coals, respectively. If the oil shales listed in Table 1 were used instead of limestone, the calculated quantity of solid waste varied from 33,800 lb/hr for high-grade shale to 35,000 lb/hr using previously combusted shale, all with Peabody A coal. For Peabody B coal, the respective range for the different shales varied from 74,100 to 98,550 lb/hr. For Salt Creek coal, the solid waste varied from 18,500 to 18,800 lb/hr. The break-even costs for the Nucla power plant are presented in Table 2 for when oil shale begins to compete with limestone at \$20.90 per ton.

Conclusions

The limestone or oil shale requirements and waste quantities generated were very strong functions of the sulfur and ash contents of the coal and the sulfur dioxide limits imposed by the regulatory agencies. The break-even point at which oil shale begins to compete economically with limestone at \$20.90 per ton varied from \$11.40 to \$26.76 per ton.

Since the passage of the Clean Air Act of 1990, the federal requirement of an additional 70% removal of sulfur, even when burning low-sulfur coals, was removed. The economics therefore now favor the burning of low-sulfur coals to meet emission standards.

Table 2. Break-Even Oil Shale Cost When Oil Shale Competes Economically with Limestone

	Peabody A Coal	Peabody B Coal	Salt Creek Coal
Combusted Shale	\$13.24	\$11.90	\$17.65
Retorted Shale	\$14.80	\$14.25	\$18.21
Low-Grade Shale	\$15.09	\$15.64	\$18.50
Medium-Grade Shale	\$17.70	\$20.49	\$20.09
High-Grade Shale	\$19.92	\$26.76	\$21.68

Related Publication

Nordin, J.S., and C.Y. Cha, 1989, The Use of Oil Shale as a Sulfur Sorbent in a Circulation Fluidized-Bed Combustor, Subtask 1.2 Technology Assessment, Subtask 1.3 Economic Evaluation. Laramie, WY, WRI-89-R016.

TREATMENT OF WELL-BLOCK PRESSURES IN RESERVOIR SIMULATION

Frank M. Carlson
Charles G. Mones

Background

A method of dealing with wells in grid blocks of reservoir simulators was developed by Peaceman (1978). This method continues to be very popular today (Desbarats 1993; Sharpe and Ramesh 1992). In the development for uniform grid spacing by Peaceman, a new definition of well-block pressure appeared along with a rather enigmatic constant, 0.2 (or more precisely, 0.198506 [Peaceman 1983]), which when multiplied by the grid size, gave an equivalent radius of the well block. Peaceman defined this well-block pressure as the steady-state flowing pressure at the equivalent radius.

Yet, there were others (van Poolen et al. 1968; Coats et al. 1974) who maintained that the well-block pressure should be the average pressure which should occur at a radius of 0.342 (or more precisely, 0.342198, to give it the same numbers of digits as Peaceman's constant) times the grid spacing. Because Peaceman's well-block pressure is neither the average pressure of the well block, nor is it located at the appropriate position for the average pressure, corrections are generally required to average pressure data obtained from pressure transient analysis before input to the simulator to accommodate Peaceman's method (Mattax and Dalton 1990).

Objective

The objective of this study was to more fully explore this controversy and to demonstrate that the more appropriate constant should indeed be 0.342198 when used with the procedure described below.

Procedures

Point-Centered Grids

Before focusing on the main issue of this study, a brief review of point-centering of grids is in order. A more complete review can be found in Aziz and Settari (1979). Figure 1 shows two examples of point-centered grids for both a one-dimensional system such as might be used in modeling a laboratory core flood and a two-dimensional system such as might be used in modeling a symmetry element of a pattern study (e.g., quarter of a five-spot).

(a) One-Dimensional Point-Centered Grid

(b) Two-Dimensional Point-Centered Grid

Figure 1. Examples of Point-Centered Grids

It is for these types of systems, where the outer boundary corresponds to an injection or production face or well, that point-centered grids are most advantageous.

To construct a point-centered grid system, one specifies the distances between grid points and then draws lines midway between the grid points. These lines delineate the grid-block boundaries as shown in Figure 1. Although, this procedure can lead to grid points that are not centered within the blocks when the grid points are unequally spaced, this study concerns itself only with grid blocks which are equally spaced. Therefore, half blocks appear at the ends of the one-dimensional system shown in Figure 1(a) and on the edges of the two-dimensional system shown in Figure 1(b). Also, quarter blocks appear in the corners of the two-dimensional system.

While having the grid points on the ends, edges, and corners of such systems has the advantage of being able to locate injection or production faces or wells at the points, it also produces a distinct disadvantage. This disadvantage is that the average pressure of the half or quarter block, which should be used in the expansion terms of the finite difference equations of the reservoir simulator, does not correspond to the grid point pressure. A similar disadvantage exists when radial wells are located at grid points in the middle of square blocks, regardless of whether the grid point is on the boundary or internal to the system; but in this case, it is the nonlinearity of the radial pressure distribution that causes the problem. Dealing with these disadvantages is the major focus of this study.

One-Dimensional System

In the lower portion of Figure 2 is shown the pressure distribution for steady-state, single-phase, incompressible fluid flow for the system shown in the upper portion of the figure. Here, five equally spaced grid points have been chosen to represent a total system length L of 100 ft. In all applications that follow, the initial pressure was set to 1000 psi, the production pressure to 1000 psi, the injection pressure

to 1100 psi, k to 1 Darcy, ϕ to 0.2, μ to 1.135 cP, and c to 1.0×10^{-6} psi $^{-1}$. The model was run until steady-state conditions prevailed. These choices are completely arbitrary and are used purely for illustration. The general form of the finite difference equation for all grid points other than grid points 1, 2, NI-1, and NI is:

$$\frac{p_{i-1}^m - p_i^m}{\Delta x} + \frac{p_{i+1}^m - p_i^m}{\Delta x} = \frac{GBV}{GP} (p_i^{n+1} - p_i^n) \quad (1)$$

where, $m = n$ or $n+1$ depending upon whether the equations are solved explicitly or implicitly (Mattax and Dalton 1990), GBV = grid block volume, Δx (Area), GP = group of variables, $6.328k$ (Area) $\Delta t / \phi \mu c$, and Area = 1 ft 2 . In the models developed for this work, all equations were solved for pressure explicitly, but the same approach, to be discussed below, was later successfully implemented in an implicit model. Equation (1) defines flow between internal grid points for a slightly compressible fluid.

Before discussing the remaining equations associated with the grid system shown in Figure 2, a comment regarding the auxiliary point is appropriate. The auxiliary point is not a new grid point added to the system. Rather, it eventually turns out to be the location of the grid point pressure for the half block on the ends displaced from its original position to a point $C \cdot \Delta x$ from the end, where C is a constant between 0 and 1, but excluding 0 and 1. The original point then becomes the boundary point of injection and is only used to implement the boundary condition.

The remaining equations describing the system shown in Figure 2 are:

$$Q_{in} = \frac{6.328k (Area) (p_{inj}^m - p_{x1}^m)}{\mu \cdot C \cdot \Delta x} \quad (2)$$

$$Q_{out} = \frac{6.328k (Area) (p_{xNI}^m - p_{prod}^m)}{\mu \cdot C \cdot \Delta x} \quad (3)$$

$$\frac{p_2^m - p_{x1}^m}{(1-C)\Delta x} + \frac{Q_{in}\mu}{6.328k(\text{Area})} = \frac{GBV}{2GP} (p_{x1}^{n+1} - p_{x1}^n) \quad (4)$$

$$\frac{p_{NI-1}^m - p_{xNI}^m}{(1-C)\Delta x} + \frac{Q_{out}\mu}{6.328k(\text{Area})} = \frac{GBV}{2GP} (p_{xNI}^{n+1} - p_{xNI}^n) \quad (5)$$

$$\frac{p_{x1}^m - p_2^m}{(1-C)\Delta x} + \frac{p_3^m - p_2^m}{\Delta x} = \frac{GBV}{GP} (p_2^{n+1} - p_2^n) \quad (6)$$

$$\frac{p_{NI-2}^m - p_{NI-1}^m}{\Delta x} + \frac{p_{xNI}^m - p_{NI-1}^m}{(1-C)\Delta x} = \frac{GBV}{GP} (p_{NI-1}^{n+1} - p_{NI-1}^n) \quad (7)$$

By specifying C and solving the system of Equations (1) through (7) for pressure through a number of time steps until steady-state conditions prevail, the pressure distribution shown in the lower portion of Figure 2 will result, Q_{in} will equal Q_{out} , and both Q_{in} and Q_{out} will equal the steady-state flow rate,

$$Q_{ssl} = \frac{6.328k(\text{Area})(p_{inj} - p_{prod})}{\mu L} \quad (8)$$

Figure 2. Developmental Point-Centered Grid and Corresponding Pressure Distribution for Linear, Steady-State Incompressible Flow of a Single-Phase Fluid

Two-Dimensional System

In the following, four sets of equations will be developed: (1) grid points other than the boundary points; (2) grid points along the left boundary excluding the injection well point, the point adjacent to the injection well, and the corner point (NI,1); (3) the corner point (NI,1); and (4) the injection well point and point adjacent to the injection well on the left boundary. The general form of the finite difference equation for all grid points other than the boundary points for the system shown in Figure 3 is:

$$\begin{aligned} & \frac{\Delta y (p_{i-1,j}^m - p_{i,j}^m)}{\Delta x} + \frac{\Delta y (p_{i+1,j}^m - p_{i,j}^m)}{\Delta x} \\ & + \frac{\Delta x (p_{i,j-1}^m - p_{i,j}^m)}{\Delta y} + \frac{\Delta x (p_{i,j+1}^m - p_{i,j}^m)}{\Delta y} \\ & = \frac{GBV}{GP} (p_{i,j}^{n+1} - p_{i,j}^n) \end{aligned} \quad (9)$$

where, $m = n$ or $n+1$ depending upon whether the equations are solved explicitly or implicitly (Mattax and Dalton 1990), GBV = grid block volume ($h\Delta x\Delta y$), GP = group of variables ($6.328kh\Delta t/\phi\mu c$), and $h = 1$ ft.

Figure 3. Developmental Point-Centered Grid for Two-Dimensional Fluid Flow in a Quarter Five-Spot Pattern

The general finite difference equation describing flow between grid points along the left boundary shown in Figure 3 for grid points other than (1,1), (2,1), and (NI,1) is:

$$\frac{\Delta y (p_{i-1,1}^m - p_{i,1}^m)}{\Delta x} + \frac{\Delta y (p_{i+1,1}^m - p_{i,1}^m)}{\Delta x} + \frac{\Delta x (p_{i,2}^m - p_{i,1}^m)}{\Delta y} = \frac{GBV}{2GP} (p_{i,1}^{n+1} - p_{i,1}^n) \quad (10)$$

The specific finite difference equation describing flow for the grid point (NI,1) in the lower left hand corner of Figure 3 is:

$$\frac{\Delta y (p_{NI-1,1}^m - p_{NI,1}^m)}{\Delta x} + \frac{\Delta x (p_{NI,2}^m - p_{NI,1}^m)}{\Delta y} = \frac{GBV}{4GP} (p_{NI,1}^{n+1} - p_{NI,1}^n) \quad (11)$$

Analogous equations to Equation (10) were written for the other boundaries and an analogous equation to Equation (11) was written for corner point (1, NJ), but these are not shown here to conserve space.

To write the equations in the vicinity of the injection and production wells shown in Figure 3, use is again made of the auxiliary point, and development of the equations will proceed very similarly to the linear case discussed above. The auxiliary point eventually will become the grid pressure to be fixed in space wherever the numerical model will produce an injection rate at steady-state conditions equivalent to the steady-state Muskat rate (Muskat 1937) for a quarter of a five-spot pattern,

$$Q_{MUSK} = \frac{19.848kh (p_{inj} - p_{prod})}{4\mu (\ln \frac{d}{r_w} - 0.619)} \quad (12)$$

where r_w is arbitrarily given the value of 0.25 ft.

For an injection pressure of 1100 psi, a production pressure of 1000 psi, a length of one side of the system in Figure 3 of 100 ft, a permeability of 1 Darcy, and a viscosity of 1.135 cP, $Q_{MUSK} = 76.445 \text{ ft}^3/\text{day}$.

The remaining equations needed to describe the flow along the left-hand boundary shown in Figure 3, (i.e., points xy1,1 and 2,1) are as follows:

$$r_x = A\Delta x \quad (13)$$

$$Q_{r_{inj}} = \frac{39.695kh (p_{inj}^m - p_{xy1,1}^m)}{\mu \ln \frac{r_x}{r_w}} \quad (14)$$

$$\frac{\Delta y (p_{2,1}^m - p_{xy1,1}^m)}{(1-B)\Delta x} + \frac{Q_{r_{inj}} \mu}{6.328kh} + \frac{\Delta x (p_{1,2}^m - p_{xy1,1}^m)}{(1-B)\Delta y} = \frac{GBV}{4GP} (p_{xy1,1}^{n+1} - p_{xy1,1}^n) \quad (15)$$

$$\frac{\Delta y (p_{xy1,1}^m - p_{2,1}^m)}{(1-B)\Delta x} + \frac{\Delta y (p_{3,1}^m - p_{2,1}^m)}{\Delta x} + \frac{\Delta x (p_{2,2}^m - p_{2,1}^m)}{\Delta y} = \frac{GBV}{2GP} (p_{2,1}^{n+1} - p_{2,1}^n) \quad (16)$$

It should be noted that xy1 (i.e., the auxiliary point) is the point which ultimately becomes the grid block pressure at point (1,1), as discussed above.

To complete the required system of equations for the model, equations analogous to Equations (14) and (15) were written for the producer and three more equations analogous to Equation 16 were written for the remaining points (1, 2), (NI-1, NJ), and (NI, NJ-1). These last five equations, however, are not shown to conserve space.

Results

One-Dimensional System

For the system described above and shown in Figure 2, $Q_{ss1} = 5.5753 \text{ ft}^3/\text{day}$. At steady state, the choice of C is arbitrary between 0 and 1, excluding 0 and 1, but because only a half block is represented at the end points, a reasonable choice for C is 0.25 which places the grid pressure at the center of the half block (i.e., at a location equivalent to the location of the average pressure of the end blocks). In a more practical model than that described here, fluid properties would be pressure-dependent and using $C = 0.25$ would allow these fluid properties to change as the average pressure of the half block changes, which seems reasonable when other possible values of C are considered. Without considering the matter further in this paper, however, it is suggested that other choices for C might be more appropriate as the compressibility of the system changes (e.g., the point where the grid block pressure equals the average pressure would be different for an ideal gas than for the slightly compressible fluid described here).

Two-Dimensional System

In the resulting model, pressures were solved for explicitly (Mattax and Dalton 1990) and the solution advanced in time until steady-state conditions prevailed. At these conditions, the injection rate and the production rate of the model should be equal and both should equal Q_{MUSK} calculated from Equation 12. Importantly, however, the choice of the constants, A and B are no longer arbitrary to get the desired rate as was C in the linear case. This is because the pressure distribution at steady-state conditions is no longer linear, but is radial in the vicinity of the wells (see Figure 4 which shows the steady-state pressure distribution along the diagonal between injector and producer and was constructed from the isobars shown in Figure 236, page 577 [Muskat 1937]). The constants A and B were specified, the model run until steady-state conditions prevailed, and the resulting rates were compared with Q_{MUSK} . By trial and error the constants were changed and the model run again until the rate from the model equaled Q_{MUSK} . For the 5×5 grid system shown in Figure 3, the required constants turned out to be $A = B = 0.3293$.

Figure 4. Steady-State Pressure Distribution along Diagonal between the Injector and Producer shown in Figure 3 for a Single-Phase Incompressible Fluid (after Muskat 1937)

For a 51 x 51 grid system, the constants turned out to be $A = B = 0.3415$. Even smaller grid spacings could have been tried, but at this point, the controversy mentioned in the introduction was recalled and the value of 0.342198 was placed in the model and the model run for 5 x 5, 11 x 11, 21 x 21, and 51 x 51 systems. These systems correspond to grid spacings of 20 ft, 10 ft, 5 ft and 2 ft respectively. The

deviation in percent was calculated between Q_{MUSK} and the model rate at steady-state conditions. These errors are small and are plotted as the lower curve in Figure 5. Note that an extrapolation of this curve to the point where the grid spacing would be equal to r_w suggests that the error would be close to zero. Actually, such a state could never be achieved, because of the singularity in Equation 14 when $r_x = r_w$.

Figure 5. Errors between Numerically Predicted Steady-State Flow Rates in a Quarter Five-Spot Pattern of an Incompressible Fluid and the Flow Rate Obtained from Muskat's Equation

This may explain the slight upward trend in error when the grid spacing is 2 ft. The upper curve represents the resulting errors for the same series of model runs, but for the case where $A=0.198506$ and $B=0$. This is equivalent to Peaceman's approach (Peaceman 1978). Note that while the errors are on the same order of magnitude in both approaches, the constant of 0.198506 is empirically based while the constant of 0.342198 is analytically based. The latter constant can be derived analytically by assuming that the well-block pressure is equal to the areal average pressure (Peaceman 1978) and is the basic assumption of Van Poolen (1968) which is clearly more intuitively appealing.

Not only does the use of the constant 0.342198 in the procedure developed here seem more appealing, but also there are several additional advantages to its use. First, as mentioned in the introduction, Peaceman's technique requires adjustments to average pressures obtained from pressure transient analysis. The technique employed here does not require such adjustments because the pressure calculated corresponds to the average pressure in the well grid block. Second, in more practical models, where fluid properties change with pressure, these properties are evaluated at the average pressure of the well block, which seems more reasonable than other possible choices. Third, for a given grid spacing, some 70% (calculated from the ratio of 0.342198 to 0.198506) larger wellbore radii can be accommodated by the technique discussed here than by using Peaceman's technique before the singularity discussed above develops. This may be important when using the apparent wellbore radius concept when wells are extensively and vertically fractured (Earlougher 1977). Fourth, even larger wellbore radii can be accommodated using the technique outlined here by leaving the constants $A = B$ subject to later change after model development. For example a choice of $A = B = 0.9$ in the 5×5 case above led to only a 1.9% error in the predicted rate from Q_{MUSK} . The choice of $A = B = 0.9$ results in a value of r_x from Equation (13) of 18 ft for

the 5×5 system. Therefore, a value for r_w can approach this value also. The potential user of this technique is cautioned, however, that when anything other than 0.342198 is used, rigor is lost and the user does so with consequences unevaluated here. Such consequences for extremely large wellbore radii should be more thoroughly evaluated before extensive use. It does seem possible that using this technique for large wellbore radii may be no worse than assuming the fracture behaves like an effective radius to begin with, an assumption that becomes less valid with increasing fracture length.

Implementation of the Procedure in an Existing Model

At first exposure, the above technique may seem quite cumbersome to implement. While more bookkeeping is necessary, it can be fairly easily implemented in existing models. For example, it has been successfully implemented in WRI's fully implicit thermal simulator.

Because in the general case wellbores may not be fully penetrating nor a well may not continuously operate during a simulation, dynamic modification of transmissibilities in the vicinity of the well block is required. This means, for example, if a well was penetrating only three of five vertical blocks, it would be desirable to modify the transmissibilities for the active blocks but not modify the transmissibilities for the inactive blocks. For simplicity, the procedure to be described here considers only one dimension, but treatment of the other dimensions would be treated analogously. Figure 6 identifies certain spatial terms to be used in this discussion. As mentioned above, when point-centered grids are used, grid block faces are assumed to be positioned midway between the grid points. The transmissibility between points i and $i+1$ is, for example:

$$T_i = \frac{kA}{\Delta x_i} \quad (17)$$

where, $\Delta x_i = x_{i+1} - x_i$

Figure 6. Representation of Transmissibilities for General Model Implementation

For a grid location containing a flowing well represented by a source term in the model, auxiliary points that locate the correct average pressure are needed to calculate the associated auxiliary transmissibility terms. For flow between adjacent grid points, two auxiliary transmissibilities are required: T_s associated with the grid point location containing the source term and T_o associated with the grid point adjacent to the grid point at which the source term is located. T_s is used to calculate interblock flow between the source point and the auxiliary point, while T_o is used to calculate interblock flow between the auxiliary point and the grid point adjacent to the grid block containing the source term.

For example, given a source term located at i , the auxiliary transmissibilities required to calculate interblock flows are as follows:

For flow between points $i-1$ and i ,

$$T_{o_{i-1}} = \frac{6.328 kA}{(1-\delta)(x_i - x_{i-1})} \quad (18)$$

for interblock flow at point, $i-1$, and

$$T_{s_{i-1}} = \frac{6.328 kA}{\delta(x_i - x_{i-1})} \quad (19)$$

for interblock flow at point i .

For flow between points i and $i+1$,

$$T_{o_i} = \frac{6.328 kA}{(1-\delta)(x_{i+1} - x_i)} \quad (20)$$

for interblock flow at point, $i+1$, and

$$T_{s_i} = \frac{6.328 kA}{\delta(x_{i+1} - x_i)} \quad (21)$$

for interblock flow at point, i .

Incorporation of this technique into WRI's fully implicit thermal simulator required two one-dimensional arrays (one for T_s and one for T_o) for each spatial dimension. The auxiliary transmissibilities are formed only once, at the same point in the code where the global (original) grid transmissibilities

are calculated. When dynamic interblock flow rates are determined about each grid point, logic within the code selects the auxiliary transmissibility T_s at any grid with an active source term and T_o at adjacent points. This procedure requires minimal computational overhead and modest additional storage.

Conclusions

- A new method has been developed which allows locating the well-block pressure at the point where the average pressure is located: (a) for the linear system, a choice of $0.25 \Delta x$ seems reasonable, (b) for the radial case, the location is fixed by the system and is located at $0.342198 \Delta x$.
- This method does not require adjusting the average pressures obtained from pressure transient analysis, as does Peaceman's approach.
- Larger wellbore radii can be accommodated using this technique than can be accommodated using Peaceman's technique for the same size grid.
- The procedure can be fairly easily implemented on existing simulators.

Nomenclature

Greek Symbols

δ	= a constant multiplied by the grid spacing to determine an equivalent radius (fraction)
Δx	= grid spacing in x direction (ft)
Δy	= grid spacing in y direction (ft)
Δt	= time step size (days)
μ	= viscosity (cP)
ϕ	= porosity (fraction)

Italicized Variables

A	= cross-sectional area open to flow for transmissibility (ft ²)
c	= compressibility (psi ⁻¹)

Other Variables

Area	= cross-sectional area open to flow (ft ²)
A	= constant multiplier of one side of a square grid block in two-dimensional system (fraction)

B	= 0, for Peaceman case A, otherwise (fraction)
C	= constant multiplier of grid block size in one-dimensional system (fraction)
d	= distance between injector and producer (ft)
GBV	= grid block volume (ft ³)
GP	= group of variables identified in text and depending upon whether system is one-dimensional (ft ⁴) or two-dimensional (ft ³)
h	= thickness (ft)
k	= permeability (darcy)
L	= system length in linear case (ft)
Q	= flow rate (ft ³ /day)
T	= transmissibility (ft ³ -cP/day-psi)
x	= distance (ft)

Subscripts

i	= grid point number in x direction
inj	= injector
j	= grid point number in y direction
MUSK	= steady-state, Muskat five-spot
NI	= maximum grid point in x direction
NJ	= maximum grid point in y direction
o	= adjacent to source term
prod	= producer
r	= radial
s	= source-term
ssl	= steady-state, linear
w	= well
x	= equivalent radius
$x1$	= auxiliary grid point at injection end for one-dimensional case
xNI	= auxiliary grid point at production end for one-dimensional case
$xy1$	= auxiliary grid point at injector in two-dimensional case

Superscripts

m	= general time step identifier
n	= time step identifier for which solution is known
$n+1$	= next time step number beyond n for which solution is unknown

Related Presentation

Carlson, F.M., and C.M. Mones, 1994, Resolution of the Inconsistency Between Peaceman's Well-Block Pressure and the Average Pressure of the Well-Block. 45th Annual Technical Meeting of the CIM, Calgary, Alberta, Canada.

THERMAL RESERVOIR MODELING

Charles G. Mones

Background

Western Research Institute had previously developed a numerical simulator (Tar Sand Reservoir Simulator [TSRS]) that describes thermal recovery processes in porous media (Vaughn 1986). The principal application of the model was to support laboratory investigations of combustion steam technologies in tar sand resources. The laboratory simulations consisted of one-dimensional tube tests in a 3-ft long reactor and two-dimensional block tests in a 3 x 3 x 2-ft sample of reservoir material.

TSRS is a highly implicit, four-phase (oil, water, gas, and coke), multicomponent, finite difference thermal simulator. The model formulation is based on a set of individual component-mass balance, energy balance, and related constraint equations that account for accumulation, vapor-liquid partitioning, chemical reaction, injection-production, heat conduction, heat loss, and the transport of mass and energy by Darcy flow. Interblock transport of mass and energy are calculated using a single-point upstream fluid mobility and enthalpy in a five-point, block-centered, finite difference scheme on fixed-sized Cartesian grids. The components described by TSRS include condensable species (oxygen and inert gas), water (liquid and vapor), oil species (light and heavy), and coke. Source-sink terms are accommodated by specification of molar-rate at a grid-block or by specification of a source-sink pressure which is used in a one-dimensional, linear flow calculation.

TSRS proved to be a useful tool for the evaluation of laboratory-scale experiments, and the formulation of its equations were satisfactory to describe thermal recovery processes (steamflooding, combustion, flooding, hot-gas pyrolysis, and hot-water flooding) in petroleum reservoir material. In fact more recently, TSRS has been used to predict field performance from CROWTM (Contained Recovery of Oil Wastes) applications. The model's nonisothermal

capability and fully-implicit formulation make it a useful tool for studying CROW, as well as other thermally-related, in situ technologies currently under development.

After its initial development, TSRS had limitations. The model was not three-dimensional and its memory management algorithms were inefficient, causing long execution times for large problems. Also, specification of input data was somewhat cumbersome and lacking in flexibility. A further limitation was that TSRS did not have provisions for well terms. TSRS permitted only the specification of a constant molar rate or a constant-pressure, linear-flow term.

Objectives

The objectives of this work were to modify and extend TSRS into a thermal simulator that is usable for field-scale problems.

Procedures

In extending TSRS for use as a field-scale, reservoir simulator, the following modifications were made to the model:

- Ability to describe one-, two-, or three-spatial dimensions
- Addition of point-centered spatial grids
- Ability to specify variable grid spacings
- Ability to describe directional permeabilities
- Ability to modify interblock transmissibilities
- Addition of radial well terms (i.e., source-sink) in both horizontal and vertical orientations
- Improvements to model numerics to reduce memory storage requirements, improve accuracy, and increase computation speed

The model was modified to accommodate one-, two-, or three-spatial dimensions by using three-, five-, or seven-point, respectively, finite difference computational gridding techniques. The model uses upstream weighting for the convective terms. The harmonic averaging method was used to compute interblock transmissivity terms, because it is believed that this method gives the most realistic results, particularly in cases of significant permeability contrasts. Provision for modifying transmissibility terms from the model input file was added to permit the user to more easily specify flow anomalies within the computational grid and to aid in performance of history matching procedures where it is more convenient to modify the transmissibility than block permeability. Provision for directional permeability was added to the model to more accurately describe vertical permeability contrasts which occur frequently in reservoirs.

Variable grid-spacing was implemented in the model. Variable grids permit improved accuracy with reasonable simulation times, by allowing the user to concentrate a fine-grid mesh in areas of rapidly changing reservoir properties or fluid velocities, and coarse grids in areas of relatively small changes in properties. A grid-centered method was used as described in Settari and Aziz (1972). This technique permits improved spatial discretization accuracy over cell-centered methods and has superior accuracy when performing pattern studies.

Vertical and horizontal well (source-sink) terms were added to the model. The method employed for calculation of the productivity indices in the model was developed by Peaceman (1983) for nonsquare, anisotropic reservoirs. The implementation permits wells to be oriented in the x-, y-, or z-direction and can be located anywhere within the reservoir. Well rates can be specified as either/or both rate controlled or pressure limited for any flowing phase. In the case of multilayer well completions, flow for each phase is partitioned among layers using a method of

weighted, dynamic-reservoir properties rather than a more commonly used weighted mobility method. The user may also specify a gravity gradient due to liquid level within the well.

The model's transport equations and numerical discretization methods were verified by comparing model results with analytical solutions from five-spot pattern studies and one-dimensional studies that used unit mobility ratios for both injected and produced fluids. Results from these tests were acceptable, giving agreement within 1% to the analytical results.

Results

The model's ability to simulate a three-dimensional thermal problem was verified by running the model with a Society of Petroleum Engineers comparative steamflood problem (Aziz et al. 1987). The problem was to steamflood a three-dimensional, nine-spot, heavy oil reservoir. One-eighth of the pattern was to be simulated. The oil was assumed to be nonvolatile. Because TSRS does not employ a nine-point difference method, the grid was oriented differently from that shown in the problem. The grid employed nine grids aligned between the injector well and the near producer with the far producer located diagonally at the corner (from the injection well) of the nine by five grid. The results with TSRS were generally within the range of the respondents for time of steam breakthrough, production pressure, and oil recovery.

Conclusions

WRI has been successful in adapting its previously developed laboratory-scale thermal model for use as a field-scale simulator. We anticipate significant use for the model in CROW field design applications.

Related Publications

Mones, C., 1993, Modifications to WRI's Thermal Model: Development Toward a Field-Scale Simulator. Laramie, WY, WRI-93-R033.

DEVELOPMENT OF THE CROWTM PROCESS

Lyle A. Johnson, Jr.

Background

The Contained Recovery of Oily Wastes (CROWTM) process removes organic contaminants from underground by adaptation of technology used for secondary and heavy oil recovery. The CROW technology has been successfully tested in the laboratory (Johnson and Guffey 1990). Presently, the process is being prepared for field demonstration in areas contaminated with wood treating wastes and byproducts of town gas production. These demonstrations will use hot-water displacement without chemical additives. The use of chemicals with the hot water to enhance displacement and solubilization of the wastes has been tested on a preliminary basis. This chemical additive testing to identify the potential of chemical addition was conducted as part of a project for the U.S. EPA SITE Program's Emerging Technology Program. The preliminary testing showed that less than 1 vol % of chemical in the initial pore volumes of hot-water flush could reduce the contaminant content by an additional 10 to 20 wt %. This testing showed the potential of chemical addition, but additional testing was needed to demonstrate the full benefit of chemical addition. The chemicals that have been tested are totally biodegradable and pose little, if any, environmental threat. However, the fate of added chemicals is considered in all testing.

The use of surfactants to enhance the solubility of polynuclear aromatic hydrocarbons (PAH) has been tested in the laboratory by researchers at Carnegie Mellon University for PAHs in water and soil-water systems (Edward et al. 1991, 1992; Liu et al. 1991; Laha and Luthy 1992). In these studies the researchers found that solubility enhancements as great as a factor of two can be attained when commercially available nonionic surfactants, such as alkyl or alkylphenol polyoxethylene, are added to the water in concentrations between 0.1 and 1.0% by

volume. This solubility enhancement resulted in 70 to 90% solubilization of the PAH. Noted in these studies was the linear decrease in the surface tension between the PAH phase and the aqueous phase as the surfactant concentration increased from the onset of surfactant micelle formation (~0.1% by volume) to the critical micelle concentration (~1% by volume). The researchers also found that the partitioning of the surfactant between the soil and solution phases increased as the degree of solubility increased. The combined effects of lowering of the surface tension and the enhancement of the PAH solubility should significantly increase the removal efficiency of the CROW process.

WRI has also conducted a limited number of other CROW screening tests with chemical enhancement. The chemicals in these tests ranged from commercial surfactants to pH modifiers for the injected water. In these tests, the surfactants performed more effectively than the pH modifiers. Results of these tests are not available for public dissemination because of the proprietary nature of the work.

Objective

The objective of this study was to obtain sufficient baseline data to show the effectiveness and environmentally safe use of chemicals, primarily surfactants, to enhance the CROW process.

Procedures

Eleven one-dimensional displacement tests were originally planned. The tests investigated the effect of three chemical concentrations (0, 0.5, and 1.0 vol %) at three temperatures (ambient, the projected optimum temperature, and 22°C (40°F) below the optimum temperature).

To begin testing, a characterization sample was prepared for each contaminated material. The bulk sample was

homogenized and composite samples taken for determination of fluid saturations. The soluble organic materials collected during the saturation determinations were combined to provide a sample for initial organic characterization. The viscosity, density, and distillation range were determined for the soluble organic material. The viscosity and density determinations were conducted at ambient, 38, and 60°C (100 and 140°F) for estimation of the optimum water injection temperature.

The reactor system used for the displacement tests was a tube reactor with a disposable chlorinated polyvinyl chloride tube. The tube was vertically oriented within a series of insulated shield heaters and equipped with six internal and six external thermocouples spaced approximately every 6 inches to monitor and control the reactor and process temperatures. The entire system was interfaced to a data acquisition computer that recorded temperatures, pressures, and flow rates every 5 minutes.

Water was injected into the bottom of the reactor by a positive displacement metering pump. The injected water passed through a heater to generate steam or hot water. Chemical, when used, was metered into the water stream by a syringe pump prior to the heater.

Produced fluids were collected from the top of the reactor through an automatic sampling valve system. Sampling intervals could be held constant or changed throughout the progress of the test. The reactor back pressure was maintained at atmospheric pressure by venting the product collection vessels to the atmosphere through a gas collection system.

All experiments were conducted in the same manner, with only the temperature and chemical concentration varied between tests. To initiate the tests, a homogenized bulk sample of the contaminated sample was packed into the reactor tube. During packing of the tube, a composite sample of the material placed in the tube was

collected for determination of the initial organic saturation of each tube. The weight of the packed material was recorded. The tube was instrumented with the appropriate thermocouples and placed into the reactor shell.

Following placement of the tube, water injection at 100 cc/min and the predetermined temperature was initiated and continued until 40 pore volumes (PV) of water had been injected. The PV of the packed tube was determined from the physical dimensions of the tube and the density and saturation of the contaminated soil. During the displacement phase, produced fluids were sampled every 2 to 4 PV for total organic carbon (TOC) determinations, and measurement of the pH and resistivity. At the end of each test, a 2-liter sample of the produced fluid was collected, labeled, and placed in cold storage until completion of the project. The purpose of these samples was to provide material for assisting in the determination of the surfactant partitioning if the post-test materials were not sufficient.

After completion of the injection phase, the injection and production ports were closed, the reactor shell opened, and the tube allowed to cool before removal. The cooled tube was then removed from the reactor shell and the weight of the contents determined and recorded. The flushed material was then extruded from the tube and divided into five even increments from the top to the bottom of the tube. Each increment was homogenized and a composite sample analyzed to determine the post-test organic saturation distribution and to track the surfactant partitioning during the test.

The planned tests were to consist of 11 one-dimensional displacement tests using a single contaminated sample. However, results of the first 11 tests indicated that a second sample would assist in interpretation of the results. The initial 11 tests were conducted in three sets of experiments, three tests without chemical addition, six tests with chemical addition, and two duplicates. In each set of tests,

three temperatures were used for the flushing water. These temperatures were based on the viscosity and density of the organic contaminate as determined during initial characterization.

Tests with the second contaminated material consisted of four tests. A single test was conducted at ambient temperature and the predicted optimum temperature with and without chemical addition. The chemical addition was at the highest concentration used in the first 11 tests.

The chemicals selected for use were Triton X-100 and Igepal CA-720, marketed by Aldrich Chemicals, and Hyonic NP-90, produced by Henkel Corporation. All three chemicals are nonionic, aerobically biodegradable surfactants. To evaluate which chemical to use, a sample of the known amount of the initial contaminated material was placed in a 1% by volume mixture and agitated for several hours. The resultant surfactant and organic mixture was decanted and the organic reduction determined. Based on these simple tests, Igepal was chosen as the chemical to be used in subsequent flushing tests. The chemical concentrations chosen for use in the flushing tests were 0.5 and 1.0% by volume. These concentrations and the initial three selected chemicals were based on the studies at Carnegie Mellon University.

The contaminated soils used in the tests were obtained from a former manufactured gas plant (MGP) site and a inactive wood treatment site. The MGP site material, the initial material, was a sandy soil contaminated with coal tars and coal cinders that was provided by Midwest Gas of Iowa. The soil from the wood treatment site was a sand contaminated with creosote and petroleum based hydrocarbons. This material was from the Baxter Tie Plant Site in Laramie, Wyoming that was provided by Union Pacific Railroad.

During the packing of the tube with the MGP soil, it was noted that the packed weights were significantly lower than with prior tested materials. The material,

instead of being a sand matrix contaminated with coke and coal tars, was determined to be mainly coke-like material with some sand. The individual coke particles were porous and the contaminant appeared to reside within the particle. Therefore, the packed tubes provided a dual porosity system consisting of primary porosity between the coke and sand particles, and secondary porosity within the individual coke particle. It was decided that testing of the material would increase the knowledge of the CROW process, so testing was continued.

Results

The initial nine tests, 128 through 136, with the MGP soil consisted of one each at approximate flushing temperatures of 18, 57, and 79°C (65, 135, and 175°F) with 0, 0.5, and 1.0% by volume chemical added to the flushing water (see Table 1). For all tests, the targeted injection rate was 100 cc/min and a total injected volume of ~40 PV. Results of the initial nine tests indicate a slight increase in the reduction of the organic contaminant with increasing flushing temperature, but no definite effect from the chemical addition (the solid symbols in Figure 1). The slight increase in organic removal is believed to be caused by the location of the contamination in the secondary porosity, where only a minor contact with the flushing water occurs. However, the TOC analyses of the produced fluids and determinations of the chemical remaining in the residual organics (organics remaining on or in the matrix following flushing) indicated that a portion of the chemical was partitioning into the contaminant.

To assist in determining the effect of the chemical addition, tests 137 and 138 were conducted at the two higher temperatures with 1.0% chemical addition, replication of the conditions in tests 132 and 135, respectively. The difference between these tests was the incorporation of an additional ~40 PV of elevated temperature flushing following the initial ~40 PV of elevated temperature flushing with chemical addition.

Table 1. Test Parameters and Results

Test No.	Init. Oil Sat., Dry	Porosity, %	Temp., °F	% Chemical Added	Inj. Rate cc/min	Inj. Water PV	Residual Sat., Dry	Organic Red., %
Midwest Samples								
128	10.27	41.74	67	0.00	109.00	33.3	8.90	13.34
129	11.11	33.62	135	0.00	89.00	44.1	9.01	18.90
130	12.55	44.71	175	0.00	93.00	33.0	9.67	22.95
133	11.77	43.84	63	0.46	107.00	33.0	9.78	16.91
136	9.85	46.51	134	0.50	92.00	31.3	8.16	17.16
134	11.75	45.61	174	0.49	102.00	35.4	9.58	18.47
131	10.62	38.04	65	0.80	99.00	38.7	10.01	5.74
132	12.14	41.99	139	0.90	96.00	36.5	9.27	23.64
135	12.23	46.03	178	0.92	100.00	34.1	9.79	19.95
137	11.78	39.75	141	1.00	98.00	76.3	7.55	35.91
138	11.00	45.04	173	0.93	99.00	64.0	6.00	45.45
Baxter Samples								
139	1.97	27.15	67	0.00	86.00	47.6	1.10	44.16
140	1.25	25.35	64	0.95	101.00	47.2	0.52	58.40
141	1.16	29.98	149	1.09	87.00	41.3	0.35	69.83
142	1.97	33.93	152	0.00	98.00	36.9	1.07	45.69

Figure 1. Organic Reduction versus Flush Temperature, Midwest Tests

As shown in Figure 1, the additional 40 PV of flushing produced a significant increase in the organic reduction. This indicates that the chemical additive is modifying the solubility and the surface tension of the contaminate such that the organic material can be removed from the secondary structure, but the process requires extended flushing following the initial chemical-added flushing.

Because the results using the MGP soil were inconclusive, it was decided that a contaminated soil with a matrix that was essentially sand might help determine the effect of chemical addition. The soil from the Baxter Tie Plant was selected. Only four tests, 139 to 141, were conducted using this material. The tests were conducted at ambient temperature and 66°C (150°F) at chemical concentrations of 0 and 1.0% by volume. These tests showed that increased flushing temperature resulted in a slight increase in organic removal, while the addition of chemical resulted in a significant increase in organic removal at all temperatures tested (Figure 2). Also noted was a significant increase in organic removal with chemical addition at the elevated temperature.

Conclusions

Results of the laboratory tests of the CROW process using chemical assisted flushing on two contaminated materials indicate:

- Elevated flushing temperatures increase the removal of the organic contaminate compared to ambient temperature flushing. This is true for both the no-chemical and chemical flushing series.
- The addition of chemical results in increased removal of the contaminate at all temperatures tested for material with primarily a sand matrix.
- Chemical added to the flushing water of a material consisting of secondary porosity systems will increase the recovery, but will require additional nonchemical flushing of the system to allow time for solubilization and surface tension modification effects to occur.
- The chemical partitioned between the aqueous and soil phases occurred with a significant concentration remaining in the residual organic. This is especially evident when the soil is comprised of porous particles.

Related Publication

Johnson, L.A., Jr., 1994, Development of the CROWTM Process. Laramie, WY, WRI-94-R017.

Figure 2. Organic Reduction versus Flush Temperature, Baxter Tests

STEAMFLOOD ENHANCEMENT IN NATURALLY FRACTURED RESERVOIRS

Robert M. Satchwell
Lyle A. Johnson, Jr.

Background

Steamflooding is the primary enhanced oil recovery process in use today, both in project number and the oil produced (Moritis 1992). However, steamflooding of naturally fractured reservoirs is currently not viable, resulting in a virtually untapped resource. Chemically enhanced steamflooding could unlock these reserves. The literature reveals several attempts to produce fractured reservoirs by conventional steamflooding with limited success (Sahuquet and Ferrier 1982; Britton et al. 1983; Dietrich 1986; Oballa et al. 1991). The DOE steamflood field tests in the Northwest Asphalt Ridge tar sand deposit (Johnson and Thomas 1985) and in the Shannon formation at National Petroleum Reserve No. 3 (NPR-3) have been influenced by heterogeneous reservoir conditions. Primary recovery from the NPR-3 Shannon formation has been projected to be less than 6% of the original oil in place, with only an additional 9% from steamflooding because of the fractured nature of the Shannon formation (U.S. Department of Energy 1988).

Improvements to the performance of the steamflood process with chemical additives can provide application to a wider range of reservoirs, including those that are naturally fractured. Laboratory investigators have shown that selected classes of new cross-linked polymers have the potential for use in the harsh steamflood environment (Sydansk 1988; Mumallah and Doe 1989; Jones and Shu 1990). These polymers have had limited field testing, but with encouraging results (Cooke and Eson 1992; Hunter et al. 1992). Foaming agents for such service have a similar status, having been developed in the laboratory (Navratil et al. 1983), but having had only limited field testing (Mohammadi et al. 1991). In the present study, a series

of laboratory experiments was conducted to evaluate various chemical enhancements. These included incorporation of surfactants, polymers, and noncondensable gases into the steamflood process.

Objectives

The objectives of this study were to identify and test potential additives that would modify flow in fractures and divert it to the porous media during steam injection. Specific tasks were to: (1) identify potential additives from a literature review, (2) test and evaluate these potential additives in one-dimensional (1-D) experiments and identify the best additive, and (3) perform three-dimensional (3-D) experiments with the best additive of the 1-D tests to verify its performance and effectiveness in modifying flow in fractures.

Procedures

The 1-D simulations were performed using fluid saturated 2-inch diameter by 12-inch long Berea sandstone cores in a rubber sleeved core holder. In all tests, a steam injection rate of 18.04 cc/hr cold water equivalent was obtained with a positive displacement pump feeding a heater. Steam flowed through a bypass system until the desired steam quality conditions were established, at which time the steam was directed into the core. In all tests, steam was injected until a residual oil saturation was achieved. Chemical injection into the sample was then initiated, as directed by the manufacturer's recommendations. During each test, the produced fluid was collected on a scheduled basis. The oil-water ratio was determined either by direct measurement or by centrifugation, if necessary. Following the tests, the core was removed from the test cell, and the water and residual oil saturations were determined by extraction.

Twenty-five 1-D tests were performed at temperatures ranging from 93 to 228°C (200 to 443°F) and outlet pressures between 1 to 217 psig, using 10 separate Berea sandstone cores with and without simulated fractures. Fractures were simulated by placing spacers between the core-halves.

Two 3-D simulations were conducted using 24 x 24 x 18-inch blocks of actual Shannon reservoir material. In both experiments, an injector and producer were located diagonally across from each other within each sample block. In both cases, an injection pressure of 250 psig was maintained during the steaming, with thermocouples monitoring the movement of the front. After the produced water cut exceeded 95%, the selected additive was injected. The first test simulated a horizontal fracture that intersected both production and injection wells. To create this fracture orientation, the large block was cut into two smaller 24 x 24 x 9-inch blocks and placed back together. The second test simulated a vertical fracture case. This fracture orientation was created by cutting the large block into two smaller 12 x 24 x 18-inch blocks. In both cases, 0.006-inch spacers were placed between each of the smaller blocks to maintain fracture width.

Results

A literature review was conducted and potential sources were contacted to gather relevant information for additives to be evaluated in 1-D simulations. The selection of the additives was dictated by high-temperature stability. The additives selected for testing were three polymers and a surfactant. The additives were: Chevron's Chaser SD 1020 (surfactant), EPT's cross-linked EPT-HY-TEMP polymer gel (Polymer 1), Pfizer's cross-linked FLOPERM 3429-340X4 (Polymer 2), and Coalplex's HCC 1000 Polymer (Polymer 3).

Results of the 1-D tests indicated that the surfactant obtained the largest additional oil recovery after steamflooding to residual oil saturation, (see Table 1). Recovery was

lower when the spacer width was increased from 0.000 to 0.006-inch with all additives, except with Polymer 1. However, the increase in recovery with Polymer 1 at higher spacer widths was statistically insignificant. Core-to-core variance was determined to be insignificant, since several tests were performed using the same core, but with different additives.

Table 1. Percentage Reduction in Oil Saturation with Respect to Spacer Width

Spacer Width	Additive Type			
	Surfactant	Polymer 1	Polymer 2	Polymer 3
Whole	1.54	na	na	0.54
0.000-inch	3.37	0.27	2.49	2.35
0.006-inch	0.56	0.47	0.71	0.80
Average of Fracture Cases	1.96	0.37	1.60	1.57

The injection of all additives caused the injection pressure to increase. However, with all polymers, the high-temperature steam removed the blockage, and subsequent injection pressure decreased.

Since the surfactant produced the best results in the 1-D simulations, 3-D simulations were performed using the surfactant. The production for the horizontal fracture case is presented in Figure 1. The figure shows the cumulative production of oil and water. Also illustrated in Figure 1 is the projected oil production for the steamflood, exclusively. Approximately 16.3% more oil was produced by the addition of the surfactant. The cumulative water production was offset, but the slope was nearly identical in the stabilized portion of the test.

Figure 1. Cumulative Production for Horizontal Fracture Case

A plot of injection pressure as a function of time is shown in Figure 2. From the data it is clear that the pressure did not increase after the surfactant was injected. Based on discussions with the manufacturer of the surfactant, it was deduced that the lack of increased pressure was caused by the high quality of steam used during the test. Lack of sufficient volume of water did not create enough stable foam to divert the flow away from the fracture.

The vertical fracture 3-D test was performed under similar conditions, except nitrogen was injected to elevate the superficial velocity of the steam. The nitrogen also reduced the partial pressure of steam, which created a more stable foam. The injection rates were tailored to the wellbore dimensions to create sufficient superficial velocity to produce turbulent flow in the injection well.

The cumulative oil and water production for the vertical fracture case is shown in Figure 3. Also included is the projected oil production for the steamflood without the

addition of surfactant. These results show that 31% more oil was produced by the addition of surfactant. Increased injection pressure was observed as shown in Figure 4. It was presumed that this increase was caused by stable foam under these test conditions. It should be noted that the increase in pressure persisted even when the injection rate was reduced from 35 cc/min to 10 cc/min. The injection pressure data are consistent with the manufacturer's claim that stable foam diverts the flow away from the fracture.

Conclusions

This study identified and tested four potential additives to modify flow in fractures and divert it to the porous media during steam injection. Several 1-D and 3-D laboratory tests were performed on fracture media.

The 1-D laboratory tests showed that a surfactant additive was more effective than the three polymers tested. The ineffective behavior of the polymers is believed to be caused by temperature degradation.

Figure 2. Injection Pressure for Horizontal Fracture Case

Figure 3. Cumulative Production for Vertical Fracture Case

Figure 4. Injection Pressure for Vertical Fracture Case

The surfactant additive was further tested in the 3-D simulations that indicated that the preferential flow path can indeed be blocked if a stable foam is created. Off-spec tests showed that even if a stable foam was not created, improved recovery can still be obtained. Increased recovery in this case is likely created by a reduction in interfacial tension between the oil and water. However, when stable foam is created, further improvement in recovery is obtained.

The results indicate that critical parameters for use of the surfactant as a foaming agent are: (1) sufficient superficial velocity of the steam, and (2) adequate water volume in the steam to create the foam.

Further testing at a pilot demonstration level is recommended in a fractured field such as the Shannon Formation at NPR-3.

Related Publication

Satchwell, R.M., and L.A. Johnson, Jr., 1994, Steamflood Enhancement in Naturally Fractured Reservoirs. Laramie, WY, WRI-94-R018.

PRELIMINARY EVALUATION OF A CONCEPT USING MICROWAVE ENERGY TO IMPROVE AN ADSORPTION-BASED, NATURAL GAS CLEAN-UP PROCESS

R. William Grimes

Background

Increased use of natural gas can enhance U.S. energy security, environmental quality, and economic strength by decreasing our reliance on imported oil. Though natural gas has many advantages as a fuel, demand has decreased since the early 1970s (U.S. Department of Energy 1992). Technologies that enlarge and stabilize the domestic natural gas reserve base will help increase the long-term availability of affordable natural gas. Technologies that clean up low quality natural gas can also increase this reserve base and do so without increased drilling activity.

Among the contaminants common in natural gas, nitrogen is one of the more difficult to remove economically. For larger gas fields cryogenic processing can be used successfully. However, due to the high capital and operating costs of cryogenic systems, their application is restricted to larger fields, typically where production exceeds 20 MMscf/day (Minteco PSA 1991).

The widespread commercial acceptance of pressure swing adsorption (PSA) for low-volume gas separations would seem to make it a natural choice for a noncryogenic method of separating nitrogen from natural gas. The application of PSA to nitrogen-methane separation has been studied extensively, and pressure/vacuum swing adsorption cycles for bulk separation of nitrogen-methane mixtures have been developed. However, the high capital and operating costs associated with vacuum regeneration of the adsorbent limits the application of the pressure/vacuum swing process. Adsorbent regeneration also has a strong influence on the efficiency of separation processes based upon cyclic adsorption. Regeneration is a major factor controlling the amount of adsorbent needed to produce a given amount of product, and

thus, the size and cost of the separation system. In fact, adsorbent regeneration tends to be the major factor in the overall economics of these processes (Lukchis 1973).

Earlier, unpublished results of work conducted at Western Research Institute involving microwave regeneration of adsorbent chars suggested the possibility that microwave energy could be used instead of vacuum pumping to regenerate adsorbents. Despite relatively high cost, microwave energy has found industrial acceptance in applications where its unique properties offer advantages that offset its cost. Direct energy transfer and homogeneous and selective heating are among the properties of microwave energy that can provide a technical advantage to compensate for the high capital cost of the equipment (Orfeuil 1987).

Williams Technologies, Inc. (WTI) has been investigating the development an economically viable wellhead PSA system to separate nitrogen contamination from natural gas. They have determined that existing PSA cycles using vacuum-assisted adsorbent regeneration are unacceptable for small gas fields. WTI investigated the performance of a variety of solid adsorbents for use in a PSA process, including various natural and synthetic zeolites and an active carbon. While they did not find a workable adsorbent, they developed process guidelines and generated data related to the performance of various solid adsorbents for the separation of nitrogen-methane mixtures. Among the zeolites tested, WTI found that the natural zeolite, chabazite, showed a strong selectivity toward methane adsorption. However, it was considered unacceptable because the adsorbed methane did not desorb on pressure reduction (Minteco PSA 1991).

Objectives

The objectives of this work were to determine if microwave energy could be used to regenerate a zeolite adsorbent and to evaluate the feasibility of using microwave energy to improve the desorption phase of a PSA process applied to the upgrading of natural gas contaminated with nitrogen.

Procedures

Because chabazite holds methane strongly, it was chosen as the adsorbent to evaluate the concept of microwave-assisted desorption. If microwave energy could increase the desorption efficiency of methane without heating of the adsorbent, it should also work with other zeolites, such as faujasite and zeolite-L, on which methane is held less tightly.

Based on the cost of nonproductive energy consumption, the criteria for evaluating the heating of the adsorbent during regeneration was set at less than 11°C (20°F) rise in adsorbent temperature due to microwave heating.

Adsorbent regeneration consists of the desorption of gas with the subsequent return of adsorptive capacity. Thus, to evaluate the concept of using microwave energy for adsorbent regeneration, an ability to measure quantities of gas adsorbed and desorbed was needed. This was accomplished using a specially designed PSA apparatus. For this evaluation, adsorption and desorption of gas was measured volumetrically. Effluent gas quantity was measured volumetrically by displacing water from six individually-selectable cylinders. The closed end of each cylinder was fitted with a rubber septum from which a sample of gas could be withdrawn for analysis. The effluent gas composition was determined using a gas chromatograph. Chabazite from the Chula Claims in Arizona was supplied by WTI for use in the tests. For each test series, approximately 100 grams of preconditioned chabazite was weighed and poured into the adsorption column.

The performance of the preconditioned chabazite was established using six adsorption-desorption pressure cycles. This also resulted in the production of saturated chabazite for the subsequent microwave desorption tests. The simple two-step pressure cycle consisted of feeding 30% N₂/70% CH₄ at a constant rate of 1183.2 scm³/min into the column until the column pressure reached 50 psig, stopping the feed, and allowing the column to depressurize from the feed end. For each cycle, all effluent gas was collected, and its volume and composition was determined and recorded. The feed time was recorded and multiplied by the feed rate to give the volume of gas fed in each cycle.

After six pressure swing cycles, the chabazite was removed from the adsorption column and placed in a 500 mL round bottom flask. The flask was connected by a length of plastic tubing to a gas collection cylinder and placed in a microwave oven. The gas collection cylinder was located outside the microwave oven. The oven was turned on for 0, 1, 2, or 3 minutes, and the effluent gas was collected, and its volume measured. The flask was removed from the oven, and the temperature in the center of the chabazite was measured with a thermocouple probe. The regenerated chabazite from the microwave oven was then reloaded into the adsorption column, and additional pressure swing cycles were run. Effluent volume and composition of the gas streams were determined and recorded and subsequently compared to the baseline values obtained for the preconditioned chabazite.

Results

Table 1 lists the volume of methane and nitrogen in the feed and effluent from consecutive pressure swing adsorption cycles using preconditioned chabazite and chabazite regenerated for 1 and 2 minutes in the microwave oven. The effluent volume of the gases from the pressurization and depressurization portions of each cycle are listed separately. Figure 1 shows the volume of methane and nitrogen adsorbed per gram of adsorbent.

Table 1. Feed and Effluent Volumes for Selected Cycles, scm³

Cycle	Feed		Effluent			
	CH ₄	N ₂	Pressurize		Depressurize	
	CH ₄	N ₂	CH ₄	N ₂	CH ₄	N ₂
Baseline 1	2518.9	1087.3	18.7	919.5	1390.0	501.8
Baseline 2	2064.7	891.2	475.1	597.1	1399.3	479.7
Baseline 3	2050.9	885.3	537.9	462.7	1347.2	521.1
Baseline 4	2064.7	891.2	680.6	395.8	1351.3	523.9
Baseline 5	2050.9	885.3	666.8	402.7	1352.8	537.6
Baseline 6	2064.7	891.2	684.0	402.7	1327.1	522.1
One Minute 1	1584.1	683.8	11.0	52.8	1090.0	539.6
One Minute 2	1418.8	612.4	4.5	57.4	1260.5	609.6
Two Minutes 1	2424.3	1046.5	39.6	697.7	1318.5	476.6
Two Minutes 2	2024.9	874.0	455.1	480.5	1335.0	502.5
Two Minutes 3	1928.5	832.4	588.7	357.0	1340.7	500.4

Figure 1. Methane and Nitrogen Adsorption for Selected Cycles

In the pressurization portion of the first cycle (Baseline 1), the preconditioned chabazite adsorbed 24 scm³ of methane per gram of adsorbent (see Figure 1). Nitrogen (adsorbed from the air while the column was being loaded with adsorbent) was replaced by methane for a negative net adsorption of nitrogen in the first cycle. Very little methane was found in the waste gas stream during the pressurization portion of the cycle (2.0%), and based upon the volume and composition of this waste stream effluent from the first cycle, it can be concluded that methane was selectively adsorbed on chabazite. The depressurization effluent from the first cycle does not show significant methane enrichment (73.5 versus 70.0%). This is probably due to the fact that the column void volume and volume in the connecting tubing are filled with nitrogen at the end of the first pressurization cycle. The rapid blow-down step used in more complex cycles (Yang 1987) would increase product purity, as would desorption of more of the residual methane held by the chabazite.

Effluent from the pressurized portion of the second cycle (Baseline 2) contains a considerable amount of methane (44.3%). Methane adsorption in the second cycle is reduced to about 12.5 scm³ per gram of adsorbent, one-half of the amount found for the first cycle. Effluent from the depressurization portion of the second cycle is very similar to that of the first cycle, with no significant methane enrichment of the product detected (74.5 versus 70.0%).

By the end of the third cycle (Baseline 3), the chabazite shows essentially no selective adsorption of methane from the gas mixture, and the composition of the effluent gas during pressurization and depressurization are nearly equal for each of the remaining three pressure swing cycles. Thus, the preconditioned chabazite

shows a strong selectivity toward methane adsorption, and a methane capacity of 24 scm³ per gram of adsorbent for the first pressure swing cycle. However, selective adsorption and capacity for methane decline rapidly, and after three cycles, there is essentially no selective adsorption of methane, and capacity is down to 10 scm³ per gram of adsorbent.

The volume of gas desorbed and the corresponding temperature rise of the chabazite after 0, 1, 2, and 3 minutes in the microwave oven were measured. Heating of the adsorbent was evident for all three microwave exposure times. Two minutes in the microwave oven were needed to regenerate the adsorbent to the activity observed for the preconditioned adsorbent. However, this exposure resulted in a 42°C (75°F) rise in adsorbent temperature, which is considerably greater than the evaluation limit of 11°C (20°F). The methane content of the products resulting from the depressurization portion of the three cycles (Two Minutes 1, 2, and 3) averaged about 73% versus 70% in feed, an enrichment comparable to that observed for the preconditioned chabazite.

Conclusions

Microwave energy can be used successfully to regenerate a zeolite adsorbent, but excessive heating of the zeolite makes the concept impractical for application in natural gas cleanup. Microwave-assisted desorption may prove useful in adsorptive purification processes where recovery of the sorbate with minimal dilution is required.

Related Publication

Grimes, R.W., 1992, Preliminary Evaluation of a Concept Using Microwave Energy to Improve an Adsorption-Based, Natural Gas Clean-Up Process. Laramie, WY, WRI-93-R003.

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ADVANCED FUELS RESEARCH

EVALUATION OF WESTERN SHALE OIL AS A FEEDSTOCK FOR HIGH-DENSITY AVIATION TURBINE FUEL

Kenneth P. Thomas

Background

The processing of alternate fossil fuels has been the subject of several studies sponsored by the U.S. Department of Energy and the U.S. Department of Defense. For the most part, these studies evaluated conventional petroleum processes for the production of specification-grade fuels. For example, Sullivan et al. (1978) and Sullivan and Frumkin (1986) studied conventional refining processes for the production of transportation fuels from shale oils and coal-derived liquids. Moore et al. (1981) studied the production of military jet fuels from western shale oil by a process that combined hydrogenation, acid extraction of nitrogen compounds, and fluid catalytic cracking. A combination of hydrogenation, acid extraction, and hydrocracking was also studied by Reif et al. (1982) for converting western shale oil to jet fuels. Other research sponsored by the U.S. Air Force investigated the conversion of tar sand oils and heavy petroleum to military jet fuels (Moore et al. 1987; Talbot et al. 1986). These studies demonstrated that conventional aircraft turbine fuels could be made from several unconventional fossil fuel sources.

Objective

The purpose of this investigation was to determine the feasibility of producing high-density aviation turbine fuel from western shale oil.

Procedures

The processes that were evaluated included acid-base extraction, solvent dewaxing, Attapulugus clay treatment, coking, and hydrogenation. Acid-base extraction was used to reduce the heteroatom content of middle distillates and atmospheric and vacuum gas oils. Solvent dewaxing was used to reduce the paraffin content of atmospheric and vacuum gas oils.

Attapulugus clay treatment was used to reduce the heteroatom content of middle distillates. Coking was used to reduce the molecular weight and distillation range of vacuum gas oils. Hydrogenation was used to reduce the heteroatom content and to saturate the aromatic rings of middle distillates and atmospheric gas oils.

A whole shale oil sample received from the Unocal shale oil production facilities located at Parachute, Colorado was distilled to produce the following distillates and residue: IBP-177°C (IBP-350°F, naphtha), 177-288°C (350-550°F, middle distillate), 288-427°C (550-800°F, atmospheric gas oil), 427-538°C (800-1000°F, vacuum gas oil), and 538°C+ (1000°F+) residue. Numerous chemical and physical properties were determined for this whole oil, its distillates and residue, and process intermediates. These analyses were conducted using either ASTM (ASTM 1985) or standard WRI procedures.

The middle distillate, atmospheric gas oil, and vacuum gas oil were selected for study because these distillates have potential for being converted into high-density aviation turbine fuel. The processes evaluated address those properties of the distillates that have to be modified to produce a turbine fuel: heteroatom and paraffin content, molecular weight, distillate range, and aromatic content.

Results

Table 1 shows the chemical and physical properties of the whole oil and the distillates that were evaluated with regard to the production of high-density aviation turbine fuel. The properties of the whole oil are typical of western shale oils, containing fairly high percentages of nitrogen and sulfur and having a specific gravity of about 0.9. The oil contained 11.8 wt % residue distilling above 538°C (1000°F).

Table 1. Chemical and Physical Properties of Western Shale Oil and Selected Distillates

Property	Whole Oil	Middle Distillate	Atmospheric Gas Oil	Vacuum Gas Oil
Elemental Composition, wt %				
Carbon	84.3	83.7	83.5	83.8
Hydrogen	12.0	13.2	13.0	12.4
Nitrogen	1.7	0.9	1.3	1.9
Sulfur	1.1	1.3	1.1	1.0
Oxygen ^a	0.9	0.9	1.1	0.9
Hydrogen-to-Carbon Atomic Ratio				
	1.70	1.88	1.86	1.76
Viscosity, cP 100°F				
	17.6	2.1	14.8	429
Specific Gravity, 60°F				
	0.9091	0.8430	0.9061	0.9530
Molecular Weight				
	320	210	270	390
Pour Point, °F				
	-	-56	57	100

^a Oxygen determined directly, elemental composition then normalized to 100 wt %

As expected, the distillates and residue contain decreasing percentages of hydrogen and increasing percentages of nitrogen with increasing boiling range. Sulfur is evenly distributed across the distillate range, and oxygen is concentrated in the higher boiling distillates and residue. In addition, the specific gravity, viscosity, and molecular weight increase with increasing boiling point.

Since the application of the acid-base extraction, solvent dewaxing, and coking processes to the appropriate distillates did not produce intermediates that warranted further evaluation as fuel candidates, they will not be further discussed here. The application of Attapulgus clay treatment to selected distillates resulted in intermediates that were evaluated as potential fuel candidates. Test fuel #1 was prepared by passing the middle distillate through an Attapulgus clay column. Test fuel #2 was

prepared by passing a 4 to 1 by volume mixture of the middle distillate and a 288-354°C (550-670°F) distillate through an Attapulgus clay column.

The chemical and physical properties of the fuel candidates are listed in Table 2. Test fuel #1 easily satisfies the hydrogen requirement of a high-density aviation turbine fuel. In addition, the amount of nitrogen is very low (39 ppm), the oxygen value is less than 0.1 wt %, and the distillation data meet the requirements of a high-density aviation turbine fuel. Also, the freeze point is only slightly above the required value of -47°C (-53°F). However, the sulfur content is too high (1.0 wt %), the specific gravity is too low (0.8180), and the net heat of combustion is too low (125,890 Btu/gal). To increase the specific gravity of the fuel candidate, a mixture was prepared containing 20 vol % of a higher boiling distillate. After clay treatment, the

specific gravity of test fuel #2 had increased from 0.8180 to 0.8259. Unfortunately, the increase was not enough to satisfy the high-density fuel requirement. In addition, the heteroatom content increased, and the freeze point increased dramatically to -25°C (-13°F). Because of the changes noted in the properties of the fuel candidates, we suspected that the paraffin content of the fuels was too high. The results of mass

spectral analysis of the fuels proved this suspicion to be true. The mass spectral data show that the alkane content of test fuels #1 and #2 are 28.0 and 37.7 wt %, respectively. The requirement for a high-density fuel is less than 10 vol %. In addition, the aromatic content is also too high, 34.7 and 40.9 wt %, respectively. The requirement for this property is a maximum of 30 vol %.

Table 2. Chemical and Physical Properties of Fuel Candidates Prepared from Western Shale Oil

Property	High-Density Fuel	Test Fuel #1	Test Fuel #2
Elemental Composition, wt %			
Carbon	-	85.2	84.5
Hydrogen	13.0 min	13.8	14.0
Nitrogen	-	trace ^a	0.2
Sulfur	0.4 max	1.0	1.2
Oxygen ^b	-	<0.1	0.1
Specific Gravity, 60°F	0.850 min	0.8180	0.8259
Freeze Point, °F	-53 max	-45	-13
Net Heat of Combustion, Btu/gal	130,000 min	125,890	127,700

^a Test Fuel #1 contained 39 ppm nitrogen

^b Oxygen determined directly, elemental composition then normalized to 100 wt %

To reduce the heteroatom and aromatic content of the distillates, hydrogenation experiments were conducted using the middle distillate and atmospheric gas oil as the feeds to the reactor. Each distillate was hydrogenated at two different temperatures. This was done to determine the level of severity that is appropriate to convert the distillates to high-density turbine fuel intermediates. As expected, heteroatom content and distillate range of the intermediates significantly decreased with respect to the original distillates. The total heteroatom content was reduced from the 3.1- to 3.5-wt % level to the part-per-million level.

Hydrocarbon-group-type analysis of the process intermediates from the middle distillate shows that the amount of alkanes increased because of the partial saturation of alkenes. Consequently, the percentage of saturates in the process intermediates was only somewhat higher than that in the original distillate. However, the amount of aromatics in the process intermediates increased from 29 to about 37 wt %. This was due to an increase in the amount of monoaromatics (alkylbenzenes and indanes/tetralins). The process intermediates from the atmospheric gas oil also had an increase in alkanes. However, not only saturation of alkenes, but also

conversion of other classes of compounds through cracking resulted in this increase. Consequently, the percentage of saturates in these process intermediates increased from the 54 wt % originally present in the atmospheric gas oil to about 86 wt %. The amount of aromatics in the intermediates from the atmospheric gas oil decreased somewhat, exhibiting a shift from diaromatics to monoaromatics (alkylbenzenes and indanes/tetralins). Even though hydrogenation reduced the level of heteroatoms to the part-per-million level, the high concentration of alkanes in the process intermediates precluded their further evaluation as high-density aviation turbine fuels.

Conclusions

Several processes were evaluated for their ability to produce intermediates for the production of high-density aviation turbine fuel. These processes included acid-base extraction, solvent dewaxing, Attapulugus clay treatment, coking, and hydrogenation. Acid-base extraction and solvent dewaxing reduced the heteroatom and paraffin content of the distillates. In addition, coking reduced the distillate range, molecular weight, and specific gravity of the vacuum gas oil. However, none of these products was suitable for evaluation as fuel candidates because the heteroatom and paraffin contents of the products were too high.

Attapulugus clay treatment reduced the nitrogen and oxygen content of the middle distillate to the part-per-million level but the amount of sulfur, alkanes, and aromatics in the test fuels were higher than the target values established by the U.S. Air Force. In addition, the specific gravity and net heat of combustion of the test fuels were too low. Because acid-base extraction and Attapulugus clay treatment did not reduce the heteroatom content to the levels appropriate for a fuel candidate,

hydrogenation was evaluated as a process to reduce heteroatoms and also to saturate the aromatic rings present in the middle distillate and atmospheric gas oil. The heteroatom content of the process intermediates was reduced to the part-per-million level. However, the amount of alkanes was too high to satisfy the requirements of a high-density aviation turbine fuel.

Because of the paraffinic nature of western shale oil, it appears that it will be quite difficult or expensive to prepare high-density aviation turbine fuel from this alternative fossil fuel.

Related Publications and Presentations

Publications

Thomas, K.P., and D.E. Hunter, 1989, The Evaluation of Western Shale Oil as a Feedstock for the Production of High-Density Aviation Turbine Fuel. Laramie, WY, DOE/MC/11076-2888.

Thomas, K.P., E.B. Smith, and D.E. Hunter, 1989, Advanced Fuels Research. Proceedings of the Ninth Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting, Morgantown, WV, DOE/METC-89/6107, 282-291.

Presentations

Thomas, K.P., 1989, Advanced Fuels Research. Presented at the Ninth Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting, Morgantown, WV.

Thomas, K.P., E.B. Smith, and D.E. Hunter, 1989, The Processing of Alternate Fossil Fuels to Produce High-Density Aviation Turbine Fuel. Presented at Confab '89, Laramie, WY.

EVALUATION OF PROCESSES FOR THE UTILIZATION OF EASTERN SHALE OIL AS A FEEDSTOCK FOR HIGH-DENSITY AVIATION TURBINE FUEL

Kenneth P. Thomas

Background

For many years, the U.S. Department of Defense and the U.S. Department of Energy have been involved in evaluating alternative fossil fuel sources as feedstocks for the production of conventional transportation fuels. For example, Sullivan and Frumkin (1986) studied conventional refining processes for the production of gasoline, diesel fuel, and jet fuel from coal-derived liquids. Moore et al. (1981) and Reif et al. (1982) evaluated various refining processes for the production of jet fuels from western shale oil. Other research sponsored by the U.S. Air Force investigated the conversion of tar sand bitumens and heavy crude oils to military jet fuels (Talbot et al. 1986; Moore et al. 1987). However, it appears that very little has been done to evaluate the process sequence and the properties of conventional transportation fuels produced from eastern shale oil.

With respect to the production of high-density aviation turbine fuel from shale oils, several papers have recently been published. For example, western shale oil was shown to not be a suitable feedstock for the production of high-density turbine fuel (Thomas and Hunter 1989a; Greene 1989). This is, primarily, because western shale oil is a very paraffinic fossil fuel. However, the only information that appears to be available concerning the evaluation of eastern shale oil as a feedstock for the production of high-density turbine fuel are the reports of Fahy and Vawter (1987) and Cha et al. (1989). They concluded that upon hydrogenation this very aromatic oil could make a good feedstock for the production of high-density aviation turbine fuel.

Objective

The objective of this study was to determine the feasibility of producing a high-density aviation turbine fuel from eastern shale oil.

Procedures

A sample of eastern shale oil was received from the Morgantown Energy Technology Center, Laramie Project Office. The oil was produced by Synfuels Engineering and Development Inc. (1989) using the Tosco II process. Normally, a routine analysis of the whole oil is made on the as-received sample. However, because of the very high solids and water content of the oil, a small portion of the oil was dissolved in toluene and then filtered to remove the solids. The water and toluene were removed from the resultant mixture by rotary evaporation. This sample constituted the "whole oil" for analysis. The distillates and residue and the subsequent process intermediates that were analyzed resulted from a rather laborious clean-up and distillation process (Thomas and Hunter 1989b). The shale oil resulting from this process was distilled to produce the following distillates and residue: IBP-177°C (IBP-350°F, naphtha), 177-288°C (350-550°F, middle distillate), 288-427°C (550-800°F, atmospheric gas oil), 427-538°C (800-1000°F, vacuum gas oil), and 538°C+ (1000°F+) residue. Numerous chemical and physical properties were determined for the whole oil, its distillates and residue, and process intermediates. These analyses were conducted using either ASTM (ASTM 1985) or standard WRI procedures.

The middle distillate, atmospheric gas oil, and vacuum gas oil were selected as the feed materials for process evaluation because these distillates have the potential of being converted into high-density

aviation turbine fuel. The processes that were evaluated included acid-base extraction, solvent dewaxing, Attapulugus clay treatment, coking, and hydrogenation. Acid-base extraction was used to reduce the heteroatom content of the middle distillate and atmospheric and vacuum gas oils. Solvent dewaxing was used to reduce the paraffin content of the atmospheric and vacuum gas oils. Attapulugus clay treatment was used to reduce the heteroatom content of the middle distillate. Coking was used to reduce the distillate range of the vacuum gas oil. Hydrogenation was used to reduce the heteroatom content and to saturate the aromatic rings in the middle distillate and atmospheric gas oil. These processes address the properties of the distillates that must be modified to produce a turbine fuel: heteroatom and paraffin content, molecular weight, distillate range, and aromatic content.

Results

The chemical and physical properties of the whole eastern shale oil and selected distillates are listed in Table 1. The data listed for the whole oil are for the oil after the solids and water were removed. An aliquot of the oil as delivered to WRI contained 17.9 wt % water, determined by azeotropic distillation with toluene, and 33.2 wt % solids, determined by filtration.

The whole oil is fairly aromatic, with a hydrogen-to-carbon (H/C) atomic ratio of 1.43, and contains modest amounts of nitrogen, sulfur, and oxygen. The specific gravity is 1.0178, reflecting its aromatic character. The viscosity and molecular weight of the whole oil are, respectively, 294 cP at 38°C (100°F) and 260 amu. The chemical and physical properties of this sample of eastern shale oil are comparable to other eastern shale oils produced by a

Table 1. Chemical and Physical Properties of Eastern Shale Oil and Selected Distillates

Property	Whole Oil	Middle Distillate	Atmospheric Gas Oil	Vacuum Gas Oil
Elemental Composition, wt %				
Carbon	84.0	85.1	85.1	85.7
Hydrogen	10.1	11.7	10.1	8.7
Nitrogen	2.0	0.7	1.6	2.0
Sulfur	1.6	1.2	1.7	1.9
Oxygen ^a	2.3	1.3	1.5	1.7
Hydrogen-to-Carbon Atomic Ratio				
	1.43	1.64	1.41	1.21
Viscosity, cP				
100°F	294	3.2	22.7	91,100
Specific Gravity,				
60°F	1.0178	0.8936	0.9690	1.0656
100°F	1.0040	-	0.9550	1.0518
Molecular Weight				
	260	200	250	380
Pour Point, °F				
	-	-35	14	77

^a Oxygen determined directly, elemental composition then normalized to 100 wt %

variety of processes (Tokairin and Morita 1983; Ewert and Scinta 1983; Faulkner et al. 1983; Roberts et al. 1988). In general, the percentages of nitrogen, sulfur, and oxygen in the distillates and residue increase with increasing boiling range, while the H/C atomic ratio decreases with increasing boiling range. The viscosity, specific gravity, molecular weight, and pour point increase with increasing boiling range.

The process conditions and properties of the process intermediates are listed in Table 2. Evaluation of these results indicated that the products from acid-base extraction, solvent dewaxing, Attapulugus clay treatment, and coking were not suitable for further investigation as fuel candidates.

Table 2. Conditions Used and Properties of Process Intermediates Obtained from the Hydrogenation of Distillates from Eastern Shale Oil

	Middle Distillate		Atmospheric Gas Oil	
<u>Process Conditions</u>				
Pressure, psig	1500	1500	2000	2200
Liquid Hourly Space				
Velocity, V_o/V_c /hr	1	1	1	1
Hydrogen Feed, scfb	5000	5000	5000	6000
Temperature, °F	600	625	700	700
Hydrogen Consumption, scfb	800	918	1250	1105
<u>Product Properties</u>				
Elemental Composition,				
Carbon, wt %	87.2	87.2	88.4	88.2
Hydrogen, wt %	12.7	12.8	11.4	11.5
Nitrogen, ppm	1470	350	990	1610
Sulfur, ppm	104	46	620	1140
Specific Gravity, 60°F	0.9348	0.9318	0.9053	0.9118
Hydrocarbon Type, wt %				
Alkanes	16.8	14.4	28.0	30.5
Alkenes	10.8	13.3	20.7	19.5
Monocyclic Alkanes	3.1	6.6	6.3	5.6
Dicyclic Alkanes	0	0.3	0	0
Tricyclic Alkanes	<u>1.6</u>	<u>1.1</u>	<u>0</u>	<u>0</u>
Total Saturate Hydrocarbons	32.3	35.7	55.0	55.6
Alkylbenzenes	9.6	10.8	6.6	7.3
Indanes/Tetralins	54.4	52.0	31.8	26.9
Naphthalenes	3.7	1.5	0.9	1.8
Fluorenes	0	0	4.5	6.3
Anthracenes/Phenanthrenes	<u>0</u>	<u>0</u>	<u>1.2</u>	<u>2.1</u>
Total Aromatic Hydrocarbons	67.7	64.3	45.0	44.4

Since the processes tested to this point did not significantly improve the properties of the distillates, specifically the heteroatom and aromatic content, hydrogenation of the distillates was conducted. Each distillate was hydrogenated at two different sets of conditions. This was done to estimate the level of severity that might be appropriate for conversion of the distillates to high-density aviation turbine fuel intermediates.

As a result of the hydrogenation process, the heteroatom content of all intermediates significantly decreased with respect to the original distillates. Based on the results of hydrocarbon-group-type analysis, the process intermediates produced from the middle distillate contain less alkanes and alkenes than the original distillate. However, the percentage of monocyclic alkanes is increased. The result is that the percentage of saturates decreased from 50 to about 34 wt %. The percentage of monoaromatics (alkylbenzenes and indanes/tetralins) is increased with respect to the original distillate. This results in an increase in the aromatics from 45 to about 66 wt %. Of particular interest is that these process intermediates contain about 53 wt % indanes/tetralins, a component that upon further hydrogenation to dicyclic alkanes is important for the production of high-density turbine fuel. The process intermediates from the atmospheric gas oil have higher percentages of alkanes and monocyclic alkanes than the distillate. This results in an increase in saturates from 40 to about 55 wt %. The percentage of aromatics in the intermediates is increased from 36 to about 44 wt %. This increase in aromatics is the result of increased amounts of monoaromatics (primarily, indanes/tetralins). During the processing, diaromatics and triaromatics were lost. As observed for the intermediates from the middle distillate, the aromatics from the atmospheric gas oil were composed of, primarily, indanes/tetralins and some alkylbenzenes. Even though the hydrogenation process reduced the heteroatom content to about 0.1 wt % or less and the alkane content is fairly low (middle distillate intermediates contain about 15 wt % alkanes), the process

intermediates were not suitable for further evaluation as a high-density turbine fuel. However, the high concentration of indanes/tetralins does suggest that eastern shale oil may be a suitable feedstock for the production of high-density aviation turbine fuel.

The middle distillate from eastern shale oil is composed of about 32 wt % indanes/tetralins. After a single-stage hydrogenation experiment, the percentage of this class of compounds is increased to about 53 wt %. In addition, the heteroatom content is reduced to about 0.1 wt % or less. It appears that a two-stage hydrogenation process may lead to the production of a high-density aviation turbine fuel from distillates of eastern shale oil. However, the first stage must be relatively mild for the removal of heteroatoms. The second stage is then more severe, for the saturation of alkenes and aromatic rings. If the conversion is not conducted using a two-staged approach, but rather a severe single-stage process, the result will be the opening of dicyclic structures to produce monocyclic structures (Thomas and Hunter 1989c).

Conclusions

Five processes were evaluated for their ability to produce intermediates from suitable distillates of eastern shale oil for the production of high-density aviation turbine fuel. The application of the acid-base extraction, solvent dewaxing, Attapulugus clay treatment, and coking processes did not result in intermediates that warranted further investigation as fuel candidates. Hydrogenation was evaluated as a process to not only reduce the heteroatom content, but also saturate the aromatic rings present in the middle distillate and atmospheric gas oil. The heteroatom content of the process intermediates was reduced to about 0.1 wt % or less. However, the saturation of aromatics and olefins was not accomplished during the application of the single-stage hydrogenation process. Consequently, evaluation of the process intermediates as fuel candidates was not conducted.

In summary, the processes evaluated did not produce materials that satisfied all of the requirements of a high-density aviation turbine fuel.

In spite of the difficulties in preparing fuel candidates suitable for evaluation as a high-density aviation turbine fuel, it is believed that a two-stage hydrogenation process can be employed to produce a high-density turbine fuel that would meet the requirements of the U.S. Air Force. This is based on the observation that the process intermediates from hydrogenation contain high concentrations of indanes/tetralins.

Hydrogenation of indanes/tetralins to dicyclic alkanes results in a class of compounds that are necessary for the production of a high-density aviation turbine fuel.

Related Publication

Thomas, K.P., and D.E. Hunter, 1989, The Evaluation of Processes for the Utilization of Eastern Shale Oil as a Feedstock for the Production of High-Density Aviation Turbine Fuel. Laramie, WY, DOE/MC/11076-3023.

EVALUATION OF A COAL-DERIVED LIQUID AS A FEEDSTOCK FOR HIGH-DENSITY AVIATION TURBINE FUEL

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Background

The conversion of coal-derived liquids to transportation fuels has been the subject of many studies sponsored by the U.S. Department of Energy and the U.S. Department of Defense. These studies evaluated conventional petroleum processes for the production of specification-grade fuels. For example, Sullivan et al. (1978) and Sullivan and Frumkin (1986) studied conventional refining processes for the production of transportation fuels from coal-derived liquids and western shale oil. Smith et al. (1988) evaluated the potential of producing conventional jet fuels from a by-product stream of the Great Plains Gasification Plant (Basin Electric). They concluded that the production of conventional military turbine fuels, JP-4 and JP-8, is possible but only through the use of large amounts of hydrogen, 3400 scfb. They also concluded that the production of a high-density aviation turbine fuel, JP-8X, is possible but only through special processing to satisfy specific gravity and freeze point requirements. As a continuation of the screening studies conducted by Smith et al. (1988), Furlong et al. (1989) evaluated various hydrogenation schemes to produce conventional jet fuels and high-density aviation turbine fuel from the tar oil (by-product) stream. They verified their process scheme, which includes three separate hydrogenation steps, by producing two barrels of JP-8 that met all of the military specifications, except the flash point. In addition, small quantities of JP-4 and JP-8X were produced. These products met all specifications except copper strip corrosion (JP-4 and JP-8X), heating value (JP-4), existent gum (JP-8X), and flash point (JP-8X). The copper strip corrosion and existent gum specifications probably would have been met if the samples had been clay-treated or if additives had been used. As a continuation of the study

reported here, Greene et al. (1989) and Greene et al. (1990) evaluated various refinery processes to produce high-density aviation turbine fuel from coal-derived liquids. Employing a series of hydroprocessing steps, they produced fuels that exceed the net heating value requirement of a high-density aviation turbine fuel.

Objective

The purpose of this investigation was to determine the feasibility of producing a high-density aviation turbine fuel from a coal-derived liquid.

Procedures

A coal-derived liquid was received from the Morgantown Energy Technology Center. The liquid was produced by Coalite and Chemical Products Limited of England using a low-temperature carbonization process (Needham 1961). The liquid was distilled to produce IBP-177°C (IBP-350°F, naphtha), 177-288°C (350-550°F, middle distillate), 288-418°C (550-785°C, atmospheric gas oil), 418-538°C (785-1000°F, vacuum gas oil), and 538+°C (1000+°F) residue. No evidence of thermal cracking was observed during the distillations. Numerous chemical and physical properties were determined for the whole coal-derived liquid, its distillates and residue, and process intermediates. These analyses were conducted using either ASTM (1985) or standard WRI procedures.

The middle distillate, atmospheric gas oil, and vacuum gas oil were selected for process evaluation because these distillates have potential for being converted into high-density aviation turbine fuel. The processes that were evaluated included acid-base extraction, solvent dewaxing, Attapulugus clay treatment, coking, and hydrogenation. Acid-base extraction was used to reduce the heteroatom content of

the middle distillate and atmospheric and vacuum gas oils. Solvent dewaxing was used to reduce the paraffin content of the atmospheric and vacuum gas oils. Attapulugus clay treatment was used to reduce the heteroatom content of the middle distillate. Coking was used to reduce the distillate range of the vacuum gas oil, and hydrogenation was used to reduce the heteroatom content and to saturate the aromatic rings in the middle distillate and atmospheric gas oil. These processes address those properties of the distillates that must be modified to produce a turbine fuel: heteroatom and paraffin content, molecular weight, distillate range, and aromatic content.

Results

The chemical and physical properties of the whole coal-derived liquid and selected distillates are listed in Table 1. As is typical

of coal-derived liquids, the whole oil is fairly aromatic, having a hydrogen-to-carbon ratio of 1.25. It also contains modest amounts of nitrogen and sulfur and a rather large amount of oxygen. The specific gravity is 1.0407, also reflecting its aromatic character, and the oil contains 8.7 wt % distilling above 538°C (1000°F). Nitrogen increases with increasing distillate range; while sulfur and oxygen are variable. The middle distillate has the highest amount of oxygen (7.3 wt %), probably phenols. As expected, the hydrogen-to-carbon ratio decreases with increasing distillate range, and the viscosity, specific gravity, molecular weight, and pour point increase with increasing distillate range. Note that the molecular weight of the vacuum gas oil was determined in pyridine rather than the customary solvent, toluene, because of the presence of preasphaltenes.

Table 1. Chemical and Physical Properties of a Coal-Derived Liquid and Selected Distillates

Property	Whole Oil	Middle Distillate	Atmospheric Gas Oil	Vacuum Gas Oil
Elemental Composition, wt %				
Carbon	82.9	82.2	85.2	85.0
Hydrogen	8.7	9.3	9.1	8.0
Nitrogen	1.1	0.5	1.1	1.4
Sulfur	1.1	0.7	0.8	1.0
Oxygen ^a	6.2	7.3	3.8	4.6
Hydrogen-to-Carbon Atomic Ratio	1.25	1.35	1.27	1.12
Viscosity, cP 100°F	67.8	42.0	83.2	97,800
Specific Gravity, 60°F	1.0407	0.9750	1.0313	1.1080
Molecular Weight	180	190	230	270 ^b
Pour Point, °F	-	-29	57	97

^a Oxygen determined directly, elemental composition then normalized to 100 wt %

^b Molecular weight determined in pyridine, all other molecular weights determined in toluene

Unfortunately, acid-base extraction, solvent dewaxing, Attapulgi clay treatment, and coking did not produce intermediates that warranted further investigation as fuel candidates. In each case, the resulting intermediates contained too high of heteroatom and aromatic contents.

Consequently, hydrogenation experiments were conducted on the middle distillate and atmospheric gas oil with the goal being

the removal of heteroatoms and the saturation of aromatic rings. The process conditions and properties of the process intermediates are listed in Table 2. Each distillate was hydrogenated at two different temperatures. This was done to estimate the level of severity that might be appropriate for conversion of the distillates to high-density aviation turbine fuel intermediates.

Table 2. Conditions Used and Properties of Process Intermediates from the Hydrogenation of Distillates from a Coal-Derived Liquid

	Middle Distillate		Atmospheric Gas Oil	
<u>Process Conditions</u>				
Pressure, psig	1750	1750	2000	2000
Liquid Hourly Space				
Velocity, V_o/V_c /hr	1	1	1	1
Hydrogen Feed, scfb	8000	8000	8000	8000
Temperature, °F	635	650	700	715
Hydrogen Consumption, scfb	2681	2835	2269	2559
<u>Product Properties</u>				
Elemental Composition,				
Carbon, wt %	86.0	85.9	87.8	87.6
Hydrogen, wt %	14.0	14.1	12.2	12.4
Nitrogen, ppm	<20	<20	270	59
Sulfur, ppm	<20	27	97	35
Specific Gravity, 60°F	0.9208	0.9178	0.9598	0.9558
Hydrocarbon Type, wt %				
Alkanes	4.2	3.8	8.8	13.7
Alkenes	34.2	35.1	17.5	17.4
Monocyclic Alkanes	34.2	36.2	18.5	17.8
Dicyclic Alkanes	0.6	1.4	1.8	1.1
Tricyclic Alkanes	0.5	0	0.2	0
Total Saturate Hydrocarbons	73.7	76.5	46.8	50.0
Alkylbenzenes	8.1	8.7	6.8	7.0
Indanes/Tetralins	18.0	14.7	42.8	40.7
Naphthalenes	0.2	0.1	0.8	0.8
Fluorenes	0	0	2.0	1.0
Anthracenes/Phenanthrenes	0	0	0.8	0.5
Total AromaticHydrocarbons	26.3	23.5	53.2	50.0

During the hydrogenation process, the heteroatom content of all intermediates significantly decreased with respect to the original distillates. The total heteroatom content was reduced from the 5.7- to 8.5-wt % level to the part-per-million level. In addition, a significant amount of thermal cracking occurred during the hydrogenation of the distillates. For the middle distillate, the conversion in distillate range was significant, the process intermediates contain about 50 wt % distilling below 177°C (350°F) rather than the original 3 wt %. For the atmospheric gas oil, a rather significant reduction in the distillate range also resulted because of the hydrogenation process. More than one-third of the material distilling in the 288-427°C (550-800°F) range was converted to the next lower reported distillate range. The specific gravity of the process intermediates was decreased with respect to the original distillates. The specific gravity of the distillates ranged from 0.9750 to 1.0313, whereas the specific gravity of the process intermediates ranged from 0.9178 to 0.9598.

Hydrocarbon-group-type analysis of the process intermediates produced from the middle distillate contained less alkanes than the original distillate. However, the percentage of alkenes in the intermediates doubled because of the processing. Monocyclic alkanes were also significantly increased. The percentage of saturates increased from 40 to about 75 wt %. The percentage of aromatics remained about the same as that in the original distillate. The aromatics were composed of, primarily, indanes/tetralins and some alkylbenzenes. The process intermediates from the atmospheric gas oil contained about the same amount of alkanes and three times the amount of alkenes as the original distillate. In addition, they contained significant amounts of monocyclic alkanes. The percentage of saturates increased from 19.7 to about 48 wt %. The percentage of aromatics also increased, in this case, from 38.1 to about 52 wt %. As observed for the intermediates from the middle distillate,

the aromatics from the atmospheric gas oil were composed of, primarily, indanes/tetralins and some alkylbenzenes. Even though the hydrogenation process reduced the heteroatom content to the part-per-million level and the alkane content was low, the intermediates were not suitable for evaluation as high-density turbine fuels because their alkene contents were too high and, for those intermediates from the atmospheric gas oil, the aromatic contents were too high. However, the high concentration of indanes/tetralins does seem to suggest that this coal-derived liquid may be a suitable feedstock for the production of high-density aviation turbine fuel.

The hydrogenation studies reported here parallel those of Smith et al. (1988). The combined results of the two studies demonstrate that during the hydrogenation of a coal-derived liquid containing high concentrations of heteroatoms, in particular oxygen, the reactions occur in the following order: sulfur removal, oxygen removal, and nitrogen removal and ring opening. Saturation of double bonds competes with these processes and results in products that are either partially hydrogenated or reflect ring-opening reactions. If these results are compared with earlier work (Smith et al. 1986) on FCC light cycle oil and pyrolysis fuel oil, there is almost complete conversion of naphthalene to dicyclic alkanes. However, the higher ring-number structures are not exclusively converted to their saturate analogs. These structures also undergo ring opening and alkyl chain cleavage to yield tetralin-type structures. It appears that two-stage hydrogenation is necessary, but the first stage must be relatively mild with the goal being the removal of heteroatoms, in particular oxygen. The second stage is then more severe, with the goal being the saturation of alkenes and aromatic rings. If the processing is not conducted using this two-stage approach, a single-stage process will result in the opening of one of the rings of the dicyclic structures to produce monocyclic structures.

Conclusions

Five processes were evaluated for their ability to produce intermediates from suitable distillates for the production of high-density aviation turbine fuel. Acid-base extraction, solvent dewaxing, Attapulugus clay treatment, and coking resulted in products that contained high concentrations of heteroatom- and aromatic-containing structures. Consequently, further evaluation of these products was not warranted.

Hydrogenation was evaluated as a process to not only reduce the heteroatom content, but also saturate the aromatic rings present in the middle distillate and atmospheric gas oil. The heteroatom content of the process intermediates was reduced to the part-per-million level. However, the saturation of aromatics and olefins was not accomplished during the application of the single-stage hydrogenation process. Consequently, evaluation of the process intermediates as fuel candidates was not conducted. In summary, the processes evaluated did not result in the production of materials that satisfied all of the requirements of a high-density aviation turbine fuel.

Despite the difficulties in preparing fuel candidates suitable for evaluation as high-density aviation turbine fuels, it is believed that a two-stage hydrogenation process can be employed to produce a high-density turbine fuel that would meet the requirements of the U.S. Air Force.

This premise is based on the observation that the process intermediates from hydrogenation contain high concentrations of dicyclic alkanes and indanes/tetralins, compounds that are necessary for the production of a high-density aviation turbine fuel.

Related Publications and Presentation

Publications

Thomas, K.P., and D.E. Hunter, 1990, Advanced Fuels Research: The Evaluation of a Coal-Derived Liquid as a Feedstock for the Production of High-Density Aviation Turbine Fuel. Proceedings of the Tenth Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting, Morgantown, WV, DOE/METC-90/6115, 490-499.

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