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**INVESTIGATION OF THE USE OF A RECYCLE STREAM TO MEDIATE
HYDROGEN TRANSFER TO IMPROVE THE CONVERSION OF EASTERN OIL
SHALE TO LIQUID PRODUCTS**

Topical Report

**By
F. A. Barbour
F. D. Guffey
K. P. Thomas
R. F. Blake**

June 1994

Work Performed Under Contract No. FC21-86MC11076

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

**By
Western Research Institute
Laramie, Wyoming**

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SUMMARY

The processing of eastern oil shale has long been known to require the addition of hydrogen to increase the oil yield. Several researchers have investigated the use of both high pressure hydrogen and hydrogen donor solvents. Much of the donor solvent work has used pure compounds such as tetralin and has not addressed the use of a more realistic solvent such as one derived from the production process itself. The work reported herein is for the research Task 1.2.2, Process Studies, in the Annual Project Plan, October 1, 1990 - September 30, 1991, of the Cooperative Agreement. In the study, a shale oil-derived, recycle oil was used to mediate the transfer of hydrogen to eastern oil shale. The work was divided into two main parts which correspond to the two main portions of the Hydrogen-Extraction (H-ETM) process: (1) the shale oil extraction which involves the use of a donor solvent to aid in the extraction of the shale oil and (2) the regeneration of the donor solvent to a hydrogen-rich state ready for recycle.

The results of the investigation to evaluate shale oil extraction using a shale oil-derived donor solvent suggest that temperature had the greatest effect on organic conversion. At a temperature of 425°C (797°F), a yield of 130% of Fischer assay was obtained using tetralin as a donor solvent. At the same temperature, only 110% of Fischer assay could be obtained using a middle distillate as a donor solvent. Increasing the oil to solid ratio to 2:1 did not appear to have any effect on the organic carbon conversion of the Sunbury Shale. Increasing the residence time appeared to have mixed effects on the conversion of Sunbury Shale in the presence of a donor solvent. Data from tests made at 375 and 400°C (707 and 752°F) suggest some increase in conversion with increasing residence time. Data from tests run at 425°C (797°F) do not always show an increase in conversion with increasing time. While a large increase was noted between the 5 and 10 minute residence times, tests using the middle distillate as a donor solvent showed decreases when the tests at 425°C (797°F) were run for 20 minutes.

Comparison of tetralin with a middle distillate indicated that tetralin was more efficient as a hydrogen donor. Not only was the organic conversion better using tetralin, but less hydrogen was needed. The extra hydrogen consumption for the distillate tests is probably the result of an increase in the cracking of the distillate fraction. Using tetralin as a donor solvent, the average hydrogen consumption was approximately 1300 scf of hydrogen needed to produce a barrel of shale oil. The average hydrogen consumption for the distillate tests was nearer 2000 scf per barrel of produced oil because of the extra hydrogen needed to satisfy radicals formed by thermal cracking.

The most effective hydrogenation conditions for regenerating the middle distillate as a donor solvent were 316°C (600°F), 1900 psi hydrogen, and liquid hourly space velocity (LHSV) = 1. Pressures above 1500 psi did not appear to influence the formation of tetralin as much as the temperature and LHSV. However, model compound studies indicated that cracking became a predominant reaction at 1200 psi. The amount of hydrogen consumed during the regeneration of the middle distillate was approximately 350 scf per barrel, at the most effective conditions.

INTRODUCTION

A considerable amount of research has been done on both western and eastern oil shales to produce an alternative source of transportation fuels. The difference in the kerogen structures of the two shales has led to the development of different methods of production (Das 1989). Western shales containing more hydrogen and being more aliphatic can be produce oil easily by thermal degradation. Most methods for the production of oil from western shales rely on thermal decomposition under relatively inert atmospheres. However, the eastern shales with much less hydrogen (Smith and Stanfield 1964) and hence, more aromatic carbon, do not react favorably to thermal treatment. Starting with comparable amounts of organic carbon, the oil yields by thermal degradation of eastern oil shales under inert atmospheres are generally half that of the western oil shales (Miknis et al. 1987). To compensate for the lack of hydrogen during thermal treatment, eastern oil shale processing methods generally incorporate the addition of hydrogen to aid in the production of oil (Matthews and Feldkirchner 1983).

Work on eastern oil shale conducted by the Institute of Gas Technology (IGT) over the past decade has dealt with hydrotreating. Results from this work indicated that high yields were obtained when the eastern shales were retorted with hydrogen at elevated pressures. More recently, IGT has developed an new method, the pressurized fluidized-bed hydrotreating process (Roberts et al. 1992). Oil yield was found to be a function of both temperature and hydrogen pressure. As the pressure increased to 1000 psi, oil yields for all studied shales increased. Temperature, however, showed an inverse relationship with oil yield. As the temperature was increased, the oil yield from Ohio Shale (Cleveland Member) decreased. Increasing the reaction temperature generally increased the amount of gas evolved.

Several researchers have examined the use of hydrogen transfer solvents as a mechanism to provide hydrogen during the retorting of eastern oil shales. Both donor, tetralin, and non-donor solvents, toluene (Baldwin et al. 1983) and mesitylene (Cronauer et al. 1983), have been examined in conjunction with the Cleveland Member of Ohio Shale.

Baldwin et al. (1983) performed tests processing the shale under both hydrogen and helium atmospheres at temperatures ranging from 375 to 450°C (707 to 842°F). The batch autoclave experiments had a nominal residence time of an hour and were charged at an ambient temperature to 800 psi. Organic carbon conversion increased with respect to the temperature of the test for both the donor and non-donor solvent in the presence of a hydrogen atmosphere. Conversions as high as 85% were obtained at the highest temperature (450°C [842°F]) using the donor solvent (tetralin). When an inert (helium) atmosphere was used, little change in organic conversion was noted for the case using the donor

solvent. However, a 50% drop in conversion was noted for the non-donor solvent (toluene).

Cronauer et al. (1983) performed tests under an inert atmosphere of nitrogen, between 400 and 425°C (752 and 797°F). The reactor was charged to 50 psi at room temperature. Temperature was again found to greatly influence the amount of soluble extractables from eastern shale. With increasing reaction time, conversion with tetralin continued to increase, while that with mesitylene decreased. The decrease with mesitylene is attributed to cracked intermediates that recombine in retrograde reactions forming heavier products. The amount of hydrogen transferred, as measured by the conversion of tetralin to naphthalene, increased with increases in time and temperature. Furthermore, the conversion of tetralin to naphthalene increased linearly with reaction time. However, the conversion of eastern shale to toluene solubles peaked at 10 minutes. A sizable level of tetralin dehydrogenation appears to occur even with spent shale.

Triad Research Incorporated (TRI) developed a process to obtain high oil yields from eastern oil shale without the addition of gaseous hydrogen to the reactor. This process is referred to as the Hydrogenation-Extraction (H-ETM) process (Addington et al. 1984). The process involves recycling a middle distillate product that is capable of hydrogen transfer during the extraction step. The hydrogen transfer provides the needed hydrogen for conversion of the organic material in the shale (kerogen). The hydrogen transfer agent is then separated from the hydrocracked product and regenerated. The regeneration step involves conventional hydrotreating over a catalyst. The hydrogen transfer distillate is then recycled into the extraction unit.

Based on the information obtained by Cronauer et al. (1983), Baldwin et al. (1983), and other proprietary work, Addington et al. (1984) designed and began the construction of a one-barrel-a-day plant. However, the plant was never completed, and the individual process steps incorporated into the plant design were not adequately tested. The operation of the plant included the use of a recycle stream derived from the process. The use of a recycle stream from eastern shale oil has sound technical merit. Work by Cha et al. (1988) and recent work by Thomas and Hunter (1989) showed that eastern shale oil is composed of a high concentration of diaromatics that upon hydrogenation are converted to indanes/tetralins, which would supply hydrogenation capability.

The objective of the work reported here was to investigate the use of a shale oil-derived, recycle oil to mediate the transfer of hydrogen to eastern oil shale. The work was divided into two main parts which correspond to the two main portions of the H-ETM process: (1) shale oil extraction which involves the use of a donor solvent to aid in the extraction of the shale oil and (2) regeneration of the donor solvent to a hydrogen-rich state ready for recycle.

A series of experiments were performed in tubing bombs to address the suitability of an eastern shale oil middle distillate as a hydrogen donor solvent. Freshly ground eastern oil shale was coprocessed with the distillate to evaluate conversion as a function of temperature and residence time. The tests were monitored by evaluation of carbon conversion and hydrogen generation.

A second series of experiments were performed using a bench-scale hydrotreating reactor to address the ability to regenerate the donor solvent after the extraction process. A large sample of spent donor solvent was prepared in the Western Research Institute (WRI) batch autoclave by coprocessing it with eastern oil shale at relatively severe conditions. The spent donor solvent and produced oil were separated from the solids for hydrotreating tests to regenerate the donor solvent capability. The degree of donor solvent regeneration was evaluated with respect to temperature, pressure, and residence time. The hydrotreating of the spent donor solvent was monitored by hydrogen consumption and gas chromatography/mass spectrometry (GC/MS)

EXPERIMENTAL

Materials

Shale Description

Sunbury Shale was ground dry and sieved to 100% less than 149 μM (-100 mesh). The initial bulk sample was thoroughly mixed and then successively riffled to obtain aliquots for the tests and analysis. A Fischer assay of the feed shale for this study is given in Table 1. The oil yield is 10.9 gal/ton and is within the range generally reported for this shale. Proximate and ultimate analyses for both the feed shale and the Fischer assay spent shale are given in Table 2.

Table 1. Fischer Assay of Sunbury Shale

Oil, wt %	4.21
Water, wt %	2.30
Spent Shale, wt %	91.14
Gas + Loss, wt %	2.34
GPT Oil	10.88
GPT Water	5.52
Specific Gravity of Shale Oil	0.9283

Table 2. Proximate and Ultimate Analyses of Sunbury Shale

Proximate Analysis						
Shale		Moisture	Ash	Volatile	Fixed Carbon	
Raw Sunbury	AR ^a	0.9	82.8	11.6	4.8	
	MF ^b		83.6	11.7	4.8	
	MAF ^c			71.2	29.4	
Spent Sunbury from Fischer Assay	AR ^a	0.0	90.3	5.0	4.7	
	MF ^b		90.3	5.0	4.7	
	MAF ^c			51.5	48.5	
Ultimate Analysis						
Shale		Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen ^d
Raw Sunbury	AR ^a	10.0	1.6	0.3	2.9	2.5
	MF ^b	10.1	1.5	0.3	2.9	1.7
	MAF ^c	61.1	9.1	1.8	17.6	10.3
Spent Sunbury from Fischer Assay	AR ^a	5.6	0.7	0.2	1.9	1.3
	MF ^b	5.6	0.7	0.2	1.9	1.3
	MAF ^c	57.7	7.2	2.1	19.6	13.4

^a AR - As Received

^b MF - Moisture Free

^c MAF - Moisture and Ash Free

^d Oxygen determined by difference

Data presented by Robl et al. (1983) suggest that mineral carbon is a very small portion of the total carbon. The principal form of carbon present in the oil shale is organic matter. The Sunbury Shale contained between 0.01 and 0.14 wt % mineral carbon. The sulfur content of Sunbury Shale was listed as 3.70 wt % with more than 80% of the sulfur present in the form of sulfide minerals, predominantly as pyrite (FeS₂).

Middle Distillate Description

The distillate shale oil tested during this work was prepared during an earlier study dealing with the evaluation of eastern shale oil as a feedstock for production of aviation fuel (Thomas and Hunter 1989). The oil was produced by Synfuels Engineering and Development Incorporated using the Tosco II process. The oil shale was from the Clegg Creek Member of the New Albany Shale, McRae Quarry, Clark County, Indiana. A description of the oil shale and the processing scheme are contained in the publication by Synfuels (1989). The oil was then distilled into naphtha, middle distillate, atmospheric gas oil, and vacuum gas oil

fractions. The middle distillate, boiling between 177-288°C (350-550°F), was tested as a hydrogen donor solvent for these experiments.

The physical and chemical properties of the middle distillate tested as a donor solvent for this work are given in Table 3. Elemental analysis indicates that the distillate contains modest amounts of nitrogen, sulfur, and oxygen. Hydrogen to carbon atomic ratio, as well as compositional data suggest that the sample contains a mixture of saturated and aromatic material. The tetralins and indanes (the hydrogen donor types of interest) make up about 32% of the middle distillate. There was no detectable water or ash in this sample.

Table 3. Physical and Chemical Properties of Middle Distillate

Elemental wt %	Carbon 85.1	Hydrogen 11.7	Nitrogen 0.7	Sulfur 1.2	Oxygen ^a 1.3
Hydrogen to Carbon Atomic Ratio			1.64		
Boiling Range, °F vol %	IBP-350 2.1		350-550 88.8		550-800 9.1
Compositional Data wt %	Saturates 49.9		Aromatics 44.7		Polar Aromatics 5.4
Indanes and Tetralins	31.9%				
Specific Gravity, 60°F	0.894				
Molecular Weight	200				
Water, wt %	ND ^b				
Ash	ND				

^a Oxygen by direct determination

^b Below analytical detection limit

A stock sample of the middle distillate was spiked with approximately 0.5 wt % tetralin to be used as an indicator of hydrogen transfer for these tests. No tetralin was detected in the original distillate, and it was assumed that the tetralin would transfer hydrogen at approximately the same rate as the indanes and substituted tetralins present in the original distillate. This would then provide a method to follow hydrogen generation taking place during the retorting experiments. While the addition of about 0.5 wt % provides adequate tetralin for analysis, it was felt that this amount would not alter the donor solvent activity of the middle distillate significantly.

Experimental Apparatus

Tubing Bombs

The tubing bombs used for the coprocessing studies were constructed from 16 cm (6.25 inches) long by 2 cm (0.75 inches) o.d. stainless tubing, with an inside diameter of 1.6 cm (0.625 inches). The ends of the tubes (bombs) were sealed with Swagelok caps. A 2.5 cm (1.0 inch) length (0.6 cm [0.25 inches] o.d.) of stainless steel tubing was welded perpendicular to the length of each tube (bomb). The 0.6 cm (0.25 inches) diameter tubing was placed 5 cm (2 inches) from one end of the bomb. The 0.6 cm (0.25 inches) diameter tubing was attached to a 0.3 (0.125 inches) diameter tubing (46 cm [18 inches] long) by means of a Swagelok reducing union. The open end of the 0.3 cm (0.125 inches) tubing was fitted with a valve to allow introduction and venting of gases.

Normally, three tests were performed at a given residence time and temperature. Each of the tubing bombs was charged differently. The first bomb was charged with 3 g of freshly ground and sized (~100 mesh) shale and 3.0 g of middle distillate donor solvent. The second bomb was charged with 2 g of shale and 4 g of the middle distillate. The third bomb was charged with 3 g of shale and 3 g of tetralin as the donor solvent. The bombs were then pressurized with nitrogen to 250 psi (pressure at room temperature). While the pressure of the bombs at reaction temperatures was not measured, it was calculated to be in the 900 to 1300 psi range. This experimental design permits comparison of a known donor solvent (tetralin) with the middle distillate as well as different solids to donor solvent ratios.

The horizontally oriented tubing bombs were heated in a preheated sand bath and shaken at a rate of 100 cycles per minute. Three temperatures were examined for these tests: 375, 400, and 425°C (707, 752, and 797°F). For each of these temperatures three different residence times were tested: 5, 10, and 20 minutes. A fourth bomb was added to the tubing bomb holder to monitor temperature. The desired temperature was reached within 2 minutes of the start of heating. This point was set as the zero point in time and residence times were counted from this point. Thus, the 5 minute residence time would actually be in the sand bath for 7 minutes. At the end of each experiment, the tubing bombs were rapidly cooled by quenching them in a bucket of water.

The tubing bombs, when at room temperature, were vented into a chamber of known volume, the pressure measured, and a sample of gas taken for analysis. The 0.3 cm (0.125 inches) riser assembly was removed from the tubing bombs, each bomb charged with 15 mL of n-pentane, capped, and sonicated for 60 minutes. The bombs were charged and sonicated two additional times with pentane. The contents were rinsed from the bombs and filtered to remove the residual solid

material. The pentane was removed from the pentane-soluble fraction with a rotary evaporator until a constant weight of the extract was achieved. The solvent rinse and sonication procedure was then repeated using toluene. The residual solid material from this extraction was dried in a vacuum oven at 80°C (176°F) for 24 hours and the weight determined. The ash content of the solid material was determined by gravimetric difference after combustion at 427°C (800°F).

The fraction of extractables (conversion) was defined as the difference between the raw shale charge and spent shale after extraction divided by the shale charge. A correction for moisture was made. In addition, a direct measurement of residual carbon on the spent shale was made by elemental analysis. The concentrations of hydrogen and other product gases were determined by gas chromatography.

Batch Autoclave

A large sample of spent, middle distillate, donor solvent was generated in the WRI batch autoclave, a stirred reaction vessel designed and built by the TEM-PRES Division of LECO. The reaction vessel is constructed of Carpenter 20 Cb-3 steel and has a capacity of 1 liter. Heating of the vessel contents is accomplished by an electric heater located around the periphery of the vessel. Agitation within the vessel is accomplished through a belt-driven magnetic stirrer. The shaft is externally cooled by circulating water and is turned at approximately 600 rpm. The autoclave is surrounded by a vertical tube furnace capable of a maximum temperature of 700°C (1292°F). The furnace provides additional heat during the initial heating of the autoclave and prevents heat loss at operational temperature assuring better temperature control of the reaction.

The batch autoclave was charged with the middle distillate and Sunbury Shale (-100 mesh) at a weight ratio of 1:1. The autoclave was sealed and charged with nitrogen at 250 psi. The autoclave was then brought to a reaction temperature of 425°C (797°F) as fast as possible and held there for 30 minutes. The reactor was cooled by opening the tube furnace and blowing air through the cooling coils attached to the reactor.

After the reactor reached room temperature, the autoclave was vented into an expansion chamber of known volume, the pressure measured, and a gas sample taken for analysis. Pentane was then added to the autoclave and stirred to dissolve the coprocessing products. The resulting slurry was then poured into a container for transfer to a Soxhlet extractor. The contents from the reactor wash were extracted with pentane for 48 hours. Toluene was then added to the autoclave and stirred to dissolve the remaining material. The toluene wash was then added to the Soxhlet after the pentane extraction had been completed and the solids were then extracted for 48 hours with toluene. The solvents were removed from the

soluble organic fractions with a rotary evaporator until a constant weight of the extracts was achieved.

Hydrotreater

The regeneration of the spent donor solvent was accomplished using a bench-scale hydrotreater. The hydrotreating reactor is based on a Chemical Data Systems 810-CD-HP dual mode catalytic reaction system. The hydrogen flow was controlled by a Brooks mass flow controller capable of delivering 0 to 500 sccm at pressures up to 2000 psi. The liquid was injected into the top of the reactor with an ISCO LC 5000 precision pump capable of delivering 0-400 mL/hr at 2000 psi.

All experiments were conducted with Shell 424 catalyst provided in the form of a 2.54 mm (0.10 inches) diameter tri-lobe extrudate. This is a widely used, commercially available Ni-Mo type catalyst in which the metals are supported on silica-improved alumina acidified with phosphoric acid. The catalyst bed was prepared in one 5-mL section with layers of 2 mL each of Ottawa sand above and below the catalyst bed.

The catalyst was presulfided using a 20 vol % solution of thiophene in n-hexane. The liquid was injected at 5 mL/hr (liquid hourly space velocity [LHSV] = 1) for 5 hours. The hydrogen flow was held at 160 mL/min at 1000 psi. The temperature was programmed in three stages: (1) 204°C (400°F) for 2 hours, (2) 316°C (600°F) for 1 hour, and (3) 371°C (700°F) for 2 hours. The flow was then reduced to 15 mL/hr and the temperature reduced to 250°C (482°F) in preparation for sample introduction.

During operation, the reactor temperature was stabilized at the selected experimental temperature and hydrogen flow raised to a point that would establish a hydrogen feed ratio of 5000 scf per barrel for the experimental liquid flow. Once temperatures and flows had stabilized, the hydrogen deficient shale oil was introduced into the top of the reactor for 2 hours. At this time, the sample collected was drained and discarded. A sample representing about 4 hours of operation was then collected for analysis and the reactor conditions readjusted for the next set of experimental conditions. This cycle was repeated until all the experimental conditions had been tested.

Samples were prepared for analysis as follows. The liquid was transferred from the receiver to a separatory funnel, weighed, and washed with cold, deionized water to remove hydrogen sulfide and ammonia. The organic phase was dried by stirring overnight with anhydrous magnesium sulfate in a closed container. The mixture was filtered to remove the salt, and samples of the filtrate were refrigerated until analysis could be performed.

Analytical Procedures

Mass Spectral Analysis

Samples obtained from both the tubing bomb experiments and the hydrotreated donor solvent were analyzed using a Hewlett Packard 5985B (GC/MS) system. A 0.2 mm by 25 m fused-silica column coated with 5% (0.33 μ m thickness) methyl silicone was used for the chromatographic separation. Each sample (1 μ L) was injected using a split ratio of 100:1 at an injection temperature of 275°C (527°F) and an oven temperature rate of 3°C/min (1.8°F/min) from 50 to 275°C (122 to 527°F). A flow rate of 0.75 mL/min was used for the helium carrier gas. An ionization voltage of 70 volts at an ion source temperature of 200°C (392°F) and electron multiplier voltage of 1600 volts were used for all experiments.

Concentrations of tetralin and naphthalene were determined using selected ions that are representative of each compound. The method relies on gas chromatographic separation to minimize interferences from fragment ions of other hydrocarbon compounds. An internal standard, not present in either the original distillate or product oil, was used to eliminate possible injection error. The method was calibrated using standard solutions of tetralin and naphthalene to determine sensitivity factors for each of the compounds of interest.

Routine Analyses

Routine analyses of oil samples from both the tubing bomb tests and the hydrotreater tests were performed after the samples had been filtered and dried. The analyses included carbon, hydrogen, nitrogen, sulfur, specific gravity, and distillation range for some of the organic products. The spent shale from the tubing bomb tests was analyzed for residual carbon and ash content. The dried solid was ashed at 427°C (800°F) for 16 hours.

RESULTS AND DISCUSSION

Shale Oil Production

Conversion of eastern oil shale requires the addition of hydrogen to achieve organic recoveries that approach those observed by thermal treatment of western oil shale. This work deals with the use of a hydrogen transfer solvent to supply the needed hydrogen for organic conversion during thermal treatment. While many researchers have studied the effects of a traditional hydrogen donor solvent (tetralin), less work has been performed to evaluate shale distillates as donor solvents for eastern oil shale conversion. The use of a middle distillate from an eastern shale oil has been proposed as the donor

solvent for TRI's H-E process. This premise is the basis of this work in which a middle distillate from an eastern shale oil was tested as a hydrogen donor solvent for the conversion of eastern oil shale.

The experimental tests and the conditions are listed in Tables 4A through 4C. Data presented in the tables provide material balance information as well as carbon conversion data calculated by different methods. The shale and oil weights are the reactant charges to the tubing bombs. The solvent solubles, spent shale, and gas weights are the product yields recovered after the tests. The conversion numbers represent the amount of carbon in the raw shale converted during the tests. Material balances range from 93 to 104% recovery with a few tests below 90%. The tests with lower recoveries were a result of the loss of the solvent soluble fractions. As all of the conversion calculations were performed using the solid material, the conversion data were unaffected by these losses.

The relative concentrations of gases detected in the produced gases change with respect to temperature and donor solvent type. The normalized gas analyses are presented in Tables 5A through 5C and have been reduced to a nitrogen-free basis in order to examine the relative amounts of gases generated at different conditions. Several trends can be noted with the various gas species.

Carbon dioxide is the first major gas to appear for the lower temperature and shorter residence time tests. For tests conducted at 375°C (707°F), the concentration of CO₂ is relatively the same regardless of the donor solvent used (distillate or tetralin). The produced gas for the shorter residence time tests also contains a fairly high concentration of CO₂ even for those tests conducted at 425°C (797°F). The concentration of CO₂ relative to other gases decreases as the residence times increase for all temperatures, but is more pronounced at higher temperatures. This decrease is probably a result of dilution by other gases produced at longer residence times and elevated temperatures and would suggest that CO₂ is probably the result of a low temperature reaction such as decarboxylation.

The production of hydrogen differs significantly between tests using the distillate and those using tetralin. Generally, the hydrogen concentration for those tests using tetralin as the donor solvent is between 45 to 60 vol % regardless of temperature or residence time. The concentration of hydrogen present in tests using the distillate as a donor solvent is generally half or less (15 to 30 vol %) that noted for the tetralin tests. The hydrogen concentration decreases significantly for the distillate tests as the temperature increases. While the amount of hydrogen in the gas is not indicative of the amount transferred to the shale oil, lower gaseous hydrogen concentrations may lead to retrograde reactions such as coking, which may reduce carbon conversion to liquids.

Table 4A. Eastern Oil Shale Tubing Bomb Material Balance for Tests Conducted at 375°C

Test Number	1A	1B	1C	2A	2B	2C	3A	3B	3C
Temperature, °C	375	375	375	375	375	375	375	375	375
Residence Time, min	5	5	5	10	10	10	20	20	20
Oil/Solid Ratio	1:1	2:1	1:1	1:1	2:1	1:1	1:1	2:1	1:1
Donor Solvent ^a	MD	MD	T	MD	MD	T	MD	MD	T
Reactants, g									
Weight Shale	2.95	2.00	2.93	3.00	2.02	3.02	3.03	2.01	3.01
Weight Oil	2.95	4.00	2.91	3.00	4.01	3.02	3.00	3.98	3.02
Products, g									
Pentane Solubles	3.05	3.92	2.94	3.08	4.14	2.88	3.06	4.13	2.94
Toluene Solubles	0.06	0.03	0.03	0.07	0.08	0.08	0.06	0.07	0.05
Weight Spent Shale	2.83	1.94	2.83	2.95	1.99	2.85	2.90	1.94	2.90
Gas	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.02	0.02
Material Balance, wt %	100	98	99	101	103	96	100	102	97
Conversion, wt %									
Ashing	5	12	10	9	9	9	21	18	17
Elemental	0	0	5	8	8	6	17	20	20

^a MD = middle distillate and T = tetralin

Table 4B. Eastern Oil Shale Tubing Bomb Material Balance for Tests Conducted at 400°C

Test	4A	4B	4C	5A	5B	5C	6A	6B	6C
Temperature, °C	400	400	400	400	400	400	400	400	400
Residence Time, min	5	5	5	10	10	10	20	20	20
Oil/Solid Ratio	1:1	2:1	1:1	1:1	2:1	1:1	1:1	2:1	1:1
Donor Solvent ^a	MD	MD	T	MD	MD	T	MD	MD	T
Reactants, g									
Weight Solids	3.00	2.03	3.06	3.02	2.01	3.01	3.06	2.16	3.03
Weight Oil	3.02	4.08	3.05	3.03	4.04	3.06	3.05	4.11	3.07
Products, g									
Pentane Solubles	3.37	4.35	2.41	3.14	3.95	2.20	3.10	3.87	3.14
Toluene Solubles	0.04	0.07	0.07	0.15	0.08	0.07	0.13	0.09	0.07
Weight Spent Shale	2.88	1.93	2.86	2.83	1.86	2.81	2.89	2.04	2.83
Gas	0.02	0.02	0.01	0.03	0.02	0.02	0.03	0.02	0.02
Material Balance, wt %	104	104	88	102	98	84	100	96	99
Conversion, wt %									
Ashing	18	20	18	27	22	24	38	37	42
Elemental	17	16	16	27	28	26	36	34	46

^a MD = middle distillate and T = tetralin

Table 4C. Eastern Oil Shale Tubing Bomb Material Balance for Tests Conducted at 425°C

Test	7A	7B	7C	8A	8B	8C	9A	9B	9C
Temperature, °C	425	425	425	425	425	425	425	425	425
Residence Time, min	5	5	5	10	10	10	20	20	20
Oil/Solid Ratio	1:1	2:1	1:1	1:1	2:1	1:1	1:1	2:1	1:1
Donor Solvent	MD	MD	T	MD	MD	T	MD	MD	T
Reactant, g									
Weight Shale	3.01	2.10	3.02	3.08	2.11	3.13	3.03	2.03	3.04
Weight Oil	3.01	4.06	3.04	3.07	4.00	3.15	3.04	4.05	3.03
Products, g									
Pentane Solubles	3.23	3.98	3.17	2.89	3.75	3.06	2.68	3.91	3.10
Toluene Solubles	0.11	0.12	0.08	0.11	0.07	0.29	0.12	0.07	0.09
Weight Spent Shale	2.84	1.98	2.85	2.81	1.94	2.79	2.77	1.87	2.75
Gas	0.02	0.01	0.01	0.06	0.05	0.03	0.10	0.07	0.10
Material Balance, wt %	103	99	101	95	96	98	93	97	100
Conversion, wt %									
Ashing	27	27	24	50	49	58	41	38	56
Elemental	17	22	20	48	45	57	39	37	57

* MD = middle distillate and T = tetralin

Table 5A. Gas Analyses for Eastern Oil Shale Tubing Bomb Tests Conducted at 375°C

Test	1A	1B	1C	2A	2B	2C	3A	3B	3C
Temperature	375	375	375	375	375	375	375	375	375
Residence Time	5	5	5	10	10	10	20	20	20
Oil/Solid Ratio	1:1	2:1	1:1	1:1	2:1	1:1	1:1	2:1	1:1
Donor Solvent ^a	MD	MD	T	MD	MD	T	MD	MD	T
Hydrogen	33.8	21.9	57.9	30.5	27.1	56.5	28.1	32.9	52.8
Carbon Monoxide	4.0	3.5	0.5	7.9	5.2	3.7	4.7	4.7	0.2
Carbon Dioxide	27.2	31.4	28.4	30.8	32.8	15.0	20.8	17.0	14.7
Methane	7.2	10.2	2.9	2.3	9.6	2.6	12.8	12.3	2.4
Ethane	4.0	3.8	1.4	6.3	4.7	1.2	6.5	6.2	1.2
Ethylene	1.2	1.2	0.5	1.5	1.1	0.2	1.3	1.1	0.2
Propane	3.1	3.6	0.6	3.3	3.2	4.2	2.7	4.8	4.3
Propylene	4.3	4.7	1.6	2.4	4.1	0.0	0.0	1.4	5.5
C ₄ s	1.5	0.7	0.0	2.1	0.6	3.9	5.6	9.0	0.1
Hydrogen Sulfide	13.7	19.1	6.2	12.9	11.8	12.7	17.5	10.5	18.6
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

^a MD = middle distillate and T = tetralin

Table 5B. Gas Analyses for Eastern Oil Shale Tubing Bomb Tests Conducted at 400°C

Test	4A	4B	4C	5A	5B	5C	6A	6B	6C
Temperature	400	400	400	400	400	400	400	400	400
Residence Time	5	5	5	10	10	10	20	20	20
Oil/Solid Ratio	1:1	2:1	1:1	1:1	2:1	1:1	1:1	2:1	1:1
Donor Solvent ^a	MD	MD	T	MD	MD	T	MD	MD	T
Hydrogen	15.5	17.8	37.5	19.0	21.1	44.5	22.3	23.3	57.6
Carbon Monoxide	4.3	3.5	2.4	4.4	3.9	2.7	3.9	5.9	1.2
Carbon Dioxide	30.2	29.1	23.6	15.2	21.3	17.7	14.2	13.2	9.9
Methane	10.0	11.0	3.3	12.8	16.7	3.7	16.3	20.7	4.1
Ethane	5.5	5.6	1.6	7.4	9.4	1.8	9.7	11.5	2.0
Ethylene	1.0	1.7	0.5	1.3	1.5	0.9	1.2	1.4	0.3
Propane	2.7	2.6	0.9	5.1	2.3	1.3	2.1	2.1	0.6
Propylene	1.7	3.4	2.0	4.1	1.4	2.2	1.6	1.4	0.4
C ₄ s	1.6	1.2	0.1	1.8	1.8	0.1	3.7	1.8	0.1
Hydrogen Sulfide	27.5	24.2	28.2	28.9	20.6	25.2	25.0	18.5	23.8
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

^a MD = middle distillate and T = tetralin

Table 5C. Gas Analyses for Eastern Oil Shale Tubing Bomb Tests Conducted at 425°C

Test	7A	7B	7C	8A	8B	8C	9A	9B	9C
Temperature	425	425	425	425	425	425	425	425	425
Residence Time	5	5	5	10	10	10	20	20	20
Oil/Solid Ratio	1:1	2:1	1:1	1:1	2:1	1:1	1:1	2:1	1:1
Donor Solvent	MD	MD	T	MD	MD	T	MD	MD	T
Hydrogen	17.4	16.0	45.1	17.0	18.7	61.7	17.2	17.5	58.3
Carbon Monoxide	4.1	5.1	1.2	3.7	5.0	0.6	2.0	4.0	1.1
Carbon Dioxide	19.9	21.3	24.3	9.1	7.5	4.8	6.3	6.5	4.1
Methane	15.1	15.8	4.6	22.5	26.9	6.2	22.0	30.0	7.3
Ethane	8.3	8.6	2.1	14.0	15.6	2.8	13.5	17.2	3.2
Ethylene	1.5	1.5	0.5	1.5	1.6	0.2	1.1	1.3	0.3
Propane	2.6	4.3	0.6	9.1	8.4	1.7	16.2	9.3	1.6
Propylene	0.0	4.7	0.9	1.2	0.9	0.9	1.3	0.8	0.6
C ₄ s	4.8	4.3	0.0	3.2	2.6	0.2	4.4	2.8	0.4
Hydrogen Sulfide	26.3	18.4	20.8	18.5	12.8	20.9	16.0	10.6	23.1
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

^a MD = middle distillate and T = tetralin

Hydrocarbon gas concentrations are affected by both donor solvent selection and reaction conditions. Hydrocarbon gases are relatively minor components when tetralin is used as a donor solvent. Tests conducted with the distillate as the donor solvent always contain larger amounts of hydrocarbon gases than those tests conducted using tetralin as a donor solvent. Methane is the most predominate hydrocarbon gas and increases with increasing residence time and reaction temperature. At higher temperatures, higher molecular weight hydrocarbons ($C_2 - C_4$) increase in concentration. The larger amount of hydrocarbon gases is probably a result of cracking the middle distillate used as the donor solvent and could be the reason for the lower hydrogen gas concentrations noted earlier.

Hydrogen sulfide production appears to take place continuously during the tests regardless of residence time. The amount of H_2S generated does not appear to be a function of the donor solvent used for most tests and is probably the result of the pyrolysis of pyrites. For a given set of conditions regardless of the donor solvent, the tests produce approximately the same amount of H_2S . It does appear that increasing the temperature from 375 to 400°C (707 to 752°F) increases the production of H_2S . At 425°C (797°F) and longer residence times there is a decrease in the relative amount of H_2S produced for tests conducted using the distillate donor solvent. This decrease is not as noticeable for the tests that use tetralin as the donor solvent. This is probably the result of the reduced amount of hydrogen available when the middle distillate was used as the donor solvent.

Organic Conversion

Traditionally, the conversion of western shales to shale oil has been defined as the amount of oil produced during a Fischer assay test. Because Fischer assay tests for eastern shales yield only about half of the carbon as oil, other methods of determining organic conversion are generally used for eastern shales. The conversion of the organic material present in oil shale (kerogen) is generally defined as the difference between the amount of organic material present in the original shale and the spent shale divided by that in the original shale. Another method is that of Das and Hamrin (1982). They calculated conversion from an ash balance using the following equation.

$$\text{Conversion} = \frac{(A - a) \times 10000}{A \times (100 - a)} \quad (1)$$

where A = % ash in spent shale

a = % ash in dry feed shale

One nice feature of this method is that errors are not introduced into the calculation by losses encountered during the test and product

recovery procedures. Another method of calculating organic conversion involves using carbon composition of the shale before and after the thermal conversion test. Cronauer et al. (1983) calculated conversion as percent extractables (n-pentane and toluene) as given by the following formula.

$$\% \text{ (solvent) extractable} = \frac{\text{wt sample} - \text{wt residue}}{\text{wt sample}} \times 100 \quad (2)$$

A correction was made for moisture in the original shale. All of these methods for calculating conversion percentage include gases generated during the thermal conversion procedure and not just the produced oil as is the case for the Fischer assay method.

The ash balance and elemental conversion calculation methods yield results that are in reasonably good agreement. This comparison is shown in Figure 1. The least squares representation of the data is depicted as a straight line in the figure. The coefficient of correlation for this line is 0.94 indicating a reasonable degree of correlation. The slope for this line is 0.89, indicating that a one to one correspondence does not exist. Examination of the data shows that generally the ash conversion data are slightly higher than the conversion calculated using elemental carbon data. This is probably due to the inorganic sulfur compounds present in the shale.

Figure 1. Comparison of Elemental and Ashing Conversion Calculation

More than 80% of the sulfur present in the Sunbury Shale is thought to be in the form of pyrites (Robl et al. 1983). Thermal conversion of the pyrites to pyrrhotite would release part of the sulfur as hydrogen sulfide. Data from the ultimate analyses on both the raw and Fischer assay spent shale indicate that about one third of the sulfur was lost during the Fischer assay test. If the sulfur present in the raw shale is indeed in the form of pyrites then this would account for nearly all of the pyrites being converted to pyrrhotite. This loss would result in a difference of approximately 7 wt % in the conversion of organic material present in the raw shale using the ash balance calculation. This would then add several percent to the conversion value calculated from ash data, particularly, at low conversion values. This can be noted in Figure 1 by the line not passing through the origin. The intercept for these data suggests that approximately 5% of the conversion value calculated by the ash balance method is due to the loss of sulfur as H_2S .

The percent solvent-extractable material and the sum of the carbon and hydrogen data from elemental analysis of the spent shale can also be used to determine organic carbon conversion. The comparison is made with the elemental composition data presented as weight percent and not as carbon conversion because the conversion values for the solvent extractable data cannot be calculated without estimating the total amount of extractable material. A data comparison is shown in Figure 2.

Figure 2. Comparison of Elemental Analyses and Solvent Solubles

The least squares representation of the data is depicted as a straight line in the figure. The coefficient of correlation for this line is 0.94 indicating a reasonable degree of correlation. The slope for this line is -1.23 indicating that a one to one correspondence does not exist and that the percent-extractable method appears to differ from the elemental-composition method more than the ash-balance method. Evaluation of the three methods, indicates that generally using elemental composition data is the best method of calculating organic conversion.

Reaction Temperature Effects

The conversion of the organic carbon increased greatly with increasing temperature. Results from the thermal conversion with a hydrogen donor, presented in Tables 4A through 4C, indicate that temperature had the greatest effect on the conversion of the Sunbury Shale. Increasing the temperature from 375 to 400°C (707 to 752°F) nearly doubled the percent conversion of the organic carbon for most residence times. Increasing the reaction temperature to 425°C (797°F) also increased the conversion of the organic carbon in the shale, but not at the same rate for each residence time as was noted from 375 to 400°C (707 to 752°F).

Increase in the organic conversion as a function of temperature using a middle distillate as a donor solvent can be noted in Figure 3. An oil to solid ratio of 1:1 was examined in the data presented in this figure. At 10 minute residence times a greater influence of temperature can be observed than for the 5 and 20 minute residence times. Very little increase with respect to temperature could be observed for the 5 and 20 minute conversion data between 400 and 425°C (752 and 797°F). However, the 10 minute residence time data at 425°C (797°F) show increases in organic conversions that are about the same as those observed from 375 to 400°C (707 to 752°F).

For comparison of the effectiveness of the middle distillate as a donor solvent, conversion data for tetralin (1:1 oil to solid ratio) are also depicted in Figure 3. At a residence time of 5 minutes the tetralin and middle distillate conversion data appear to be quite similar at each temperature examined. A difference between the two solvents is quite obvious at a residence time of 20 minutes for all temperatures examined. The conversion data for the tetralin donor solvent tests all show a significant increase when compared to the same reaction conditions using the middle distillate. Less difference can be noted in the 10 minute residence time data. The 375 and 400°C (707 and 752°F) test data show very little difference between the two donor solvents. However, tetralin appears to be significantly better at 425°C (797°F).

Figure 3. Effect of Reaction Temperature on Organic Conversion

Increasing the oil to solid ratio to 2:1 does not appear to have any effect on the organic carbon conversion of the Sunbury Shale. Data from tests using the middle distillate as the donor solvent at the same temperature and residence times, but a different oil to solid ratio, are depicted relative to temperature in Figure 4. It can be noted that most of the data points are quite similar for all of the test conditions. This similarity would suggest that the hydrogen donor capability of the middle distillate has not been depleted at an oil to solid ratio of 1:1.

Figure 4. Comparison of Oil to Solid Ratio and Organic Conversion with Respect to Reaction Temperature

Residence Time Effects

Increasing the residence time appeared to have mixed effects on the conversion of Sunbury Shale in the presence of a donor solvent. The effect on the organic conversion as a function of residence time can be noted in Figure 5. An oil to solid ratio of 1:1 was examined in the data presented in this figure. Data from tests made at 375 and 400°C (707 and 752°F) suggest some increase in conversion with increasing residence time. Data from tests run at 425°C (797°F) do not always show an increase with increasing time. While a large increase was noted between the 5 and 10 minute residence times, tests using the middle distillate as a donor solvent show marked decreases when the tests at 425°C (797°F) were run for 20 minutes.

Figure 5. Effect of Residence Time on Organic Conversion

For comparison of the effectiveness of the middle distillate as a donor solvent, conversion data for tetralin (1:1 oil to solid ratio) are also depicted in Figure 5. At a reaction temperature of 375°C (707°F), the tetralin and middle distillate conversion data appear to be quite similar at each residence time examined. A difference between the two solvents is quite obvious at a reaction temperature of 425°C (797°F) for the 10 and 20 minute residence times. The conversion data for the tetralin donor solvent tests at 10 and 20 minute residence times show a significant increase when compared to the middle distillate data. Less difference can be noted in the 400°C (752°F) reaction temperature data.

Increasing the oil to solid ratio to 2:1 does not appear to have any effect on the organic carbon conversion of the Sunbury Shale. Data from tests using the middle distillate as the donor solvent at the same temperature and residence times, but a different oil to solid ratio, are depicted relative to residence time in Figure 6. It can be noted that most of the data points are quite similar for all of the test conditions. Of greatest interest are the data at 425°C (797°F) because of the decrease in the organic carbon conversion at 20 minute residence times. Similar trends were noted by Cronauer et al. (1983) for tests that involved the use of mesitylene as a donor solvent.

Figure 6. Comparison of Oil to Solid Ratio and Organic Conversion with Respect to Residence Time

Mesitylene was used by Cronauer et al. (1983) as a comparison to tetralin in a donor solvent type test for eastern oil shale conversion. It was chosen because it was a relatively poor donor solvent. A decrease in conversion was noted with the use of mesitylene with residence times greater than 5 minutes. The decrease was attributed to thermal cracking with the cracked intermediates being recombined into heavier products at longer residence times. Good hydrogen transfer solvents would suppress this retrogressive reaction by transferring hydrogen to the free radicals formed during pyrolysis.

Hydrogen Generation and Transfer

The success of a thermal extraction process using a donor solvent is dependent on the ability to transfer hydrogen from a donor solvent in such a manner that the ability to reverse the transfer has not been destroyed. The evaluation of the amount of hydrogen transferred then becomes of great importance to the overall concept. Two measurements were made to follow the generation of hydrogen during oil shale conversion. The level of total hydrogen generation was calculated by following the conversion of tetralin to naphthalene. In addition, gaseous hydrogen formed during the shale conversion was measured. The hydrogen transferred is then assumed to be the difference between the two measurements.

Calculation of the total amount of hydrogen generated for tests using tetralin as a donor solvent is straight forward. It is based on the amount of naphthalene generated during the test as measured by GC/MS and that 2 moles of hydrogen are formed for every mole of naphthalene generated. The amount of gaseous hydrogen along with other light hydrocarbons formed during the thermal treatment was determined by gas chromatography.

The amount of hydrogen generated for tests using tetralin as a donor solvent is depicted in Figure 7. Both the total amount of hydrogen and the gaseous hydrogen generated as grams of hydrogen per 100 grams of shale are shown in the figure. The results show increases in both the total amount and the amount of gaseous hydrogen generated with increases in time and temperature. While the total amount of hydrogen generated for the 10 and 20 minute residence times generally paralleled each other with increases in temperature, the amount of gaseous hydrogen increased dramatically between 400 and 425°C (752 and 797°F) at the 20 minute residence time. This indicates that, even though more hydrogen was generated at the longer residence time, it was not consumed by the organic material in the shale. The organic conversion data presented in a previous section demonstrate similar results in that the conversion appeared to level off after 10 minutes at 425°C (797°F). Work reported by Cronauer et al. (1983) reported similar trends and suggested that a sizable amount of tetralin dehydrogenation occurred as a result of spent-shale mineral catalysis.

Figure 7. Hydrogen Generation during Tests using Tetralin as a Donor Solvent

Estimating the total amount of hydrogen generated during tests using the middle distillate as a donor solvent was more complicated and required some assumptions. It was assumed that only about 32 wt % of the distillate was capable of acting as a donor solvent. This was based on type analysis performed on the distillate in another study (Thomas and Hunter 1989). The data are presented in Table 3. A second assumption made with respect to the hydrogen donor material present in the distillate was that it was equally distributed between substituted indanes and tetralins. Finally, it was assumed that the substituted indanes and tetralins would dehydrogenate at about the same rate as the tetralin spike that was added to follow hydrogen generation. This would mean that only three hydrogen atoms would be generated as a result of one mole of donor distillate dehydrogenation. Based on these assumptions the hydrogen generated during tests with the distillate as a donor solvent was calculated by the following method.

$$\text{Mass of Hydrogen} = \frac{(\text{wt } \% \text{ N}) \times (\text{mass oil}) \times (0.32) \times (3)}{(\text{wt } \% \text{ T}) \times (\text{MW oil}) \times (\text{mass shale})} \quad (3)$$

where

wt % N = weight percent of naphthalene formed

wt % T = weight percent of tetralin charged (0.46 wt %)

MW oil = molecular weight of oil

The mass of hydrogen calculated by this method is in grams of hydrogen per gram of shale. For more convenient representation the results were multiplied by 100 and presented as grams of hydrogen per 100 grams of shale. The amount of gaseous hydrogen measured during the middle distillate tests was approximately half of that generated during the tetralin tests.

The hydrogen consumed during these tests was estimated by subtracting the amount of gaseous hydrogen measured from the total amount of hydrogen generated. This was assumed to be the amount of hydrogen used in the production of shale oil. Hydrogen consumptions for the tetralin and middle distillate tests are shown in Figure 8. At 375°C (707°F) there is not a great deal of difference between tetralin and middle distillate tests regardless of residence time. When a temperature of 400°C (752°F) was examined, more spread could be noted at the different residence times. At residence times of 5 minutes, little difference could be noticed between the middle distillate and tetralin tests. As the residence times increased, more hydrogen consumption was noted when the middle distillate was used than when tetralin was used as the donor solvent. At 425°C (797°F) the differences between the middle distillate and tetralin tests becomes even more pronounced. The tests performed using the middle distillate as the donor solvent exhibit three to five times more hydrogen consumption than the tetralin tests. However, this extra hydrogen consumption does not appear to increase the conversion of the organic carbon as was noted in the previous discussion on conversion.

The increase in hydrogen consumption for the middle distillate tests can probably be attributed to an increase in the cracking of the middle distillate fraction. The presence of alkyl-substituted compounds would decrease the thermal stability of the middle distillate fraction and make it more prone to thermal cracking. The breaking of bonds to form smaller molecules would then require a substantial amount of hydrogen to satisfy the cleaved bonds. Support for this can be found in the gas analyses data presented in Tables 5A through 5C. The hydrocarbon gases generated during tests using the middle distillate as the donor solvent are present in much greater concentrations than for those tests using tetralin. Those tests showing large increases in the hydrocarbon gases also show a corresponding decrease in the hydrogen concentration.

Figure 8. Hydrogen Consumption during Tubing Bomb Tests

The hydrogen consumption reported in the previous discussion was based on the hydrogen generated per mass of shale. To evaluate the hydrogen requirement of a thermal extraction process, these data were converted to hydrogen consumption required to produce a barrel of shale oil. Using tetralin as the donor solvent, an average hydrogen consumption calculated for the 400 and 425°C (752 and 797°F) tests is approximately 1300 scf of hydrogen to produce a barrel of shale oil. Because of the extra hydrogen needed to satisfy radicals formed by thermal cracking, the average hydrogen consumption for the middle distillate tests is nearer 2000 scf per barrel of produced oil.

Hydrotreating of Recycle Oil

The ability to regenerate a donor solvent is of great importance to the overall success of the thermal extraction process. The middle distillate needs to be hydrogenated in such a manner to avoid loss of the distillate to lower boiling fractions. The concept of using a donor solvent as a hydrogen source requires that the donor solvent be removed from the shale and a portion of it hydrogenated before it can be returned to the thermal extraction process. A large sample of spent donor distillate was generated in a 1-liter batch autoclave for the purpose of evaluating hydrotreating parameters for regeneration of the recycle donor solvent. The same middle distillate was used for the hydrotreater study that was used for the tubing bomb extraction tests. A tetralin spike was used to follow the hydrotreating process. Naphthalene and decalins were also monitored to evaluate the severity of the hydrotreating process.

Model Compound Studies

Model compounds were studied to determine the best operating parameters for the regeneration of the spent middle distillate. Because tetralins are the most prevalent hydrogen donors in the middle distillate and upon donating hydrogen form naphthalene, naphthalene was included as a model compound for the hydrotreating study. A mixture of model compounds (phenol, toluene, naphthalene, 1-octene, 1,3-pentadiene, cyclohexene, pyridine, and thiophene) were hydrotreated using a Chemical Data Systems reaction system. The variety of model compounds selected was based on simulating the chemical functional groups that may be present in shale oil. Approximately 2 wt % of each compound was dissolved in hexane. The sample was then hydrotreated at temperatures of 204, 218, 232, 246, 260, 274, 288, 302, and 316°C (400, 425, 450, 475, 500, 525, 550, 575, and 600°F) and pressures (1200, 1700, and 1900 psi). The product from each test was analyzed by GC/MS to obtain qualitative and quantitative information.

The results from the model compound hydrotreating studies indicate a narrow temperature range that is acceptable for regenerating a donor solvent. Figure 9 depicts the data from the 1700 psi tests performed on the model compound mixture. The results from tests performed at other pressures are similar.

Naphthalene was almost completely converted to products at 288°C (550°F) regardless of the operating pressure. At 1700 and 1900 psi, nearly all of the naphthalene could be accounted for by addition of the main products (t-decalin, c-decalin, and tetralin). At 1200 psi, only about 75% of the naphthalene and its products could be accounted for. Of these products only tetralin is useful as a hydrogen donor solvent. Once naphthalene is converted to one of the decalins, it can no longer function as a hydrogen donor solvent. The best conditions for maximizing the conversion to tetralin appear to be at 270°C (518°F) and 1700 psi.

Figure 9. Model Compound Distribution during Hydrotreating Tests

The reactor pressure did not appear to change the temperature at which conversion took place. However, the pressure was important with respect to the type of reaction taking place. At pressures of 1700 psi and above, the conversion of the model compounds appeared to be mainly via hydrogenation of the unsaturated bonds. At 1200 psi, cracking appeared to become more prevalent with loss of the desired product, tetralin. Pressures between 1200 and 1700 psi need to be examined to determine the lowest pressure that can be used with the current catalyst without loss of the desired tetralin due to cracking.

Middle Distillate Hydrogenation Studies

The recycle oil used for the hydrogenation tests was made by processing the middle distillate with Sunbury Shale in a batch autoclave. The tetralin and naphthalene concentrations were measured by monitoring selected ions (104 - tetralin and 128 - naphthalene) using a GC/MS. Other ions that were monitored included 132 (methylindanes), 138 (decalin), and 146 (methyltetralins). Measurements for tetralin and naphthalene made on the original middle distillate indicated that no tetralin itself was present in the oil and that approximately 0.2 wt % of naphthalene was present. Prior to the batch autoclave test, the middle distillate was spiked with 0.46 wt % tetralin and the concentration was confirmed by the GC/MS technique. After the middle distillate had been used as a donor solvent in the batch autoclave test, the tetralin had been reduced to about 0.13 wt % and the naphthalene concentration had increased to 0.55 wt %.

The mild hydrotreating conditions suggested by the model compound tests were used as a starting point for the donor solvent regeneration tests. Following the tetralin and naphthalene concentrations indicated that these conditions (274°C [525°F] and 1700 psi) did not regenerate the tetralin species to the starting level. The naphthalene data depicted in Figure 10 show very little change until the temperature is in excess of 302°C (575°F). The legend for the figure denotes pressure and liquid hourly space velocity (LHSV) used for the particular test. The naphthalene concentration returned to approximately the starting point only when a temperature of 316°C (600°F) was used. This was achieved only when a LHSV = 1 was tested. When the higher space velocity (2) was tested only about half of the naphthalene was converted. It is also interesting to note that the pressure did not have as much of an effect on the conversion as the temperature and the space velocity.

The appearance of tetralin closely followed the disappearance of the naphthalene. The data depicted in Figure 11 indicate that the tetralin concentration approaches the starting value (0.46 wt %) at the most severe conditions of 316°C (600°F) and LHSV = 1. As was indicated in the naphthalene data, the pressure does not appear to influence the formation of tetralin as much as the temperature and LHSV. However, it is important to bear in mind that the model compound study indicated that hydrocracking became a major reaction when pressure was dropped to 1200 psi.

Decalin was monitored throughout the hydrogenation tests to determine if the processing conditions were too severe. The appearance of decalin was only noted at the highest processing temperature (316°C [600°F]) and that was only in barely detectable quantities. This would indicate that very little of the naphthalene was hydrotreated passed tetralin and would, therefore provide a reversible donor solvent system.

Figure 10. Effect of Hydrotreater Temperature on Naphthalene Concentration

The tetralin, decalin, and naphthalene data provided thus far only deal with the tetralin spike that was added to the original middle distillate plus some naphthalene that was indigenous to the distillate. To expand on the knowledge obtained from the hydrotreating tests, attempts were made to monitor all of the substituted tetralins and indanes. The values obtained for the amount of substituted tetralins and indanes are only for comparison between tests and are not an absolute concentration present in the oil sample. This is a consequence of not being able to determine sensitivities for these compounds.

Figure 11. Effect of Hydrotreater Temperature on Tetralin Concentration

Figure 12 depicts the data obtained on the methyltetralins. While the data contain more scatter than that of tetralin, a general trend can still be noted. These data suggest that the substituted tetralins are formed at a lower temperature than was observed for tetralin itself. Perhaps the hydrogenation could be performed near 302°C (575°F) and lessen the chance of losing donor solvent. The data for the substituted indanes are less definitive and contain a lot of scatter. However, the data do indicate that the indanes appear to form at a lower temperature also.

The amount of hydrogen consumed during the hydrotreating of the spent middle distillate was approximately 350 scf/bbl for the most severe conditions at 316°C (600°F) and LHSV = 1. This value was calculated from elemental analyses of the feedstock and product oils.

Figure 12. Effect of Hydrotreater Temperature on Substituted Tetralin Concentration

Comparison of the amount of naphthalene measured by the GC/MS technique and the elemental hydrogen consumption can be seen in Figure 13. While some scatter can be noted there is still a definite trend. Calculation of hydrogen consumption based on the tetralin-naphthalene balance, as was done for the tubing bomb tests, resulted in values that were about 70% of those calculated using elemental analyses of the feedstock and product oils. This would suggest an error was made in assuming that only three hydrogen atoms would be available from each mole of donor compound (substituted indanes and tetralins) from the middle distillate. A better choice may have been four, which would suggest that most of the hydrogen donor compounds were substituted tetralins. While GC/MS analysis of the middle distillate indicated the concentration of indanes was about that of tetralin, the data may have been in error because no sensitivity factors were available. Another reason could be that the substituted indanes do not donate hydrogen as readily as the substituted tetralins.

Figure 13. Comparison of Naphthalene Concentration and Hydrogen Consumption during Hydrotreater Tests

Product Characteristics

Products from the tubing bomb tests were evaluated by elemental and simulated distillation analyses. The evaluation of the data was difficult because it was impossible to separate the donor solvents (middle distillate and tetralin) from the shale oil generated during the thermal process. However, changes observed in the results of the elemental analyses can be used to evaluate the shale oil properties.

The elemental analyses indicate that the shale oil generated by hydrogen thermal extraction is probably similar in nature to other eastern shale oils. The data from these analyses are presented in Table 6. As the temperature of the tests increases, two changes in the results can be noted. First, as the test conditions became more severe, the hydrogen to carbon atomic ratio decreases slightly, indicating a slight increase in the aromatic character of the oil. This could result from either increased conversion of oil shale to liquid products or the formation of aromatic species as a result of hydrogen transfer reactions taking place during the conversion of the oil shale. Second, there appears to be an increase in the heteroatom content of the product oil with increasing temperature of the tests. This increase is probably a result of the increased production of shale oil. These changes would suggest the produced oil is probably similar to the eastern shale oil from which the middle distillate was derived (Thomas and Hunter 1989).

Table 6. Elemental Analyses of Oils from Tubing Bomb Tests

Temperature, °C	375	375	375	375	375	375
Residence Time, min	5	5	10	10	20	20
Oil/Solid Ratio	1:1	2:1	1:1	2:1	1:1	2:1
Conversion, %	0	0	8	8	17	20
Carbon, wt %	85.90	85.40	85.40	85.40	85.40	85.60
Hydrogen, wt %	11.70	11.60	11.60	11.70	11.60	11.60
Nitrogen, wt %	0.50	0.50	0.70	0.80	0.70	0.70
Sulfur, wt %	1.10	1.10	1.10	1.10	1.10	1.10
Hydrogen to Carbon Atomic Ratio	1.63	1.63	1.63	1.64	1.63	1.63
Temperature, °C	400	400	400	400	400	400
Residence Time, min	5	5	10	10	20	20
Oil/Solid Ratio	1:1	2:1	1:1	2:1	1:1	2:1
Conversion, %	17	16	27	28	36	34
Carbon, wt %			85.30	85.60	85.70	85.60
Hydrogen, wt %			11.60	11.60	11.50	11.30
Nitrogen, wt %			1.50	1.30	1.00	1.40
Sulfur, wt %			1.10	1.10	1.20	1.20
Hydrogen to Carbon Atomic Ratio			1.63	1.63	1.61	1.58
Temperature, °C	425	425	425	425	425	425
Residence Time, min	5	5	10	10	20	20
Oil/Solid Ratio	1:1	2:1	1:1	2:1	1:1	2:1
Conversion, %	17	22	48	45	39	37
Carbon, wt %	85.70	85.70	85.80	85.50	85.70	85.70
Hydrogen, wt %	11.50	11.50	11.30	11.30	11.20	11.40
Nitrogen, wt %	1.00	0.90	1.70	1.10	0.80	1.00
Sulfur, wt %	1.20	1.20	1.10	1.10	1.30	1.20
Hydrogen to Carbon Atomic Ratio	1.61	1.61	1.58	1.59	1.57	1.60

Simulated distillation data suggest that the produced oil does not contain as much high molecular weight material as had been observed in the whole eastern shale oil that was the source for the middle distillate used for this project. Boiling point distributions for selected products are given in Table 7. The data were obtained for tetralin-derived products with the tetralin contribution subtracted from the total distillation curve. The results indicate that approximately 90% of the material was distillable below 316°C (600°F), which is considerably lighter than the whole eastern shale oil examined by Thomas and Hunter (1989).

Table 7. Boiling Point Distribution of Oils from Selected Tubing Bomb Tests, °C

Temperature, °C	400	425	425
Residence Time, min	20	10	20
Oil/Solid Ratio	1:1	1:1	1:1
IBP	157	126	123
5%	193	182	180
10%	207	191	190
20%	219	204	202
30%	232	213	212
40%	243	221	219
50%	253	227	226
60%	263	234	233
70%	276	241	241
80%	289	247	250
90%	307	265	289
95%	316	371	422
FBP	555	589	601

The elemental and simulated distillation analyses suggest that there is enough similarity between the produced shale oil and the whole oil studied by Thomas and Hunter (1989) that similar methods of upgrading would probably be necessary. In the study by Thomas and Hunter (1989), five processes (acid-base extraction, solvent dewaxing, Attapulugus clay treatment, coking, and hydrogenation) were evaluated for upgrading eastern shale oil. Of these methods, some degree of success was achieved in removal of nitrogen species by Attapulugus clay treatment, coking, and hydrogenation. Only hydrogenation (single stage) showed much success in increasing the hydrogen to carbon atomic ratio and even then the products were not suitable for the direct production of transportation fuels. It was suggested by the authors that a two-stage hydrogenation process would probably be required to produce intermediates for the production of transportation fuel.

CONCLUSIONS

In this study, we evaluated the use of a shale oil-derived, recycle oil to mediate the transfer of hydrogen to eastern oil shale. The work was divided into two main parts which correspond to the two main portions of the H-ETM process: (1) shale oil extraction which involves the use of a donor solvent to aid in the extraction of the shale oil and (2) the regeneration of the donor solvent to a hydrogen-rich state ready for recycle. From the results of this investigation, the following conclusions can be made:

1. The conversion of the organic carbon increased greatly with increasing temperature. At a temperature of 425°C (797°F), a yield equivalent to 130% of Fischer assay was obtained using tetralin as a hydrogen donor solvent. At the same temperature, a yield equivalent to 110% of Fischer assay was obtained using an eastern shale oil-derived middle distillate as a donor solvent.
2. Increasing the oil to solid ratio from 1:1 to 2:1 did not appear to have any effect on the organic carbon conversion of the Sunbury Shale. Results from tests using the middle distillate as the donor solvent at the same temperature and residence times, but different oil to solid ratio, indicated that the data were quite similar for all of the test conditions.
3. Increasing the residence time appeared to have mixed effects on the conversion of Sunbury Shale in the presence of a donor solvent. Data from tests made at 375 and 400°C (707 and 752°F) suggest some increase in conversion with increasing residence time. Data from tests run at 425°C (797°F) do not always show an increase in conversion with increasing time. While a large increase was noted between the 5 and 10 minute residence times, tests using the middle distillate as a donor solvent show marked decreases at 425°C (797°F) and 20 minutes.
4. Comparison of tetralin with the middle distillate indicated that tetralin was more efficient as a hydrogen donor. Not only was the organic conversion better using tetralin, but also less hydrogen was required. The extra hydrogen consumption for the distillate tests was attributed to an increase in the cracking of the middle distillate fraction. Using tetralin as a donor solvent, an average of hydrogen consumption would be approximately 1300 scf per barrel of shale oil. The average hydrogen consumption for the middle distillate tests would be nearer 2000 scf per barrel of produced oil because of the extra hydrogen needed to satisfy radicals formed by thermal cracking.

5. The most effective hydrogenation conditions for regenerating the middle distillate as a donor solvent were 316°C (600°F), 1900 psi hydrogen, and LHSV = 1. Pressures above 1500 psi did not appear to influence the formation of tetralin as much as the temperature and LHSV. However, model compound studies indicated that cracking became a predominant reaction at 1200 psi. The amount of hydrogen consumed during the hydrotreating of the spent middle distillate was approximately 350 scf/bbl for the most severe conditions.

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DISCLAIMER

Mention of specific brand names of models of equipment is for information only and does not imply endorsement.

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