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Western Oil Shale Conversion Using the ROPE© Process

Topical Report

C.Y. Cha
L.J. Fahy
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December 1989

Work Performed Under Cooperative Agreement No.: DE-FC21-86MC11076

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

By
Western Research Institute
Laramie, Wyoming

MASTER

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SUMMARY

Western Research Institute (WRI) is continuing to develop the Recycle Oil Pyrolysis and Extraction (ROPE©) process to recover liquid hydrocarbon products from oil shale, tar sand, and other solid hydrocarbonaceous materials. The process consists of three major steps: (1) pyrolyzing the hydrocarbonaceous material at a low temperature ($T \leq 400°C$) with recycled product oil, (2) completing the pyrolysis of the residue at a higher temperature ($T > 400°C$) in the absence of product oil, and (3) combusting the solid residue and pyrolysis gas in an inclined fluidized-bed reactor to produce process heat.

Many conventional processes, such as the Paraho and Union processes, do not use oil shale fines (particles smaller than 1.27 cm in diameter). The amount of shale discarded as fines from these processes can be as high as 20% of the total oil shale mined. Research conducted to date suggests that the ROPE© process can significantly improve the overall oil recovery from western oil shale by processing the oil shale fines typically discarded by conventional processes. Also, if the oil shale fines are co-processed with shale oil used as the heavy recycle oil, a better quality oil will be produced that can be blended with the original shale oil to make an overall product that is more acceptable to the refineries and easier to pipeline.

Results from tests conducted in a 2-inch process development unit (PDU) and a 6-inch bench-scale unit (BSU) with western oil shale demonstrated a maximum oil yield at temperatures between 700 and 750°F (371 and 399°C).

Test results also suggest that the ROPE© process has a strong potential for recovering oil from oil shale fines, upgrading shale oil, and separating high-nitrogen-content oil for use as an asphalt additive.

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BACKGROUND

Western Research Institute (WRI) is continuing to develop the Recycle Oil Pyrolysis and Extraction (ROPE©) process to recover liquid hydrocarbon products from oil shale, tar sand, and other solid hydrocarbonaceous materials. As discussed in earlier publications (Cha et al. 1987; Cha et al. 1988), the process consists of three major steps: (1) pyrolyzing the hydrocarbonaceous material at a low temperature ($T \leq 400°C$) with recycled product oil, (2) completing the pyrolysis of the residue at a higher temperature ($T > 400°C$) in the absence of product oil recycling, and (3) combusting the solid residue and pyrolysis gas in an inclined fluidized-bed reactor to produce process heat.

Under the previous DOE cooperative agreement, the ROPE© process was studied in a 2-inch-diameter process development unit (PDU) using Asphalt Ridge tar sand and eastern New Albany oil shale. A 6-inch-diameter bench-scale unit (BSU) was also constructed.

The results from the early New Albany oil shale tests indicated the ROPE© process had the potential to produce oil yields greater than Fischer assay yields. The increase in oil yield is mainly due to the decrease in the gas production compared to Fischer assay.

During 1988, modifications were made to the PDU and BSU reactor systems. Three New Albany oil shale tests were conducted in the PDU, and a 10-day test was conducted in the BSU (Cha et al. 1988). As in earlier tests, oil yields greater than Fischer assay were generally achieved. The oils produced from the New Albany oil shale tests were of significantly higher quality than the original starting oil. The product oils were also considered a good feedstock for BTX (benzene, toluene, and xylene) and high-density fuels.

Various operational problems have been encountered when retorting oil shale with the ROPE© process. The BSU eastern oil shale test, conducted in 1988, was initially planned as a long-term test to determine steady-state conditions. Plugging problems associated with the heavy oil injection system resulted in this objective being only partially met. Modifications to the equipment were made after the oil shale test, and a 100-hour tar sand test was conducted continuously without plugging of the heavy oil injection system. Also, plugging problems can be reduced by screening oil shale particles less than 0.318 cm in diameter from the feed material. These smaller particles can be processed; however, additional filters and screening equipment, currently not available, will have to be added to the reactor systems.

Another problem associated with processing oil shale resulted from loss of the starting heavy oil. To date, no temperature range has been found that will consistently produce heavy oil. The conversion of the oil shale kerogen to oil produces a predominantly light oil. Both the starting shale oil and the oil produced from the kerogen is vaporized and swept from the system by the nitrogen purge. The loss of heavy oil has been overcome by continuously adding oil to the heavy oil recycle system.

Adding product oil to the heavy oil system eliminates fluctuations of the oil level in the pyrolysis reactor and reduces the viscosity of the existing heavy oil, which makes it easier to pump. Also, this tendency to convert the heavy recycle oil makes this process an attractive method for upgrading a relatively heavy oil while simultaneously recovering oil from oil shale or some other hydrocarbonaceous material.

RESEARCH STRATEGY

Many conventional processes, such as the Paraho and Union processes, do not use oil shale fines (particles smaller than 1.27 cm in diameter) (Jones 1977; Snyder and Pownall 1978). The amount of shale discarded as fines from these processes can be as high as 20% of the total oil shale mined. Recovering oil from the fines will significantly improve the process oil recovery and reduce the overall shale oil production costs.

A deterrent to producing oil from western oil shale is the high sulfur and nitrogen content of the oil shale, which must be reduced before it can be used as a refinery feedstock. In contrast, the high nitrogen content in shale oil is beneficial when the oil is used as an asphalt binder. Therefore, it is desirable to develop a process that can concentrate the nitrogen and sulfur in a shale oil residue while upgrading a lighter fraction that will be relatively low in nitrogen and sulfur.

Research conducted to date has shown that the ROPE© process can significantly improve the overall oil recovery from western oil shale by processing the oil shale fines that are typically discarded by conventional processes, such as Paraho and Union. Also, if oil shale fines are co-processed with shale oil, a better quality oil may be produced. This product oil can be blended with the original shale oil to make an overall product that is more acceptable to the refineries and easier to pipeline.

Objectives

WRI used western, Green River Formation oil shale to conduct three PDU tests and one long-term BSU test. The objectives of this research were to determine the applicability of co-processing shale oil with oil shale fines to:

- Upgrade shale oil by separating high-nitrogen-content oil and removing waxy components
- Recover oil from oil shale fines

Equipment Modifications

The PDU system was modified to address the problems discussed previously (Figure 1). Overall, the modifications resulted in a much simpler system. The pyrolysis-zone screw conveyor angle was decreased from 15 degrees to 3 degrees from horizontal to allow for more liquid-gas disengagement area. The low angle was similar to earlier versions of the system, which appeared to give better oil yields from eastern oil shale.

The size of the transition between the horizontal screw pyrolysis reactor and the drying or inclined screw pyrolysis reactor was increased to reduce plugging by the oil shale fines. Four knockouts (KO1-KO4) were installed to remove the gas and oil vapors.

After the PDU system was successfully operated, the BSU system was modified to a similar configuration (Figure 2). The number of knockouts in the BSU system was decreased to three by combining the KO2 and KO3 knockouts into one (KO2). The heavy oil injection system was also modified. The system was set up for only shale oil injection with no recycle of the heavy return oil. This was done to more closely simulate a co-processing system where the shale oil injection and the heavy oil return were minimized.

The 4-inch preheat screw conveyor previously used in the BSU system was removed and replaced with a larger diameter (7-inch) screw conveyor. The heating mechanism was changed from external heaters to a superheated steam-jacketed system, which provided excellent heating capacity and control.

Experimental Conditions

Western oil shale from two different locations was used in the PDU tests and the BSU test. The PDU tests were conducted with the first reference shale obtained from the Exxon mine (Owen 1987). Because of the large quantities of shale required for the BSU test, Anvil Points shale, which had previously been stockpiled, was used. The Fischer assays for the two western oil shales are listed in Table 1. The shale used in the BSU test had a slightly lower oil yield. More importantly, the Anvil Points shale Fischer assay gas yield was only one-half as large as the gas yield from the reference shale. The differences in gas yield may have been caused by the way the shale was stored. The reference shale was stored in sealed drums under a nitrogen blanket, whereas the Anvil Points shale was simply stockpiled and exposed to atmospheric conditions.

Previous PDU tests with eastern oil shale showed that a pyrolysis temperature of 650°F (344°C) produced the best oil yield (Cha et al. 1988). The best retorting temperature for western oil shale was determined by the three PDU tests (Table 2).

The first PDU test was conducted for 42 hours with an average pyrolysis temperature of 650°F (344°C). The first test and all subsequent PDU tests were started using western shale oil produced from the 10-ton retort as the starting pyrolysis-zone recycle oil (Merriam et al. 1986).

For all three tests, after 16 hours of operation, sufficient KO3 and KO4 product oils were available. These product oils were then used as makeup oil as the heavy oil level in the system decreased. The last two PDU tests were conducted for 26 hours with an average pyrolysis temperature of 700 and 760°F (371 and 405°C), respectively. Because the main objective of the PDU tests was to determine the optimal pyrolysis temperature for western oil shale, efforts were made to keep the same temperature along the length of the pyrolysis zone.

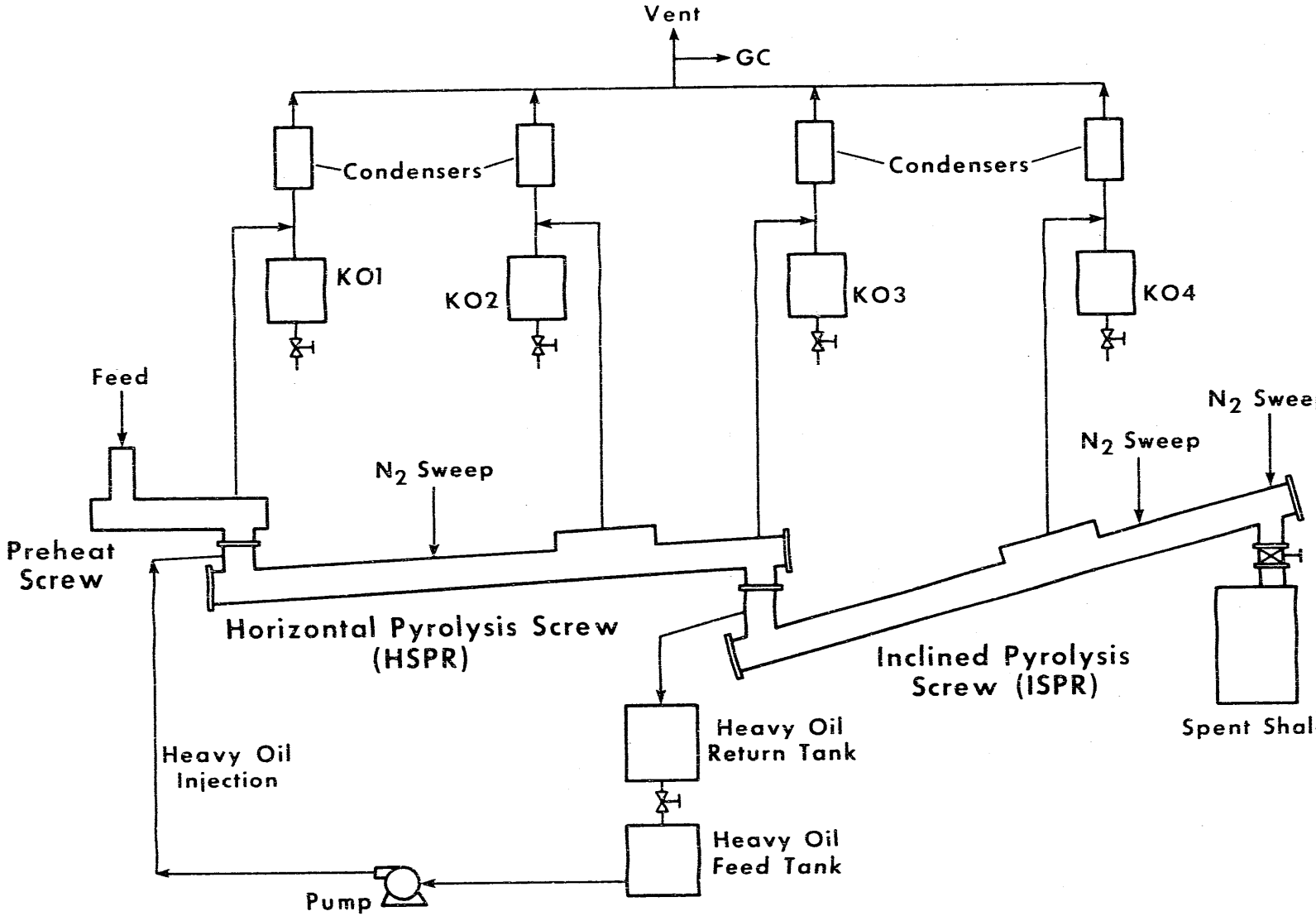

Figure 1. 2-Inch Process Development Unit Reactor System

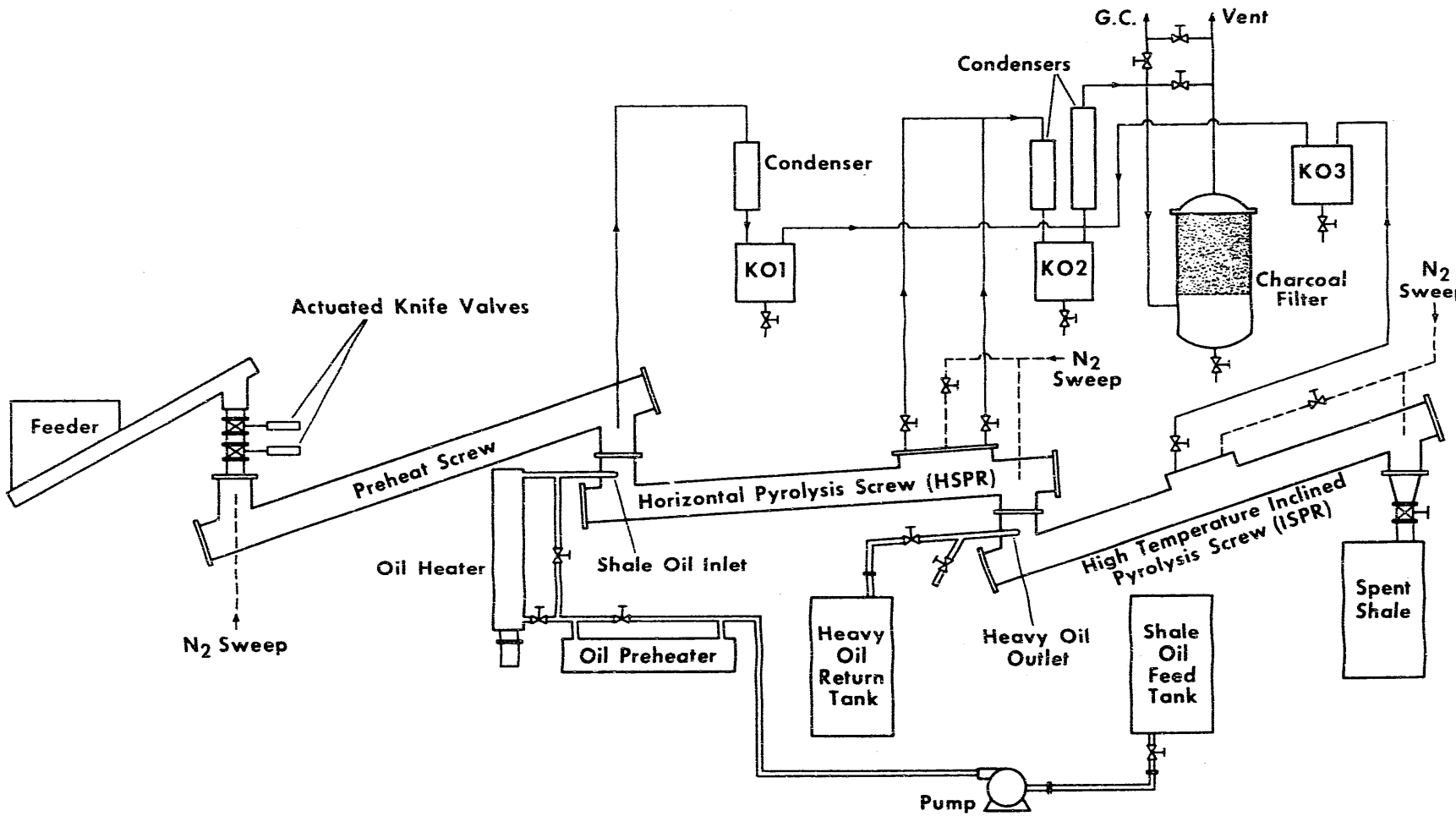

Figure 2. 6-Inch Bench Scale Unit Reactor System

Table 1. Oil Shale Fischer Assay Comparison

	2-Inch PDU Shale	6-Inch BSU Shale
Oil Yield, gpt	28.7	27.7
Oil, wt %	10.7	10.5
Water, wt %	1.5	1.2
Gas, wt %	5.2	2.5
Spent Shale, wt %	82.6	85.8
Spent Shale Organic Carbon, wt %	3.9	3.8

Table 2. Test Operating Conditions

	2-inch PDU Tests			6-Inch BSU Test
	1	2	3	
Test Duration, hr	42	26	26	103
Shale Feed Rate, kg/hr	3.0	3.0	3.0	36.8
Heavy Oil Injection Rate, kg/hr	2.0	2.8	2.5	17.2
Heavy Oil Return Rate, kg/hr	1.3	1.8	0.9	1.9
Preheat Zone Temperature, °F	475	485	465	615
Horizontal Pyrolysis Zone Average Temperature, °F	650	700	760	--
Inclined Pyrolysis Zone Temperature, °F	975	975	975	970

The BSU test was conducted with three different temperature configurations in an attempt to maximize oil yield (Figure 3). During the first 40 hours of the test, the pyrolysis-zone temperature was held constant at approximately 705°F(374°C). After 40 hours of operation, a temperature gradient was imposed across the pyrolysis zone such that the temperatures averaged 645°F (341°C) at the inlet (zone 1), 700°F (371°C) at the midpoint (zone 2) and 735°F (391°C) at the exit from the pyrolysis zone (zone 3). During the last 14 hours of the test, the pyrolysis-zone exit temperature was increased to 750°F (400°C).

Heavy oil was not circulated in the BSU test. Fresh shale oil was injected at a low rate to minimize the amount of heavy oil returned from the system (Table 2). The heavy oil that did return was collected separately and not recycled. This mode of operation was different from the PDU operation, in which the heavy oil was circulated, but is the anticipated mode of operation for co-processing oil shale fines with shale oil.

As each test was conducted, material entering or leaving the reactor was carefully measured. Samples of the raw and spent shale and the oil products were also routinely collected. From these samples, composite samples, representative of the feed material, the spent shale, the starting shale oil, and the product and heavy oils were prepared and analyzed. Gas analyses were taken hourly and an average gas analysis was calculated. The total gas produced was calculated by use of the nitrogen balance.

At the end of each test, all material was removed from the reactor and measured to determine the overall material balance. The oil yield was determined for each test from an oil balance. At the end of the test, the total product oil and remaining heavy oil was determined. From this amount, the starting shale oil was subtracted. The remaining amount of oil was the net oil produced for the test. The oil yield was calculated by dividing the net amount of oil produced from the test by the total weight of shale processed. This value is expressed as a weight percent. The amount of oil that would have been theoretically produced by a Fischer assay was determined by multiplying the total weight of shale processed by the weight percent oil determined from the Fischer assay analysis of the composite shale feed sample. Once the theoretical amount of oil produced by Fischer assay was known, the oil yield as a percent of Fischer assay could also be determined. This was done by dividing the net amount of oil produced for the test by the theoretical amount of oil produced by Fischer assay.

From the material balance, the amounts of gas, water and spent shale produced were also known. These yields were determined as a weight percent by dividing the total amount of each species produced by the weight of the shale processed.

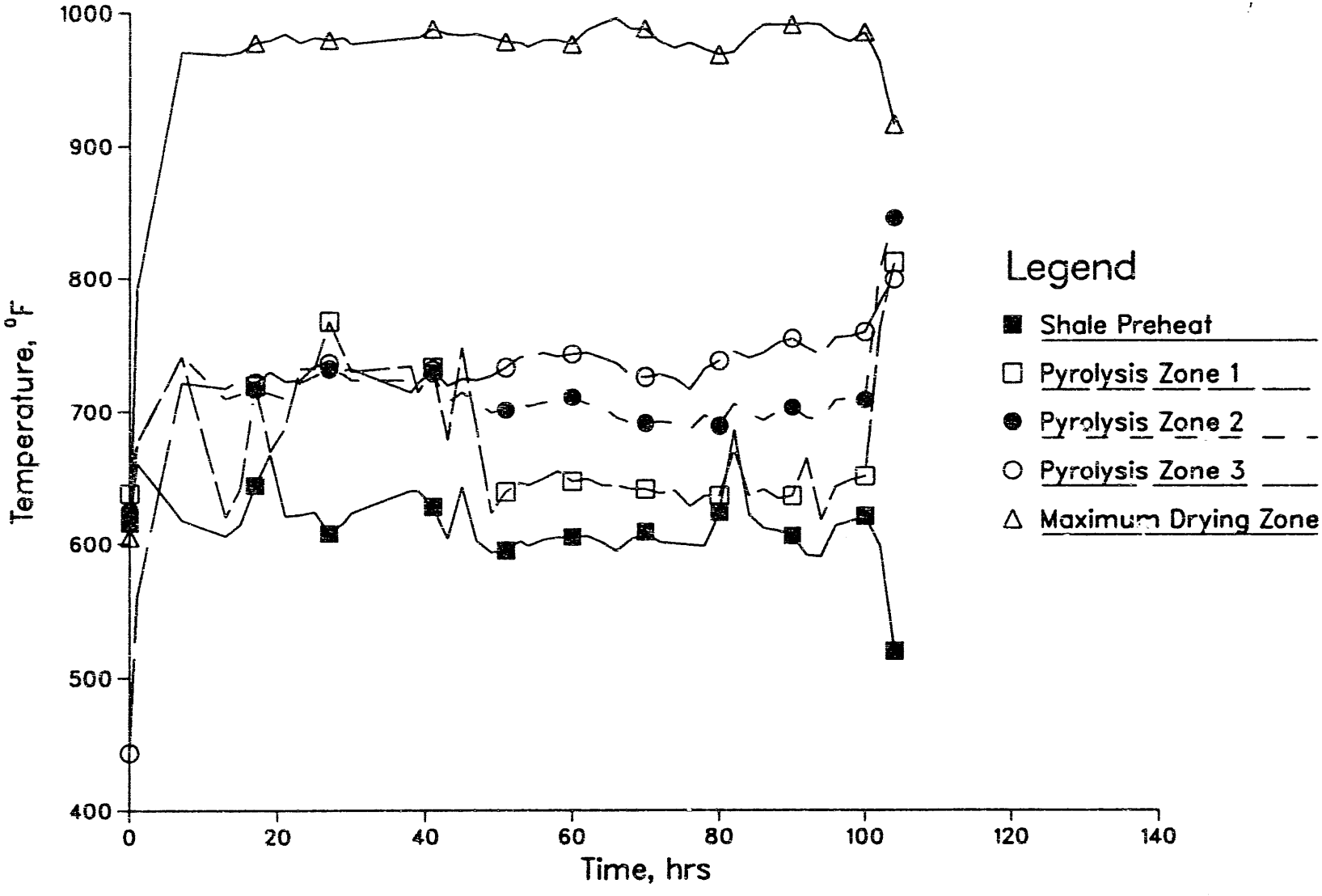

Figure 3. 6-Inch BSU Test Temperature History

RESULTS

The three PDU tests using western oil shale were conducted with essentially no problems. Modifications to the system appear to have solved most of the mechanical problems that were experienced in the past.

Because of the low oil yield at 650°F (344°C), it was determined that a higher pyrolysis temperature was needed, compared with the conditions used in the eastern oil shale ROPE© tests. Consequently, the last two tests were conducted at 700 and 760°F (371 and 405°C).

Product yields from the western oil shale tests are summarized in Table 3. The average gas compositions are listed in Table 4, and the actual amounts of shale and shale oil processed are summarized in the material balance summary tables (Tables 5-8) which will be discussed in more detail later.

Ash balance closures of 100% were achieved for the first two PDU tests. However, the third PDU test and the BSU test ash balance closures were only 95%. Attempts to force these two ash balances resulted in unrealistic variations in the oil yield. Because of these discrepancies, the actual oil yields for these two tests may be more conservative than indicated in Table 3.

For clarification, an example of how the oil yield was calculated is presented here using data from Tables 1, 3, and 5. The first PDU test was arbitrarily chosen for this example. From Table 5, a total of 43,316 g of product and heavy oil was recovered at the end of the test. A total of 37,681 g of shale oil was used to start the test. By subtraction, 5,635 g was the net amount of oil produced from the oil shale during this test. Table 5 shows that 124,500 g of oil shale was processed. From the data in Table 1, this shale would theoretically yield 10.7 wt % oil or 13,322 g of oil if the oil shale had been processed by Fischer assay. Comparison of the net oil produced from the PDU test with the theoretical Fischer assay oil yield shows that less oil was produced during this particular PDU test than if the shale been processed by Fischer assay. By dividing the net oil produced from the PDU test (5,635 g) by the theoretical Fischer assay oil yield (13,322 g) and multiplying by 100%, an oil yield value of 42.3% of Fischer assay was determined for the first PDU test (Table 3).

As indicated above, the first PDU test, conducted at 650°F (344°C), had an oil yield of only 42.3% of Fischer assay. However, the second PDU test had an oil yield of 91.6% of Fischer assay. The results in Table 3 show that the 650°F (344°C) temperature was too low to pyrolyze the oil shale effectively, and more carbon was left on the spent shale compared with Fischer assay. At 760°F (405°C), the temperature was too high, and coking and cracking losses reduced the oil yield. This is shown by the relatively high gas yield and also the increase in the organic carbon content on the spent shale in the third PDU test compared to Fischer assay results and the second PDU test results.

Table 3. Oil Shale ROPE© Test Product Yields

	2-Inch PDU Tests			6-Inch
	1	2	3	BSU test
Pyrolysis Temperature, °F	650	700	760	---
Oil Yield, % Fischer assay	42.3	91.6	92.0	108.3
Oil, wt %	4.5	9.7	9.8	11.3
Gas, wt %	5.4	5.6	6.8	2.9
Water, wt %	1.5	1.5	1.5	1.2
Spent Shale, wt %	88.6	83.2	81.8	84.6
Organic Carbon on Spent Shale, wt %	8.6	6.1	6.9	5.9

Table 4. Average ROPE© Test Product Gas Compositions, vol %

	2-Inch PDU Tests			6-Inch
	1	2	3	BSU Test
H_2	15.5	17.7	21.5	19.5
CO	3.0	4.8	5.9	3.0
CO_2	46.6	43.9	39.9	17.2
CH_4	7.2	8.9	8.6	17.2
C_2H_6	2.3	3.1	3.0	8.4
C_2H_4	2.1	1.6	1.7	2.8
C_3H_8	1.8	1.9	1.9	4.5
C_3H_6	1.1	1.4	1.4	3.1
C_4	2.3	2.2	2.0	4.4
C_5	1.5	1.8	1.4	0.5
C_6	1.6	1.8	1.5	0.3
C_7	0.6	0.5	0.5	0.3
C_8	0.7	0.5	0.6	0.2
C_9	0.2	0.3	0.3	-
C_{10}	0.2	0.1	0.2	-
H_2S	13.5	9.5	9.7	18.8
Total	100.2	100.0	100.1	100.2

Table 5. First PDU Test Material and Elemental Balance Summary

	Material	Total Carbon	Mineral Carbon	Organic Carbon	Hydrogen	Nitrogen	Sulfur
IN							
Oil Shale, g	124,500	22,161	5,603	16,558	1,743	872	1,494
Shale Oil, g	37,681	31,652		31,652	4,635	641	678
Total In, g	162,181	53,813	5,603	48,210	6,378	1,513	2,172
OUT							
Spent Shale, g	110,336	14,454	4,965	9,489	582	883	1,103
Heavy Oil, g	11,835	9,930		9,930	1,349	201	107
Product Oil, g	31,481	26,941		26,941	3,616	555	283
Water, g	1,868				208		
Gas, g	6,744	2,566	638	1,928	423		816
Total Out, g	162,264	53,891	5,603	48,288	6,178	1,639	2,309
% Closure	100.1	100.1	100.0	100.2	96.9	108.3	106.3

Table 6. Second PDU Test Material and Elemental Balance Summary

	Material	Total Carbon	Mineral Carbon	Organic Carbon	Hydrogen	Nitrogen	Sulfur
IN							
Oil Shale, g	76,500	13,617	3,672	9,945	1,377	612	918
Shale Oil, g	47,819	40,598		40,598	5,834	669	717
Total In, g	124,319	54,215	3,672	50,543	7,211	1,281	1,635
OUT							
Spent Shale, g	64,245	6,617	2,698	3,919	128	450	707
Heavy Oil, g	10,500	8,904		8,904	1,323	116	116
Product Oil, g	44,820	37,955		37,955	5,365	711	493
Water, g	1,148				128		
Gas, g	4,364	1,794	974	820	296		388
Total Out, g	125,077	55,310	3,672	51,638	7,240	1,277	1,704
% Closure	100.6	102.0	100.0	102.2	100.4	99.7	104.2

Table 7. Third PDU Test Material and Elemental Balance Summary

	Material	Total Carbon	Mineral Carbon	Organic Carbon	Hydrogen	Nitrogen	Sulfur
IN							
Oil Shale, g	72,000	12,816	3,456	9,360	1,008	504	1,008
Shale Oil, g	56,522	47,252		47,252	6,896	961	735
Total In, g	128,522	60,068	3,456	56,612	7,904	1,465	1,743
OUT							
Spent Shale, g	58,908	6,716	2,651	4,065	101	412	648
Heavy Oil, g	15,094	12,483		12,483	1,560	242	166
Product Oil, g	48,516	41,102		41,102	5,406	777	
Water, g	1,032				115		
Gas, g	4,919	1,976	805	1,171	334		461
Total Out, g	128,469	62,277	3,456	58,821	7,516	1,431	1,809
% Closure	100.0	103.7	100.0	103.9	95.1	97.7	103.8

Table 8. 6-Inch BSU Test Material and Elemental Balance Summary

	Material	Total Carbon	Mineral Carbon	Organic Carbon	Hydrogen	Nitrogen	Sulfur
IN							
Oil Shale, kg	3696.1	654.2	173.7	480.5	66.5	22.2	40.6
Shale Oil, kg	1482.5	1239.3		1239.3	177.9	22.2	26.7
Total In, kg	5178.6	1893.5	173.7	1719.8	244.4	44.4	67.3
OUT							
Spent Shale, kg	3117.5	346.0	162.1	183.9	9.3	15.6	21.8
Heavy Oil, kg	209.7	177.0		177.0	23.5	3.8	2.3
KO1 Product Oil, kg	1267.6	1062.3		1062.3	158.4	17.7	13.9
KO2 & 3 Product Oil, kg	423.3	350.9		350.9	50.3	7.6	4.7
Water, kg	44.4				4.5		
Gas, kg	106.6	48.8	11.6	37.2	12.3		24.1
Total Out, kg	5169.1	1985.0	173.7	1811.3	253.3	44.7	66.8
% Closure	99.8	104.8	100.0	105.3	105.7	100.7	99.3

Similar gas compositions were obtained for the three PDU western oil shale tests (Table 4). In the first PDU test, conducted at 650°F (344°C), more H_2S was made at the expense of hydrogen. Whereas, in the third test, conducted at 760°F (405°C), more cracking occurred, more hydrogen was produced, and CO_2 concentration was lower due to dilution. The concentration of CO increased with temperature, whereas the concentration of methane increased when the temperature increased from 650°F (344°C) to 700°F (371°C) and remained constant.

Based on the oil yield and gas analysis information from the PDU tests, it was determined that the long duration, BSU test should be operated with a pyrolysis zone temperature between 700 and 750°F (371 and 400°C). As mentioned above, a higher temperature is necessary to pyrolyze western oil shale compared to eastern shale. The higher temperature may be necessary because the chemical structures of eastern and western shale oils are different. It takes more energy to break the straight chains in the paraffinic western shale oil than it does to cleave off side chains from the aromatic eastern shale oil (F.D. Guffey, personal communication, 1989).

The BSU test was continuously operated for 103 hours (Table 2). Even though slight pyrolysis zone temperature changes were made in an attempt to improve oil yield, after the system stabilized, shale oil injection and oil production reached fairly steady rates. These rates were maintained throughout most of the test (Figures 3 and 4).

The BSU test had a measured oil yield of 108.3% of Fischer assay; however, this value has not been corrected for the low ash balance closure. The organic carbon balance for this test was also high (Table 8). If these two balances had both been closer to 100%, the oil yield would have approximated the yield from the second PDU test.

The material and elemental balances for the first two PDU tests had acceptable closures (Tables 5 and 6). Except for the ash balance closure, the third PDU test also had acceptable balance closures (Table 7). Hydrogen content is difficult to determine experimentally and commonly results in significant variations in the balance closure. The sulfur balance closures from the four tests also varied from 100%. As with hydrogen, sulfur content, particularly in the solid material, is difficult to determine accurately. Nitrogen content of the product oils proved to be difficult to measure; however, the nitrogen balance closures were generally close to 100%.

The BSU test gas yield and composition are summarized in Tables 3 and 4, respectively. The amount of gas produced from the BSU test was significantly lower than that from the three PDU tests. However, the amount was approximately equal to the Fischer assay value (Table 1). The composition of the BSU test gas was also different from the PDU tests; the former was significantly lower in CO_2, indicating much less mineral decomposition. The BSU test gas was also higher in methane and H_2S. The variations in the amounts and composition of the western oil shale gases may be caused by differences in the shale sources. Also, the Anvil Points shale, used in the BSU test, may have been affected by weathering.

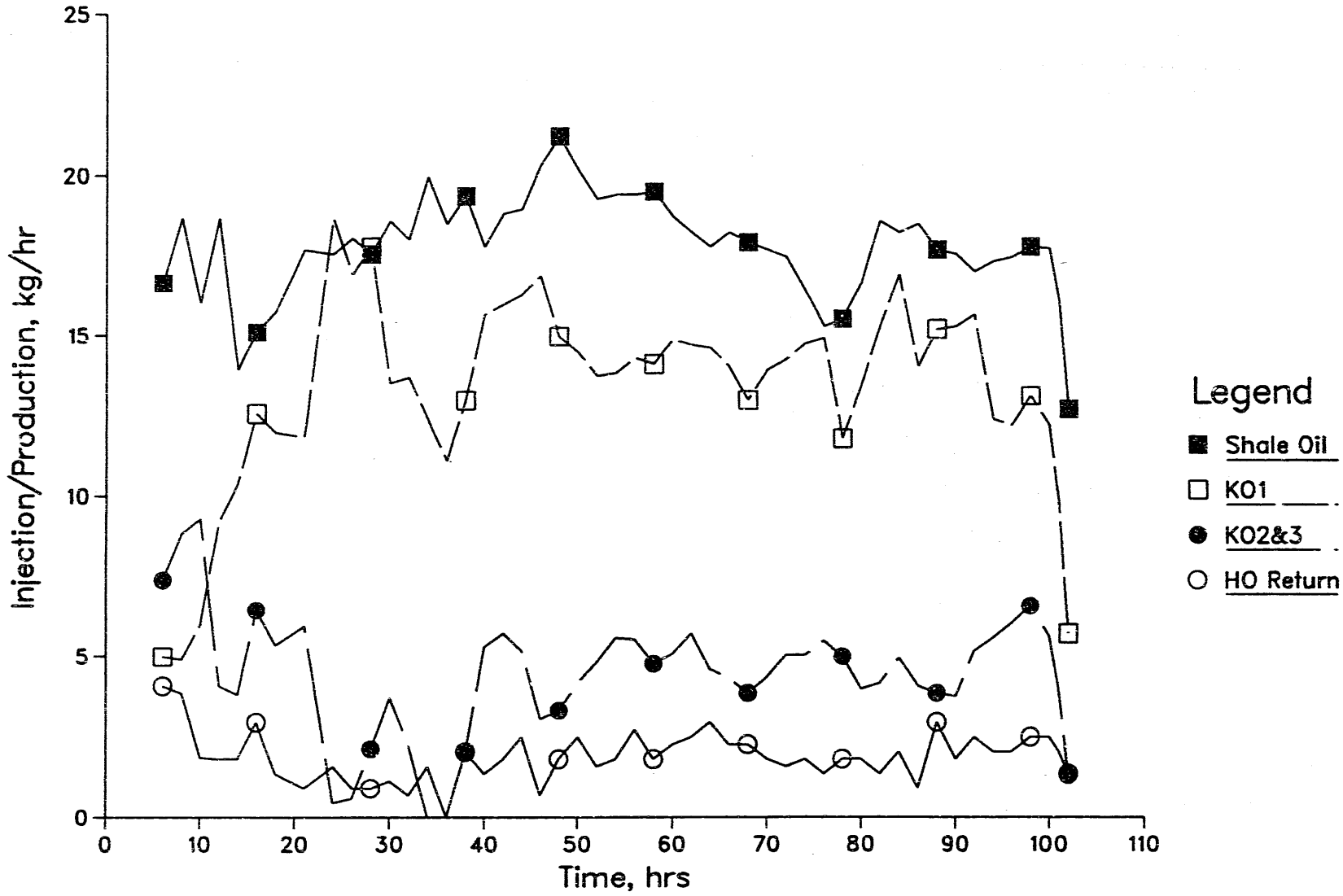

Figure 4. 6-Inch BSU Test Oil Injection and Production History

A key indicator of the efficiency of the process is the comparison of the organic carbon left on the spent shale after a Fischer assay (Table 1) with the organic carbon left on the spent shale after applying the ROPE© process (Table 3). Data in Table 1 show that the spent shale from the Fischer assay tests of the western oil shales had an organic carbon content of approximately 3.8 wt %. The second PDU test, conducted at 700°F (371°C), was higher at 6.1 wt %. The first and third PDU tests conducted with lower and higher temperatures, respectively, had more carbon left on the spent shale, indicating more coking had occurred than in the second PDU test. The BSU test had a spent shale organic carbon content of 5.9 wt %, which was approximately the same as the second PDU test.

One significant difference between the PDU tests and the BSU test involved the oil production. In the PDU tests, the majority of the product oil was produced from the second and third knockouts (KO2 and KO3), whereas almost no oil was produced from the first knockout (KO1) (Figure 5). Conversely, the majority of the oil produced in the BSU test was produced from the first knockout (KO1) (Figure 4). The higher KO1 oil production during the BSU test was predominantly caused by the distillation of the injected shale oil. The BSU test product oil that came from pyrolysis of the oil shale was mainly produced from KO2.

The average elemental compositions of the injected and produced oils are summarized in Table 9. In general, the elemental compositions of the product oils were not significantly altered from the starting 10-ton shale oil. However, the atomic hydrogen-to-carbon (H/C) ratios from the BSU test oils were lower than those from the PDU tests. There was also a tendency toward an increase in nitrogen concentration in the oil produced from KO4 on the PDU system and KO3 on the BSU system. This suggests that high-nitrogen-content oil may be separated and concentrated in the heavy product oil ends for use as an asphalt additive.

In addition to the composite oil samples that were used for material balance calculations, selected oil samples were analyzed to study the change in the elemental composition of different product oils with time. The heavy return oil from the first PDU test was analyzed because this oil was recycled for the longest time (Figure 6). The KO1 oil from the BSU test was analyzed because this was the main oil produced from that test (Figure 7). The KO2 oil from the second PDU test was analyzed because this was the main oil produced during the PDU tests (Figure 8).

The only significant changes in composition with time were a decrease in the sulfur content of the KO1 oil and an increase in the nitrogen content of the KO2 oil. This is also a desirable trend for upgrading the lighter shale oil products and concentrating the nitrogen in the heavier fractions for use as an asphalt additive. The heavy oil remained remarkably unchanged with time after the system reached steady-state conditions.

Table 9. Average Elemental Composition of Western Oil Shale Test Product Oils

2-Inch PDU	6-Inch BSU	Carbon				Hydrogen				Atomic H/C Ratio			
		2-Inch PDU			6-Inch	2-Inch PDU			6-Inch	2-Inch PDU			6-Inch
		1	2	3	BSU	1	2	3	BSU	1	2	3	BSU
KO1	KO1	85.0	84.6	84.7	83.8	13.4	13.2	14.7	12.5	1.88	1.86	2.07	1.78
KO2		85.3	85.2	85.1		12.3	12.1	13.2		1.72	1.69	1.85	
	KO2				85.2				12.1				1.69
KO3		85.4	85.0	84.8		12.5	12.0	13.1		1.74	1.68	1.84	
KO4	KO3	81.9	84.5	84.6	83.9	11.3	11.7	12.5	10.6	1.64	1.65	1.76	1.51
Shale Oil		85.1	84.7	-	83.5	12.5	12.2	-	12.0	1.75	1.72	-	1.71
Heavy Oil Recycle/Return		84.1	84.8	83.9	84.4	11.6	12.6	12.3	11.2	1.64	1.77	1.75	1.58

2-Inch PDU	6-Inch PDU	Nitrogen				Sulfur			
		2-Inch PDU			6-Inch	2-Inch PDU			6-Inch
		1	2	3	BSU	1	2	3	BSU
KO1	KO1	0.5	0.6	0.6	1.4	0.8	1.2	1.4	1.6
KO2		1.4	1.6	1.5		1.2	0.9	1.0	
	KO2				1.8				1.4
KO3		1.3	1.5	1.6		0.9	1.0	1.1	
KO4	KO3	1.7	2.0	2.4	2.5	0.8	0.7	0.6	0.9
Shale Oil		1.3	1.3	-	1.5	1.0	1.2	1.3	1.8
Heavy Oil Recycle/Return		1.5	1.1	1.8	1.8	1.0	1.2	1.4	1.1

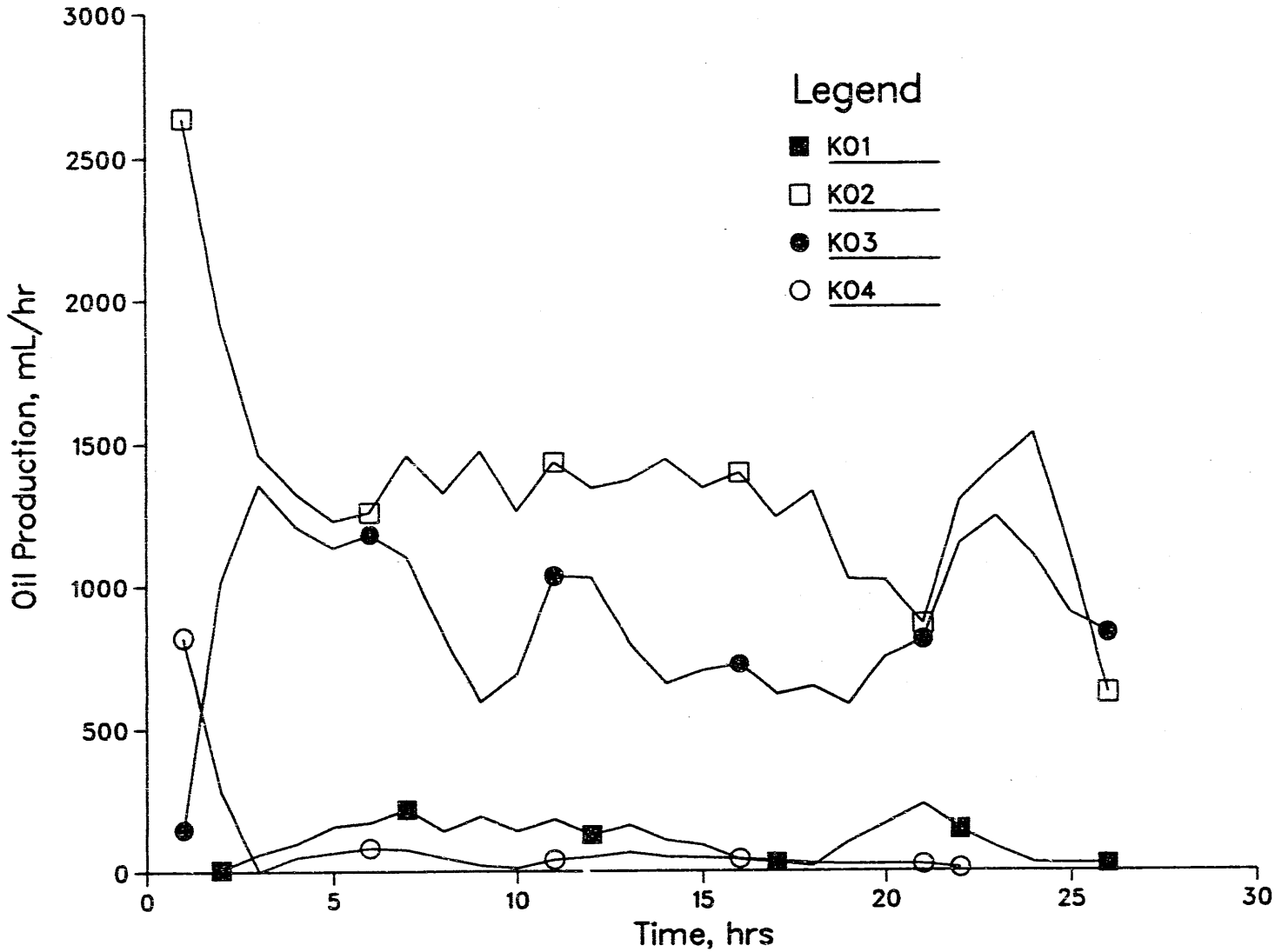

Figure 5. Third 2-Inch PDU Test Oil Production History

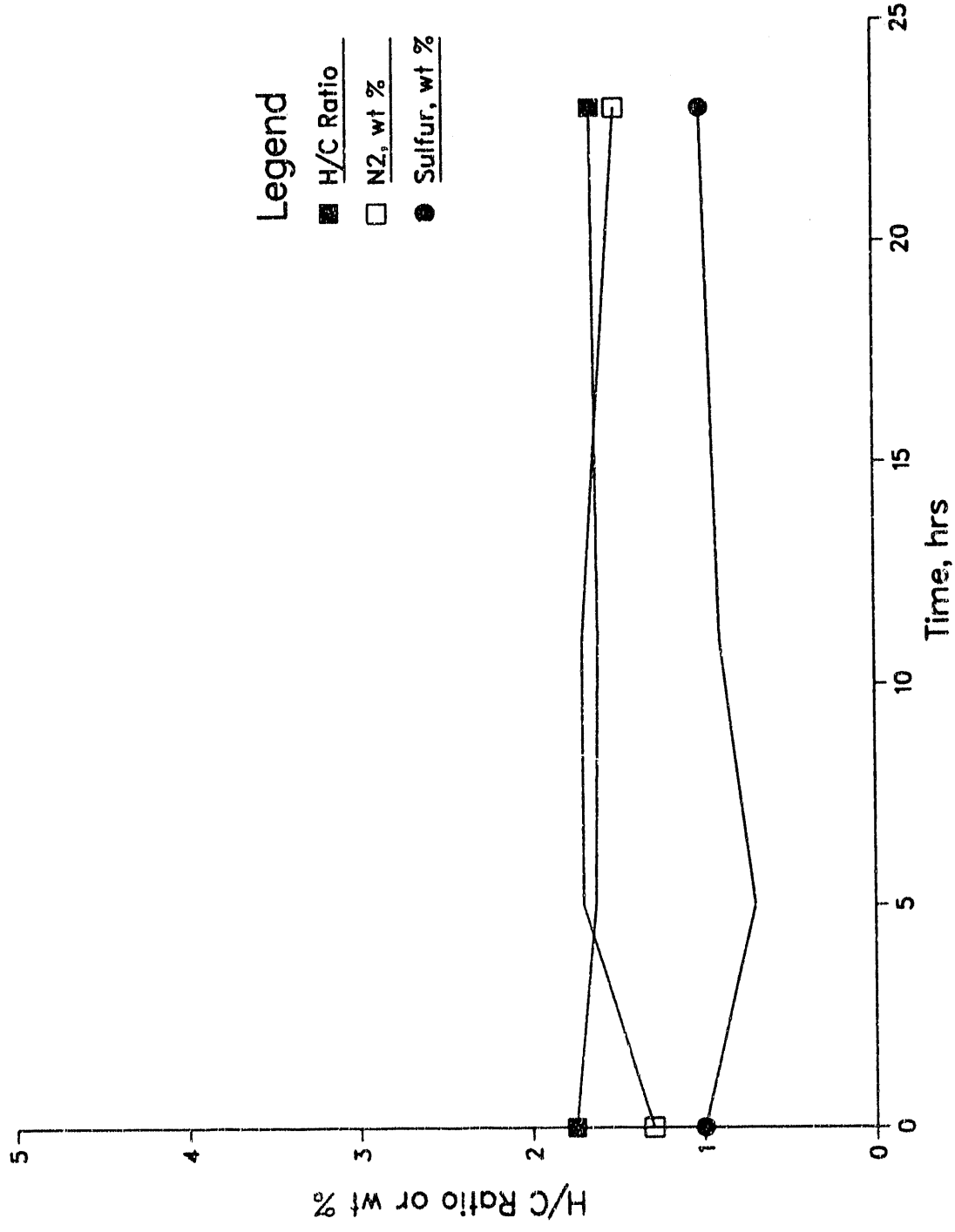

Figure 6. First 2-Inch PDU Test Heavy Oil Composition

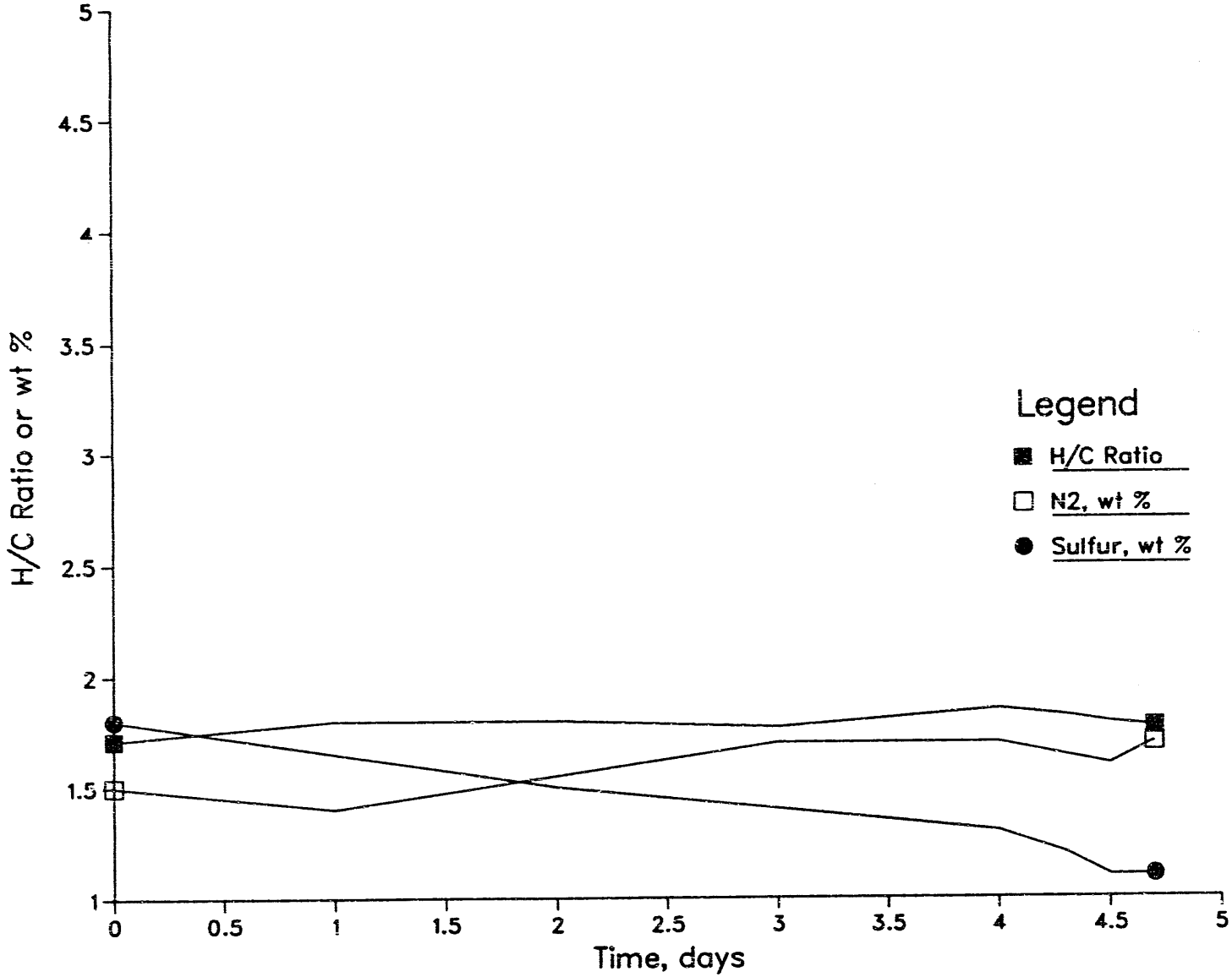

Figure 7. 6-Inch Test K01 Product Oil Composition

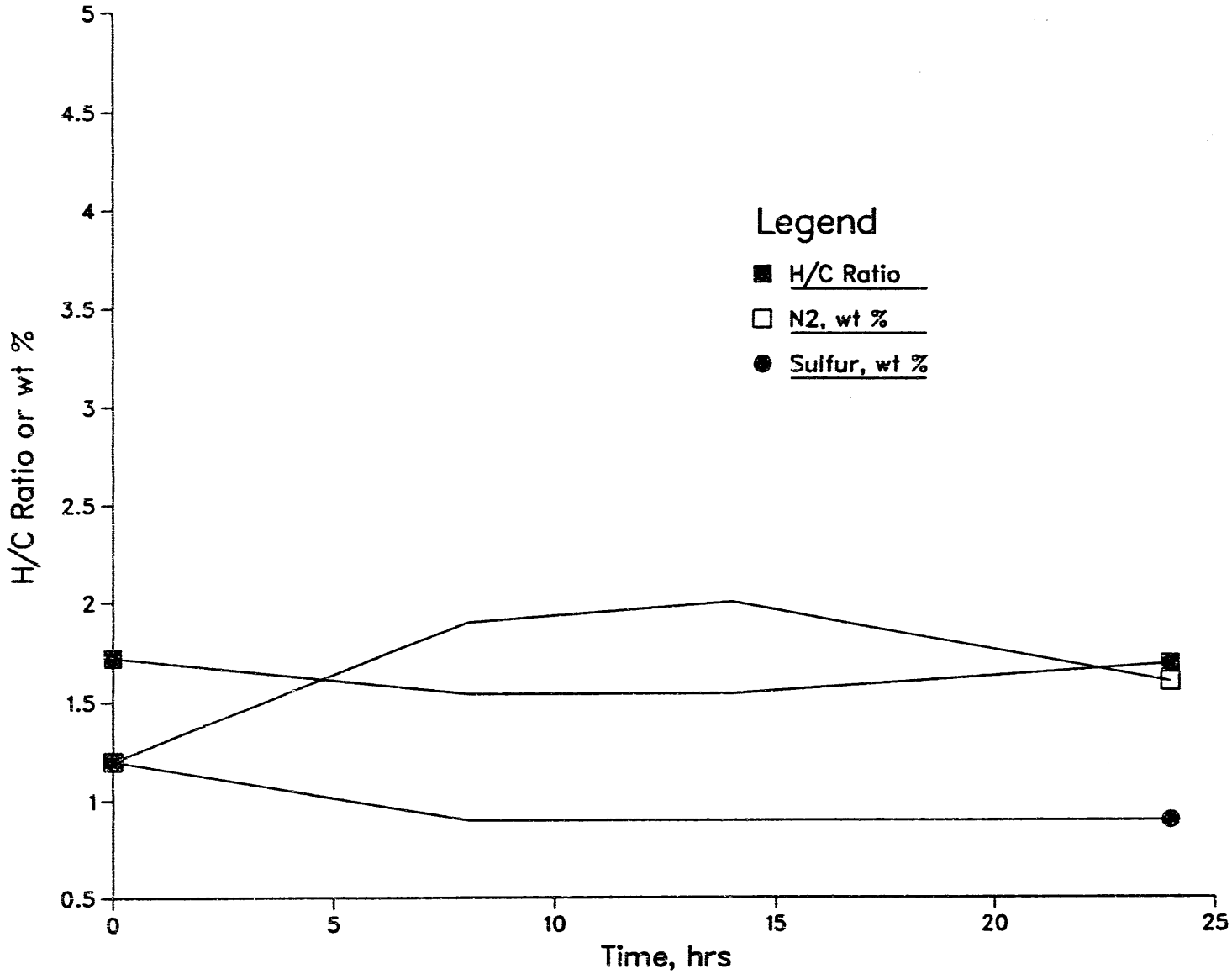

Figure 8. Second 2-Inch PDU Test K02 Product Oil Composition

The average physical properties of the product oils and the daily specific gravity and viscosity results of the KO1 product oil produced from the BSU test are summarized in Tables 10 and 11, respectively. The KO1 product oil was upgraded as it had a significantly lower specific gravity and viscosity than the starting shale oil. There was essentially no change in the physical properties of the KO1 oil with time. The heavy return oil and the KO3 oil from the BSU test had higher specific gravities and viscosities than the starting shale oil. The KO2 product oil had a specific gravity and viscosity that was similar to the starting shale oil. Reducing the specific gravity and viscosity of the KO1 oil while increasing the specific gravities and viscosities of the KO3 and the heavy return oil was caused by distillation of the injected shale oil and also by removing the waxy components from the KO1 product oil.

Simulated distillation results of the BSU test product oils are shown in Figure 9. The KO1 oil initial boiling point was 236°F (113°C) compared to 294°F (146°C) for the starting oil. The KO1 oil was also 100% distillable at 1000°F (538°C), whereas the original shale oil was only 92% distillable at 1000°F (538°C). The KO2 and KO3 product oil fractions contained more heavy ends and fewer light ends than the starting shale oil and the KO1 product oil. These results are consistent with the specific gravity and viscosity results.

Co-processing of the shale oil to produce an upgraded product is an important part of the ROPE© process if it is to be applied to western oil shale. Therefore, determining the decomposition rate of the shale oil during these tests was an important consideration. In all four tests, the amount of shale oil or heavy oil injected into the pyrolysis zone and the amount of heavy oil that was returned from the pyrolysis zone was measured with time. The difference between the oil injected and the oil returned was the amount of oil that was decomposed and recovered in the knockouts. The shale oil decomposition rates were determined for each test as a percentage of the total shale oil and kerogen fed into the reactors. This was done to normalize the results between the PDU and BSU systems which operate with feed and oil injection rates that differ by approximately one order of magnitude.

The shale oil decomposition rates were then plotted as a function of temperature (Figure 10). As expected, there was an increase in the shale oil decomposition rate with temperature as determined from the PDU tests. There was also a higher decomposition rate in the BSU test than in the PDU tests. In the BSU test, fresh shale oil was continually injected, and an abundance of light ends was continually available for distillation. Conversely, in the PDU tests, the shale oil was continually recycled, and fresh shale oil was added only when necessary to maintain a sufficient amount of heavy oil for recycling. Consequently, the heavy oil that was being recycled always had less light distillable fractions than what was available in the BSU test.

Table 10. 6-Inch BSU Test Average Product Oil Physical Properties

	Distillation Temperature, °F	Pour Point, °F	Specific Gravity, 60°F	Viscosity, 100°F(38°C) cP
Shale Oil	--	57	0.9171	15.7
KO1 Oil	670	57	0.8833	5.1
KO2 Oil	735	--	0.9121	19.5
KO3 Oil	905	--	0.9570	72.9
Heavy Oil Return	--	--	0.9610	116.8

Table 11. 6-Inch BSU Test Daily KO1 Product Oil Physical Properties

	Specific Gravity	Viscosity, cP
Day 1	0.8843	3.9
Day 2	0.8912	6.3
Day 3	0.9012	5.5
Day 4	0.8754	5.0
Day 4.3	0.8665	4.0
Day 4.5	0.8823	5.8
Day 4.7	0.8843	5.6

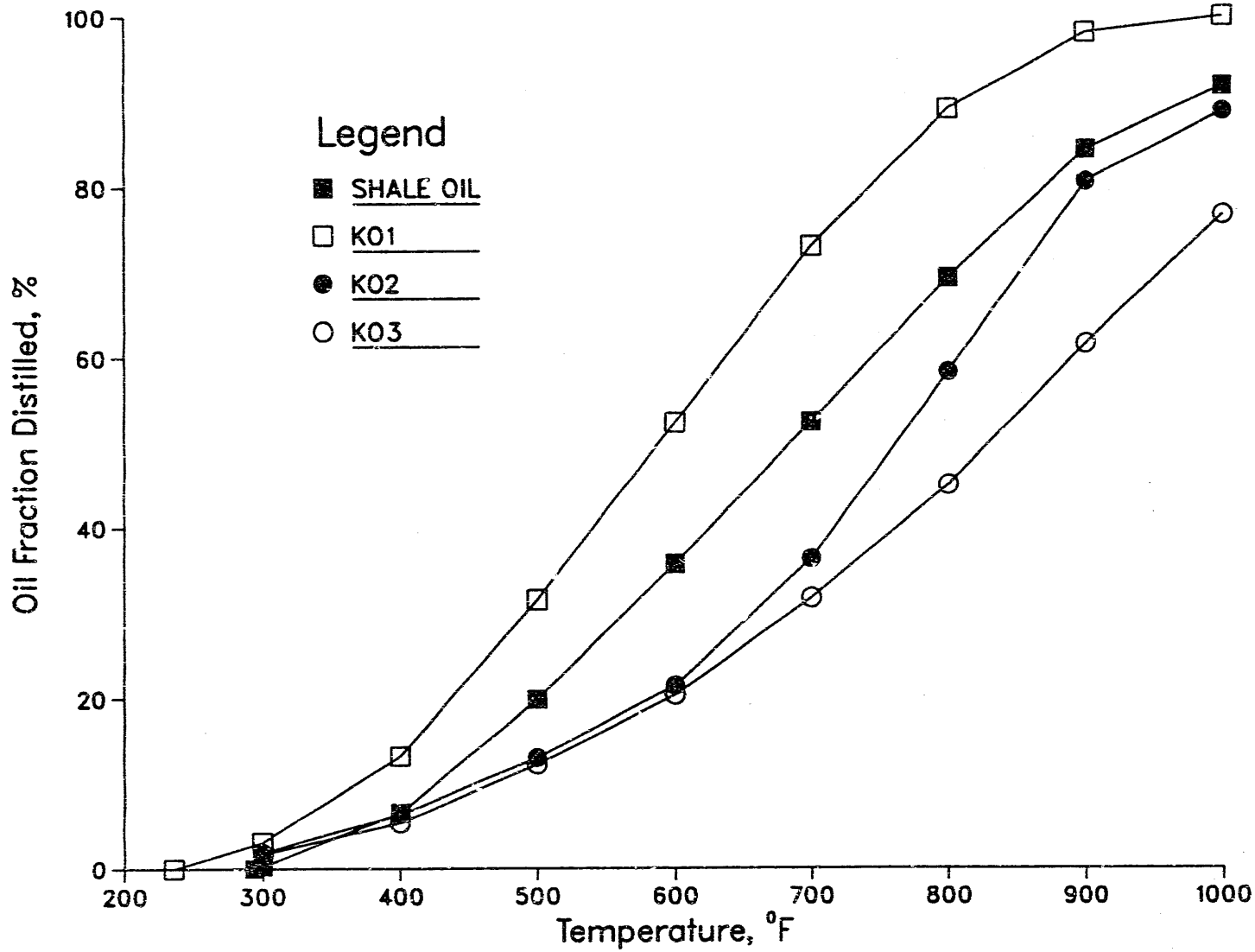

Figure 9. 6-Inch BSU Test Product Oil Simulated Distillation Comparison

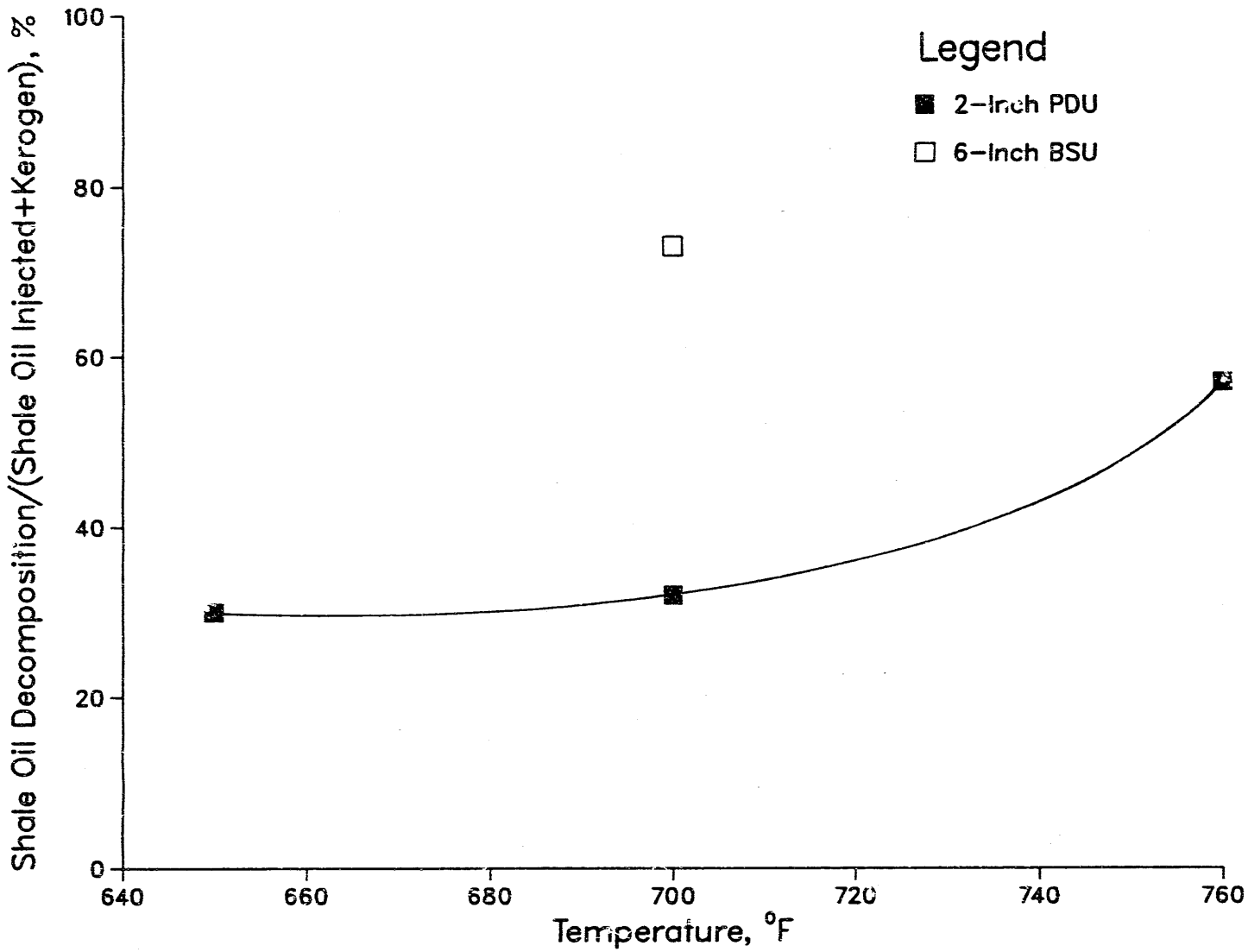

Figure 10. Shale Oil Decomposition

The decomposition rate curve generated from the PDU test data is typical of the heavy oil decomposition rates from a multiple-pass, heavy-oil recycle system. The BSU decomposition rate is typical of a commercial system that was co-processing oil shale fines with a single-pass shale oil.

CONCLUSIONS

Results from tests conducted in a 2-inch process development unit (PDU) and a 6-inch bench-scale unit (BSU) with western oil shale demonstrated a maximum oil yield at temperatures between 700 and 750°F (371 and 399°C).

Test results suggest that the ROPE© process has a strong potential for recovering oil from oil shale fines, upgrading shale oil, and separating high-nitrogen-content oil for use as an asphalt additive.

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DISCLAIMER

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

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