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ANALYTICAL PYROLYSIS EVALUATION OF THE RETORTING POTENTIAL OF
KENTUCKY OIL SHALE

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INTRODUCTION

The utilization of oil shale as a source of synthetic fuels has been increasingly promoted in recent years. While oil shales in the western United States have been extensively studied for many years, eastern shales have received serious consideration only recently.

The value of a shale resource is determined by a variety of factors. The mining and reclamation aspects of the resource, processing requirements, the product composition and the overall economics are some of the more significant variables. However, the overall resource quality, which is represented by its magnitude, accessibility and oil content, is perhaps the most important.

The standard measure of oil shale quality (oil yield potential) has been the Fischer Assay. In its various experimental forms, this assay results from the physical measurement of the amount of oil produced from the retorting of a shale sample under a standardized set of conditions. This assay and modified forms of it have, for the most part, been the accepted and standard basis for judging the retorting potential of shales worldwide.

The true utility of a standard assay is, however, its predictive ability. Fischer Assays have been shown to be an acceptable measure of the conventional retort potential of western U. S. shales. This, however, has not been shown to be true for eastern oil shales. The overwhelming acceptance of the Fischer Assay yield has, in large part, been responsible for underestimating the value of and, therefore overlooking, eastern oil shale as a synfuel resource. The current interest in eastern shale is due in part to the realization of its retorting characteristics and true oil generation potential.

Work at the Institute for Mining and Minerals Research (IMMR) (1, 2) and others (3, 4) have shown that the Fischer Assay of eastern oil shales typical of Kentucky are low with respect to the shale's true retorting potential. Retorting eastern oil shales under rapid heating, vacuum, steam addition, fluid bed, hydrogen atmosphere and donor solvent conditions (2, 5-8) have consistently produced yields in excess of Fischer Assay values. Assay yields have been exceeded by as much as 25-100% when eastern oil shales have been retorted under these conditions. A more complete discussion of eastern oil shale and their retorting characteristics can be found in the literature (9-12).

On an analytical scale, pyrolysis techniques have been used widely in many organic-analytical applications. Geochemical applications have included the evaluation of source rock potential and oil shale organic geochemistry (13-16). These techniques provide the opportunity to: pyrolyze materials under highly controlled thermal conditions, determine the material's response to pyrolysis and characterize the products of the pyrolysis.

Eastern shale oil yields are sensitive to retorting parameters and, in particular, to thermal conditions (1). The ability to carefully control thermal conditions in analytical pyrolysis experiments suggested that these techniques may be useful in evaluating shale retorting behavior. Preliminary evaluation of eastern oil shales by pyrolysis/gas chromatography analysis has examined the yield and product composition trends related to pyrolysis conditions (17, 18).

The work presented here represents an examination of an analytical pyrolysis technique as a method for determining oil shale retorting potential. A carefully selected and prepared set of oil shale samples was evaluated by three methods: Fischer Assay, bench scale fluid bed retorting and the analytical pyrolysis method described below.

EXPERIMENTAL METHODS

Oil Shale Samples

Samples of Sunbury, Cleveland and Huron shales obtained from a ninety foot oil shale core

were used for comparison of the pyrolysis and Fischer Assay yield determinations. A 1.5 inch diameter core (identified as "T-16") was drilled in Madison County, Kentucky and has been thoroughly characterized (19). Since only limited amounts of core material were available, additional samples from the Cleveland Member of the Ohio Shale and the New Albany Shale were selected for a further comparison of the pyrolysis measurement with Fischer Assay and fluid bed yields. Bulk samples of the Ohio Shale were obtained from Fleming County, Kentucky; samples of the New Albany Shale from Henryville, Indiana.

Shales were crushed, blended, sieved and split to produce representative and homogeneous aliquots for each of these analyses. Samples were prepared in 8 x 30, 18 x 20 and -325 mesh sizes for the Fischer Assay, fluid bed and pyrolysis methods, respectively. These samples were stored under an argon atmosphere until used.

Fischer Assay Analysis

The modified Fischer Assay procedure used at the IMMR has been described previously (1). These assays were performed on 100 gm aliquots in the stainless steel retort illustrated in Figure 1. A Lindberg electric furnace equipped with a programmable temperature controller was used to heat the retort under the following conditions: heated to 150°C for 30 minutes, increased from 150 to 550°C at a rate of 13±1°C/minute and held at 500°C for 20 minutes.

Oil yields were determined from the weight change of the entire liquid collection apparatus less the weight of water also collected (1). The density of each oil sample was determined on a Mettler DMA 40 density meter and was used to express oil weight on a gallons per ton (gal/t) oil yield basis.

Fluid Bed Retorting

A bench scale fluid bed retort, developed at the IMMR, used in this study is shown in Figure 2. Operating conditions for this unit were: a bed temperature of 550°C, helium gas at a linear fluidizing velocity of 25.6 m/min, a shale residence time of 20 min and a calculated theoretical heating rate of approximately 20,300°C/min. A detailed description of the operation and product trapping system used in this apparatus is given by Rubel et al. (20).

Analytical Pyrolysis

Oil shales were subjected to pyrolysis using a Chemical Data systems Model 820GS pyrolysis system. The instrument was operated in its "rapid P1/P2" mode and can be viewed as having essentially the instrumental configuration illustrated in Figure 3. In this mode of operation, the sample is heated to pyrolysis temperature under an inert atmosphere while the pyrolysate evolution is continuously monitored by a flame ionization detector (FID). The FID signal is recorded continuously and integrated by a Hewlett-Packard Model 3390A reporting integrator.

Small samples (3-5 mg) of -325 mesh shale are weighed into quartz capillaries (4 x 15 mm) and held in place with small quartz wool plugs. The sample is inserted into the pyrolysis chamber and is flushed for three minutes with helium. The sample is rapidly heated, under a 50 cc/minute helium flow, from ambient temperature (50-60°C) to 300°C, held at this temperature for nine minutes, heated at 60°C/minute to 600°C and held at this final temperature for fifteen minutes. The pyrolysis temperature program and the corresponding FID response are illustrated in Figure 4.

The FID is predominately sensitive to organic carbon containing compounds. The monitor's response, therefore, represents organic carbon pyrolysate and does not include significant contributions from water, carbon dioxide, hydrogen sulfide or other inorganic species. The material evolved up to 300°C represents the distillable (P1) fraction of the shale's organic content. The pyrolysis product (P2) is derived from the kerogen fraction of the shale. The total FID response (P1 + P2) per milligram of shale relative to that of a standard oil shale is the basis for correlating pyrolysis data to Fischer Assay.

RESULTS AND DISCUSSION

Shale Analyses

A complete discussion of the retorting and analytical characteristics of the T-16 core samples is beyond the scope of this work. These samples have been thoroughly examined and these results have been reported (19). Core data useful to the following discussion has been summarized in Table I along with data for the group of bulk samples.

Carbon and hydrogen analyses were determined using a Carlo-Erba Model 1106 elemental analyzer according to standard ASTM procedure D3178. Inorganic carbon was determined by measurement of acid-evolved carbon dioxide and was used to calculate organic carbon from total carbon.

TABLE I
SUMMARY OF CHARACTERISTICS FOR OIL SHALES

<u>Sample</u>	<u>Shale Designation</u>	<u>Depth Interval (ft.)</u>	<u>Organic Carbon (%)</u>	<u>Hydrogen/Carbon</u>
T-16 001	Sunbury	4-6.7	13.34	1.17
T-16 003	Cleveland	7-10	10.96	1.31
T-16 004	Cleveland	10-12	14.62	1.21
T-16 005	Cleveland	12-14	11.60	1.21
T-16 006	Cleveland	14-16	16.57	1.21
T-16 007	Cleveland	16-18	15.67	1.21
T-16 008	Cleveland	18-20	10.75	1.26
T-16 009	Cleveland	20-22	11.81	1.21
T-16 010	Cleveland	22-24	11.85	1.25
T-16 011	Cleveland	24-26	10.67	1.27
T-16 014	Cleveland	30-32.4	8.65	1.35
T-16 017	Huron	35.8-38	7.78	1.31
T-16 018	Huron	38-40	8.31	1.31
T-16 019	Huron	40.5-44	7.43	1.31
T-16 020	Huron	44-48	7.51	1.42
T-16 021	Huron	48-52	7.74	1.41
T-16 022	Huron	52-56	7.98	1.38
T-16 023	Huron	56-60	8.51	1.35
T-16 025	Huron	64-67	8.64	1.33
NALB-1	New Albany	-	13.31	1.28
NALB-2	New Albany	-	12.79	1.33
CLE 982C	Cleveland	-	11.65	1.41
CLE 82C	Cleveland	-	11.13	1.49

Yield Determinations

Fischer Assays were performed on the shales described above with mass and carbon balances in the 99-100% range. Oil yields were measured in weight percent and converted to gallons per ton using the individually determined oil densities. Oil yields, for the T-16 core samples, based on this classical method, varied from 7.1 to 19.0 gal/t. For Kentucky shales examined at the IMMR, Fischer Assay values parallel shale organic carbon content and yield about 1.1 gal/t for each weight percent organic carbon. The organic carbon versus Fischer Assay correlation (r) equalled 0.96 for the T-16 core samples. The data describing the Fischer Assay analyses are summarized in Table II.

Under fluid bed retorting conditions, oil yields from the bulk shale samples varied from 7.1 to 8.1% of the raw shale. Mass and carbon balances of 98 to 100% were obtained. These yields reflect a 130 to 145% enhancement of the values determined by Fischer Assay. This is presented in Table III.

Analytical Pyrolysis

Shale samples from the T-16 core were pyrolyzed as described earlier, and a value representing the FID response per milligram of shale was determined. This measurement reflects the amount of hydrocarbons evolved but is not used directly as an indication of yield. Because of potential day to day variations in the FID response, this value (response per mg) is normalized to that of a standard. The standard in this case was a shale sample with a known Fischer Assay value and permitted day to day comparison of our pyrolysis data and facilitated the conversion of response per milligram data to a gallons per ton basis. The data from other oil shales examined here were treated similarly. Table IV contains a summary of the normalized pyrolysis response data.

Data Correlations

Very good correlations were found between the normalized pyrolysis response values and the results from Fischer Assay. For T-16 core samples, the correlation (r) between the analytical pyrolysis and Fischer Assay data was 0.966. A similar relationship was found for the bulk shales examined. The T-16 core pyrolysis correlations with Fischer Assay and organic carbon are illustrated in Figure 5.

The fluid bed versus pyrolysis yield correlations for the bulk samples were also very good ($r=0.962$). Due to the nature of the fluid bed experiment and the method of oil collection, yield data were only available on a weight percent basis. The results summarizing the Fischer Assay,

fluid bed and pyrolysis evaluation of these samples are presented in Figure 6.

TABLE II
SUMMARY OF RESULTS FROM THE FISCHER ASSAY EVALUATION OF
T-16 CORE OIL SHALE SAMPLES

T-16 Sample	Fischer Assay (gal/t)	Fischer Assay (Wt %)	Oil Density
001	13.9	5.40	.932
003	13.2	5.01	.910
004	18.3	6.97	.913
005	13.9	5.23	.902
006	19.0	7.20	.908
007	17.6	6.68	.910
008	13.0	4.99	.920
009	13.7	5.19	.909
010	12.1	4.62	.914
011	12.9	4.92	.914
014	9.4	3.62	.924
017	9.3	3.44	.887
018	7.8	-	-
019	8.0	3.02	.906
020	7.8	2.96	.910
021	7.3	2.75	.902
022	9.6	3.63	.906
023	10.0	3.79	.909
025	9.3	3.51	.904

TABLE III
SUMMARY OF BULK SHALE RETORTING RESULTS FROM
FLUID BED AND FISCHER ASSAY EXPERIMENTS

Sample	Fischer Assay (Wt %)	Fluid Bed (Wt %)
NALB-1	6.1	8.1
NALB-2	5.9	7.8
CLE 982C	5.2	7.1
CLE 82C	4.7	6.7

The correlation of T-16 pyrolysis data with organic carbon (Figure 5b) is notably better than the correlation with Fischer Assay values (Figure 5a). Although the correlations for both sets of data are very good, the scatter in the pyrolysis versus organic carbon data appears smaller. In part, this reflects the smaller error associated with the determination of organic carbon as opposed to the greater experimental error associated with Fischer Assay determinations. The retorting assay methods have several contributing sources of error related to the control of thermal conditions, product trapping efficiency, product isolation, manipulative losses and density measurement among others. The pyrolysis approach has superior control over thermal parameters and no losses related to product handling. Potential problems related to reproducible FID response, standardization, weighing and sampling small samples and the preparation of representative samples exist. There are also several fundamental differences between retorting and analytical pyrolysis methods.

The measurement of yield by retorting assay methods are essentially volumetric determinations (gallons per ton) and reflect both the mass of organic matter produced and its density. The response of the FID in the pyrolysis experiment only reflects the mass of the organic matter evolved and, therefore, its yield is independent of product density. This difference between methods can be minimized by correlating oil yield data on a wt % rather than a gal/t basis. The uniformity in the oil densities for the T-16 products suggests similar pyrolysis correlation by either approach. The wt % based correlation between these methods for the T-16 core samples plotted in Figure 7 is virtually indistinguishable from the gal/t basis.

While retorting assay methods quantify yields on the basis of recovered liquid products, the FID based pyrolysis technique reflects the production of both gaseous and liquid hydrocarbons

without distinction. In the evaluation of the T-16 core shales, the amount of organic carbon evolved in the form of gases was fairly constant in the 1 to 2% range. This relatively small and constant amount of gaseous hydrocarbon contributes to the pyrolysis versus Fischer Assay correlation. The noncondensable hydrocarbon fraction is generally overlooked by retort assay methods and, in this regard, the FID response gives a more accurate measurement of the total hydrocarbon product evolved.

TABLE IV
SUMMARY OF NORMALIZED PYROLYSIS RESPONSE DATA FOR THE
T-16 CORE AND BULK OIL SHALE SAMPLES

Sample	Pyrolysis ^a Response	No. of Samples	Relative % Deviation
T-16 001 ^b	1.00	-	-
T-16 003	0.92 ± 0.02	5	2.2
T-16 004	1.17 ± 0.07	8	6.0
T-16 005	0.96 ± 0.04	7	4.2
T-16 006	1.33 ± 0.05	2	3.8
T-16 007	1.21 ± 0.04	5	3.3
T-16 008	0.93 ± 0.02	3	2.1
T-16 009	1.07 ± 0.04	2	3.7
T-16 010	1.00 ± 0.05	4	5.0
T-16 011	0.99 ± 0.05	4	5.1
T-16 014	0.77 ± 0.03	5	3.9
T-16 017	0.75 ± 0.02	3	2.7
T-16 018	0.73 ± 0.00	2	-
T-16 019	0.64 ± 0.05	3	7.8
T-16 020	0.71 ± 0.04	2	5.6
T-16 021	0.74 ± 0.04	4	5.4
T-16 022	0.72	1	-
T-16 023	0.83 ± 0.01	2	1.2
T-16 025	0.78 ± 0.05	8	6.4
NALB-1	1.13 ± 0.04	3	-
NALB-2	1.07 ± 0.01	3	-
CLE 982C	0.96 ± 0.05	3	-
CLE 82C	0.96 ± 0.01	3	-

a. Mean ± standard deviation.

b. Sample used as pyrolysis reference standard.

The work described above has been a part of an overall Kentucky oil shale resource characterization effort. The T-16 core has been extensively examined and the pyrolysis results closely parallel a variety of characterization parameters in addition to Fischer Assay values. A more complete discussion of the T-16 core trends appears elsewhere in the literature (19). The T-16 core samples represent a wide range of compositions with varied geologic ages, depth of burial, organic content and depositional history. For purposes of evaluating down core trends, the pyrolysis results compare very favorably to other measurements.

SUMMARY

It is evident from the data presented above that an analytical pyrolysis based assay is an acceptable alternative to more traditional methods. This approach was also shown to be predictive of the yield of several different shales under fluid bed retorting conditions. Further, there are several distinct advantages that the pyrolysis method offers. These principally relate to sample size requirements, speed of analysis and ancillary analytical capabilities.

Classical assay methods require large amounts of sample in comparison to an analytical pyrolysis technique. The Fischer Assay determinations described above used approximately 100 g and fluid bed evaluations normally consume more. While sample availability is not usually a factor in bulk sample analyses, it is a major limitation in evaluating drilled core. To measure Fischer Assay yields on a typical 1.5-inch diameter core, one-half of the core is consumed and material covering 2-foot intervals combined. The milligram scale pyrolysis sample requirement can preserve most of the core and provide more detailed yield and resource information as a result of the

substantially smaller sampling interval used. It is in the core analysis and resource characterization context that analytical pyrolysis may be of greatest use.

The pyrolytic analyses described here can be performed at a rate of nearly two per hour. Fischer Assays and fluid bed evaluations, however, require as much as two hours in retorting time alone.

The pyrolysis experiment described here represents only one aspect of the capabilities of this technique. The ability to carefully control the pyrolysis conditions (e.g., temperature limits, rates and residence times) should permit the evaluation of the relationship between yield and thermal treatment. The products from the above analytical pyrolysis were not examined but the capability to perform capillary gas chromatography is an additional feature of the Chemical Data Systems' 820 GS instrumentation. The integration of the pyrolysis yield, thermal treatment and product analysis capabilities are currently under evaluation in an effort to determine relationships between retorting conditions, product yield and product composition.

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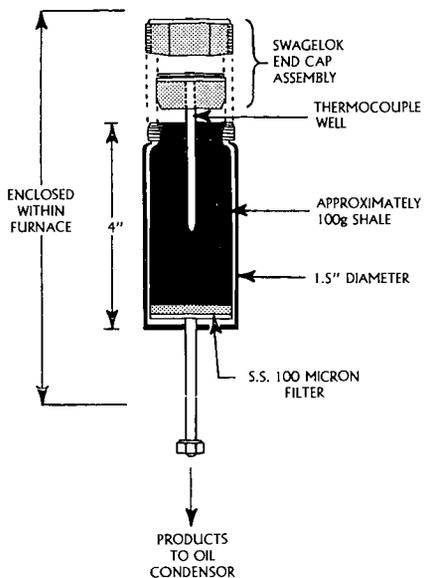


Figure 1. The modified Fischer Assay retort used to determine oil yields.

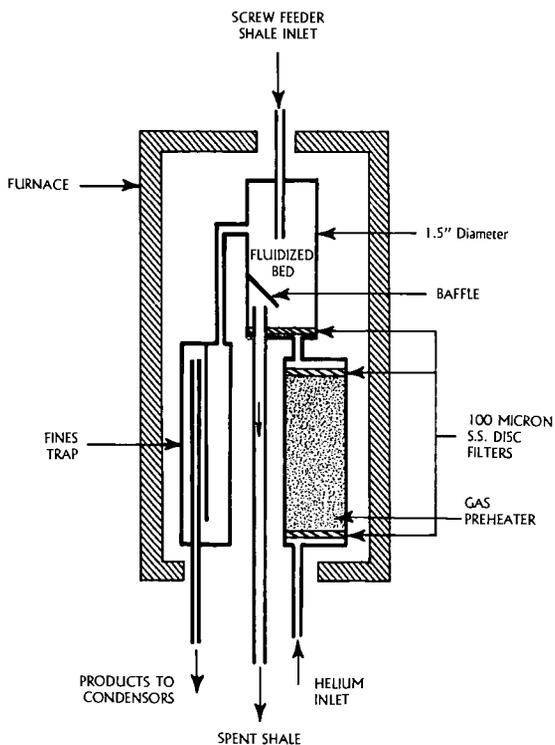


Figure 2. The fluid bed retort system developed at the IMHR for evaluating oil shale retorting under rapid heating and short product residence time conditions.

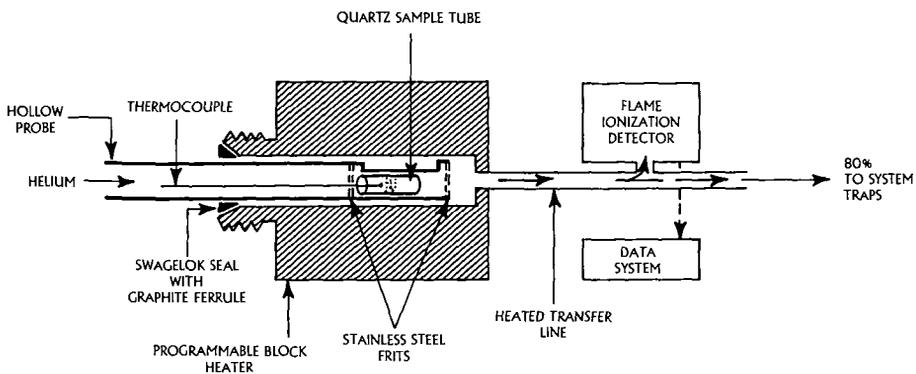


Figure 3. Simplified schematic of the Chemical Data Systems 820 GS pyrolysis system in its "rapid P1/P2" mode of operation.

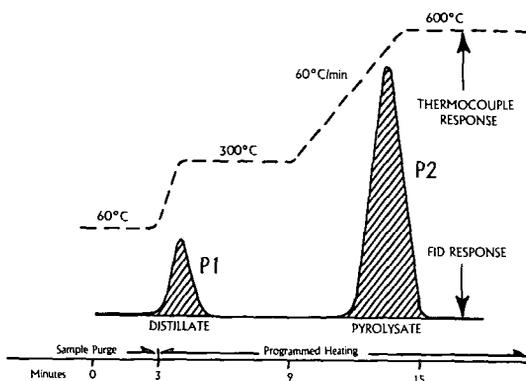


Figure 4. Illustration of the pyrolysis temperature program and the corresponding FID response reflecting pyrolysate evolution.

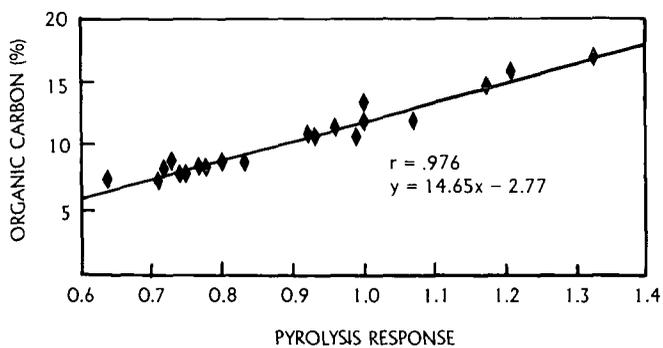
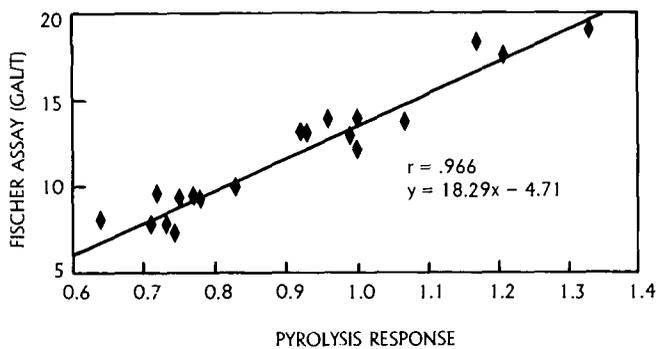


Figure 5. Normalized pyrolysis response data for T-16 core shales; correlations to: (a) Fischer Assay values and (b) organic-carbon content.

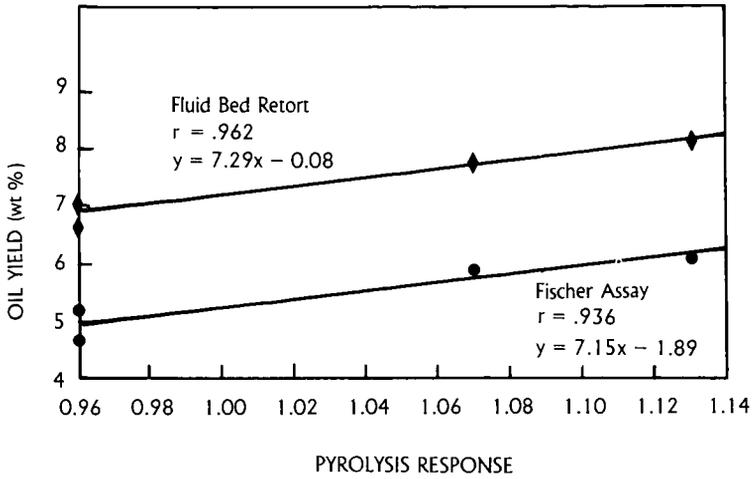


Figure 6. Correlation of normalized pyrolysis response with Fischer Assay and fluid bed yield data for a group of different bulk shales.

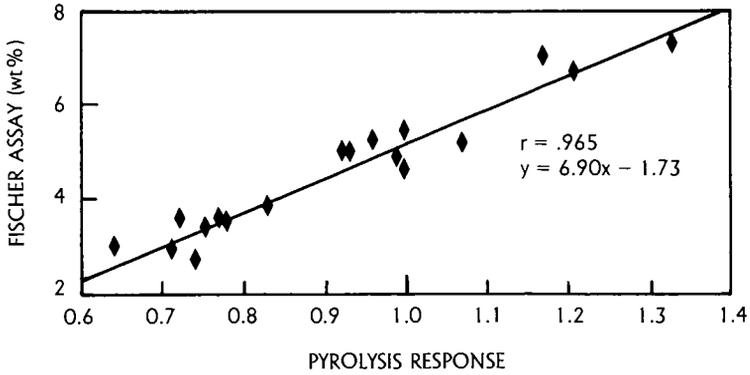


Figure 7. Normalized pyrolysis response data vs. Fischer Assay on a weight percent basis for T-16 core shales.

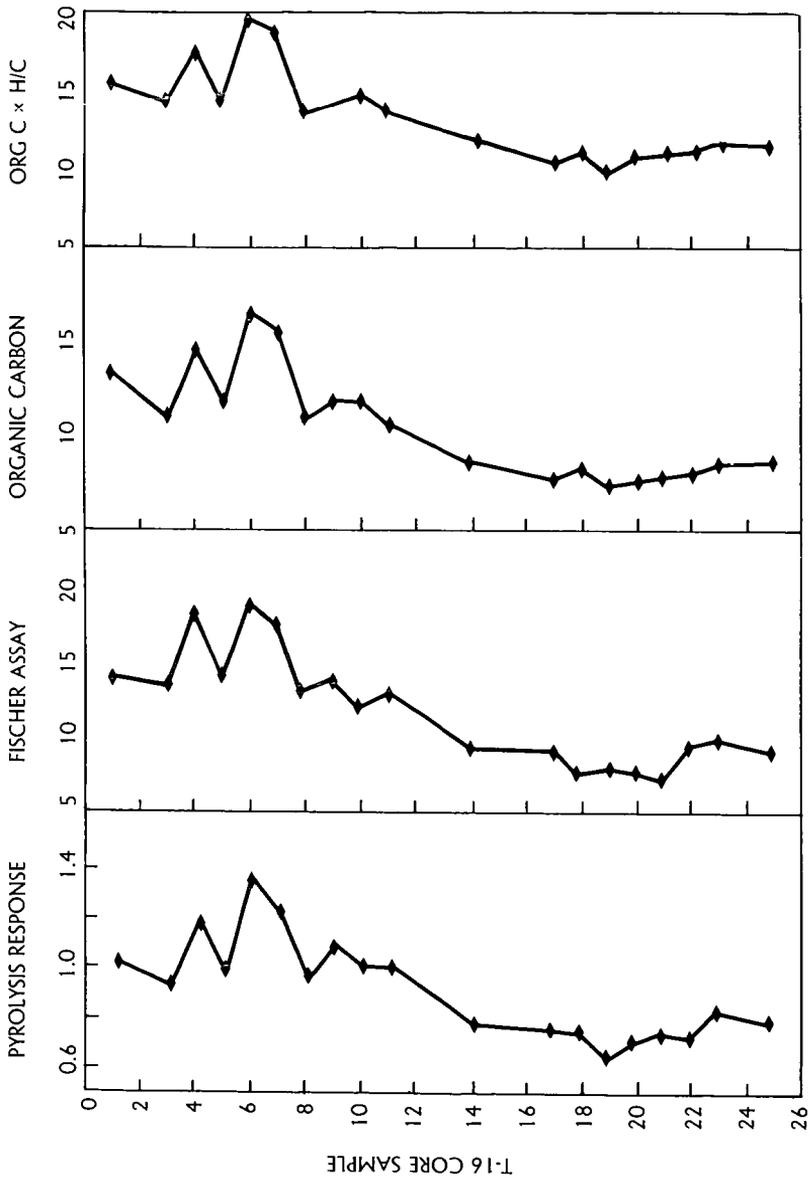


Figure 8. Comparison of pyrolysis, Fischer Assay, and organic carbon down core trends for T-16 shales.

LITERATURE CITED

- (1) Coburn, T. T., Rubel, A. M. and Henson, T. T., "Eastern Oil Shale Retorting I. Pyrolysis of the Sunbury Shale of Kentucky", University of Kentucky Inst. for Mining and Minerals Research, Report No. IMMR81/062 (1981).
- (2) Rubel, A. M. and Coburn, T. T., In: 1981 Eastern Oil Shale Symp. Proceedings, p. 21, Univ. of Kentucky Insti. for Mining and Minerals Research, Report No. IMMR82/066 (1982).
- (3) Richardson, J. H., Huss, E. B., Ott, L. L., Clarkson, J. E., Bishop, M. O., Taylor, J. R., Gregory, L. J. and Morris, C. J., UCID-19548, Lawrence Livermore Natl. Lab. (1982).
- (4) Burnham, A. K., Richardson, J. H. and Coburn, T. T., UCID-87587, Lawrence Livermore Natl. Lab. (1982).
- (5) Margolis, M. J., In: 1981 Eastern Oil Shale Symp., p. 151, Univ. of Kentucky Insti. for Mining and Minerals Research, Report No. IMMR82/066 (1982).
- (6) Margolis, M. J., Hagan, M., Cummins, W. and Toney, D., "Donor Solvent Extraction Behavior of Eastern Kentucky Oil Shale", Submitted to Fuel Processing Technology.
- (7) McKay, J. F. and Chong, S. L., In: Symp. Papers, Synthetic Fuels from Oil Shale and Tar Sands, p. 389, Insti. of Gas Technology, May 17-19 (1983).
- (8) Feldkirchner, H. L. and Janka, J. C., In: Symp. Papers, Synthetic Fuels from Oil Shale, Insti. for Gas Technology, December (1979).
- (9) "Synthetic Fuels from Oil Shale II, Symp. Papers", Nashville, TN, Insti. of Gas Technology, October 26-29 (1981).
- (10) "1981 Eastern Oil Shale Symp. Proceedings", Lexington, KY, Univ. of Kentucky Insti. for Mining and Minerals Research, November 15-17 (1981).
- (11) "1982 Eastern Oil Shale Symp. Proceedings", Lexington, KY, Univ. of Kentucky Insti. for Mining and Minerals Research, October 11-13 (1982).
- (12) "Synthetic Fuels from Oil Shale and Tar Sands Symp. Papers", Louisville, KY, Insti. of Gas Technology, May 17-19 (1983).
- (13) Espitalie, J., Laporte, J. L., Madec, M., Marquis, F., Leplat, P., Paulet, J. and Boutefeu, A., Rev. Inst. Fr. Pet. 32, 23-42 (1977).
- (14) Larter, S. R., J. Anal. Appl. Pyrolysis 4, 1-19 (1982).
- (15) Aizenshtat, Z., Israel J. Chem. 22, 266-272 (1982).
- (16) Leventhal, J. S., Chem. Geol. 18, 5-20 (1976).
- (17) Reasoner, J. W., Sturgeon, L., Naples, K. and Margolis, M. J., In: 1981 Eastern Oil Shale Symp. Proceedings, p. 11, Univ. of Kentucky Insti. for Mining and Minerals Research, Report No. IMMR82/066 (1982).
- (18) Reasoner, J. W., Naples, K. V. and Margolis, M. J., In: 1982 Eastern Oil Shale Symp. Proceedings, Univ. of Kentucky Insti. for Mining and Minerals Research, Report in press.
- (19) Rubel, A. M., Koppelaar, D. W., Taulbee, D. N. and Robl, T. L., In: 16th Oil Shale Symp. Proceedings, p. 132, Colorado School of Mines (1983).
- (20) Rubel, A. M., Margolis, M. J., Haley, J. K. and Davis, B. H., In: 1983 Eastern Oil Shale Symp. Proceedings, Univ. of Kentucky Insti. for Mining and Minerals Research (in press).