AIM

Association for Information and Image Management

1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202

Centimeter

Inches

MANUFACTURED TO AIM STANDARDS
BY APPLIED IMAGE, INC.

1 of 1

**The Development of An Integrated Multistage
Fluid Bed Retorting Process**

**Quarterly Report
January - March 1994**

**S. Carter
J. Stehn
A. Vego
U. Graham**

July 1994

Work Performed Under Cooperative Agreement No.: DE-FC21-90MC27286

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

**By
University of Kentucky
Center for Applied Energy Research
Lexington, Kentucky**

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, 175 Oak Ridge Turnpike, Oak Ridge, TN 37831; prices available at (615) 576-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650.

**The Development of An Integrated Multistage
Fluid Bed Retorting Process**

**Quarterly Report
January - March 1994**

**S. Carter
J. Stehn
A. Vego
U. Graham**

Work Performed Under Cooperative Agreement No.: DE-FC21-90MC27286

**For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880**

**By
University of Kentucky
Center for Applied Energy Research
3572 Iron Works Pike
Lexington, Kentucky 40511**

July 1994

ABSTRACT

This report summarizes the progress made on the development of an integrated multistage fluidized bed retorting process (KENTORT II) during the period of January 1, 1994 through March 31, 1994 under Cooperative Agreement No. DE-FC21-90MC27286 with the Morgantown Energy Technology Center, U.S. Department of Energy. The KENTORT II process includes integral fluidized bed zones for pyrolysis, gasification, and combustion of the oil shale. The purpose of this program is to design and test the KENTORT II process at the 50-lb/hr scale. Modifications to the system were completed that improved the start-up burner system and reduced thermal losses. Final shakedown tests were performed that demonstrated gasification zone and combustion zone temperatures of 800 and 900°C, respectively, at a raw shale feed rate of 50 lb/hr. Ash agglomeration and slagging was encountered during some of these tests, and these materials were analyzed by scanning electron microscopy and energy dispersive X-ray analysis. By limiting the combustion plenum chamber to 1100°C during heat up and by maintaining sufficient solid recycle to the combustor, it is believed that ash agglomeration difficulties will be eliminated.

ACKNOWLEDGMENTS

The work described herein was performed at the University of Kentucky Center for Applied Energy Research under Cooperative Agreement DE-FC21-90MC27286 with the Laramie Project Office of the Morgantown Energy Technology Center (METC), U.S. Department of Energy.

TABLE OF CONTENTS

LIST OF TABLES	v
LIST OF FIGURES	v
INTRODUCTION AND BACKGROUND	1
OBJECTIVES	2
SYSTEM MODIFICATIONS	3
Burner/Plenum Configuration	3
Distributor Plates	3
Gasifier Standpipe	3
Steam Generator	3
SYSTEM OPERATION	6
KT940222	6
KT940308	6
KT940310	7
KT940317	7
KT940329	8
ASH AGGLOMERATION AND FUSION	9
REFERENCES	14

LIST OF TABLES

Table 1.	Average temperatures (and standard deviation) recorded during the periods of raw shale input to the pyrolysis zone for runs: KT940222 and KT940317.	6
Table 2.	Ash fusion analysis (ASTM D-1857) of the master oil shale sample.	7

LIST OF FIGURES

Figure 1.	Flow diagram of the 50-lb/hr KENTORT II process demonstration unit. . . .	4
Figure 2.	Top and side views of (a) the original plenum chamber and top view of (b) the modified plenum chamber without the elbow fitting.	5
Figure 3.	SEM photograph of shale agglomerate at x70 magnification illustrating a glassy phase engulfing shale particles.	10
Figure 4.	Enlarged view of the sample shown in Figure 3 at x900 magnification illustrating the fibrous nature of the glassy melt.	10
Figure 5.	a) SEM photograph of the mineral clusters between the glassy phases of the agglomerated shale at x5000 magnification; b) EDX analyses of the mineral clusters.	11
Figure 6.	a) SEM photograph of red deposits at x450 magnification; b) EDX analysis of the red deposits.	13

INTRODUCTION AND BACKGROUND

It is now well accepted that fluidized bed pyrolysis of oil shale at near-zero hydrogen partial pressure will generate higher than Fischer assay oil yields. This enhancement varies according to shale type, but for most shales, it can be significant. It has been shown that fluidized bed pyrolysis of eastern and western U.S. oil shales can enhance oil yields by 50%^{1,2,3,4,5} and 10%^{6,7} above Fischer assay, respectively. In addition, fluidized bed technology offers the advantages of rapid pyrolysis kinetics (short solid residence time), total use of mined shale, and thermal efficiency. The Center for Applied Energy Research (CAER) has developed a commercial retorting concept, KENTORT II, which is based on fluidized bed technology. This process has been successfully demonstrated in a 3-inch diameter, 5-lb/hr system at the CAER using eastern U.S. oil shale.⁸ The objective of the current program is to scale the KENTORT II process to a 6-inch diameter, 50-lb/hr reactor.

Approximately 40% of the original carbon remains in the spent shale following fluidized bed pyrolysis of Eastern shale. This is more carbon than is required to provide process heat, and an intermediate gasification stage was included in the KENTORT II design to utilize this excess carbon for synthesis gas production. The gasification section is also important because it permits steam/iron sulfide reactions to go nearly to completion. These reactions remove the majority of the sulfur from the shale in the case of eastern shale because approximately 90% of its sulfur is present as iron sulfides. The removal of sulfur from the shale as H_2S prior to combustion creates a relatively concentrated stream of H_2S which is easier to scrub than a dilute stream of SO_2 from combustion. The H_2S serves as feedstock for elemental sulfur production which improves process economics because of the by-product credit. For shales which do not contain large amounts of residual carbon and/or iron sulfides following pyrolysis, the gasification step provides few benefits and can make the system more complicated than necessary.

Following gasification, the remaining carbon in the shale is combusted to provide process heat. The heat of combustion is transferred to the gasification and pyrolysis zones via recirculation of the processed shale because sufficient heat cannot be transferred using gases alone. Following combustion, essentially all of the carbon and sulfur in the shale have been removed. This has important environmental implications because the potential for acid drainage by the disposed spent shale is significantly reduced when the sulfur content is low.^{9,10}

Operation of the KENTORT II process was shown to be viable at the 5-lb/hr scale during the previous cooperative agreement, but serious questions relative to scale-up remain. One of the most critical issues are the effects that scale-up will have on the extent of solid-recycle induced cracking and coking losses in the pyrolysis zone. The scaled-up retort will also provide the opportunity to conduct tests on larger quantities of oil products. Investigation of the production of new materials from the shale oil which will have higher value at lower cost than transportation fuels is a main focus of the program.

OBJECTIVES

The primary objective of this program is to perform the research necessary to design, construct, test, and optimize the KENTORT II process at the 50-lb/hr scale. The tasks for the program are listed below.

Task 1 - Design and Construction of the KENTORT II Prototype Unit

- 1.1 - Cold-Flow Modeling of the Reactor
- 1.2 - Mini-Plant Investigation of Solids Recycle (Cracking and Coking Kinetics)
- 1.3 - Final Design and Construction of the KENTORT II Prototype Unit

Task 2 - Operation of the Prototype Unit

- 2.1 - Reactor and System Shakedown
- 2.2 - Prototype Operational Runs

Task 3 - Shale Acquisition and Product/By-Product Characterization

- 3.1 - Collection and Characterization of the Oil Shale Feedstock
- 3.2 - Characterization of the KENTORT II Materials and Products for Utilization and Environmental Characteristics
 - 3.2.1- Characterization of KENTORT II Products for Asphalt Application
 - 3.2.2- Characterization of Nitrogen and Mineralogic Transformations in the KENTORT II Process
- 3.3 - Economic Evaluations

SYSTEM MODIFICATIONS

As described in the technical progress report for the previous quarter,¹¹ several parts of the 50-lb/hr KENTORT II process demonstration unit (PDU) (see Figure 1) required modification to ensure efficient operation. These modifications were completed midway through the current quarter and final testing of the system was completed. Plans for these revisions were described in the previous quarterly report, but for completeness, the implemented modifications will be described in the following sections.

Burner/Plenum Configuration. The failure of the elbow-joint fitting between the propane-gas burner and the combustor plenum was the most serious problem to be addressed. In the original configuration (Figure 2a), the hot gases from the burner impinged directly onto the elbow joint, causing it to overheat and eventually rupture. The elbow fitting and the distance of the burner from the plenum also caused significant heat loss. To resolve both problems, the burner was mounted horizontally so that a short, straight length of pipe could direct the hot gases to the plenum (Figure 2b). To prevent the same sort of heat-related failure that the elbow fitting experienced, the entire surface of the plenum was aluminized and then the inside surfaces were lined with a 0.5-inch thick layer of castable ceramic (SiO_2). The ceramic layer serves to protect the metal and to reduce heat losses from the plenum. In addition, a ceramic-sheathed R-type thermocouple was installed in the plenum chamber to more efficiently control the operation of the burner and the fluidized bed combustor.

Distributor Plates. To prevent passage of particles through the holes of the combustion and cooling zone distributor plates, new distributors with smaller holes (0.0625 inch diameter) were fabricated and aluminized. The new distributors have the same open area as the original ones.

Gasifier Standpipe. To double the height of the gasifier bed, a 30-inch long pipe was aluminized and was placed over the existing 15-inch pipe.

Steam Generator. To enhance the steam production rate of the steam generator a feed-water tank and an inlet pump were installed so that the operating pressure could be raised above 100 psig. This arrangement also permits the recycle of condensed steam in the system.

Figure 1. Flow diagram of the 50-lb/hr KENTORT II process demonstration unit.

a) Original Burner/Combustor Plenum Configuration

b) Modified Configuration

top view

Figure 2. Top and side views of (a) the original plenum chamber and top view of (b) the modified plenum chamber without the elbow fitting.

SYSTEM OPERATION

Following the completion of the system modifications midway through the quarter, a final series of shakedown runs was performed. All the runs utilized nitrogen for fluidization to simplify the operating procedures. Since steam fluidization is required for efficient light oil trapping, the oil yields generated during these runs were not considered representative and will not be reported. The emphasis of these shakedown runs was to establish proper temperatures and solid-recycle rates among the zones. A synopsis of each run will follow to emphasize the successes and the difficulties that were encountered.

KT940222. This was a successful first run for the PDU following the extended down time for system modifications. Raw shale was continuously fed to the pyrolyzer for over three hours and the temperatures that were achieved for each of the zones were within the design ranges (see Table 1). Significant amounts of oil were collected in the electrostatic precipitator (ESP), so this run provided an opportunity to develop and refine oil-yield-measurement procedures.

While this was considered to be an excellent non-steam run in most respects, a disappointing aspect was that the temperatures of the gasifier and the combustor were approximately 100°C cooler than what was expected. Gasification temperatures of approximately 800°C are required for the steam/carbon gasification reaction to proceed at a reasonably fast rate, so an increase of least 100°C is required in this regard. Additionally, higher gasifier temperatures are required for the solid-recycle rate to the pyrolyzer to be reduced. In the previous burner configuration, the plenum and the burner-inlet pipe were not thickly insulated because of the material-failure problems in the region. Therefore, thermal losses were tolerated in order not to over heat the plenum area.

This approach was carried forth to the new configuration, but these heat losses essentially negated the thermal-efficiency gains of the new burner arrangement. Consequently, additional layers of thermal insulation were added to the exterior of the plenum region. Also, more insulation was added to the lift pipes for the pyrolyzer and the combustor to further reduce thermal losses from the system.

Table 1. Average temperatures (and standard deviation) recorded during the periods of raw shale input to the pyrolysis zone for runs: KT940222 and KT940317.

		Temperature, Std. Dev. (C)					
		<u>KT940222</u>		<u>KT940317</u>			
Pyrolysis	Bed	516	8	520	20		
	Lift	632	13	704	26		
Gasification	Bed	701	15	809	30		
Combustion	Bed	788	18	896	25		
	Lift	670	15	801	25		

KT940308. The purpose of this run was to test the

temperature capabilities of the combustor and gasifier with the new layers of insulation intact. During the start-up period, the propane burner was used aggressively to quickly raise the temperature of the combustor by maintaining the plenum chamber above 1200°C. A disturbance in the system during heat up resulted in the loss of solid recycle between the combustor and gasifier. Since solid recycle is the primary means of removing heat from the combustor, the temperature of the combustor rose quickly to over 950°C for several minutes before the flow of fuel to the burner could be ceased. Following this event, the recycle of solids between the combustor and gasifier could not be resumed and the whole system became inoperable. The system was then cooled down for examination on the following day. Large, fused masses of shale which had been previously in a molten state were found in the combustor. These slag-like materials were primarily located on the gas distributor and needed to be broken loose using a hammer and chisel. The combination of the high plenum temperature (>1200°C) and the temporarily high bed temperature in the combustor (950°C) probably caused the temperature near the gas distributor to well exceed 1000°C and reach the melting point of the minerals in the shale. Ash-fusion analysis of the shale according to ASTM D-1857 indicated that initial deformation occurred at 1168°C (see Table 2). It should be noted that slagging or ash agglomeration has been observed at temperatures hundreds of degrees lower than the initial deformation temperature of this test. According to the ASTM test and the temperatures that seemed to cause the agglomeration, the Cleveland oil shale should experience temperatures of no more than 950°C for safe, non-slagging processing.

KT940310. The slag was removed from the retort and a repeat of the run was attempted with the exception of maintaining the plenum temperature below 1200°C. Early in the heat-up process, it became apparent that something had clogged either the J-valve or the lift pipe to the combustor. To avoid additional slag formation, the retort was immediately cooled down. A marble-sized piece of agglomerated shale (apparently from run KT940308) was found to be trapped in the J-valve and was definitely determined to be the cause of the malfunction. To facilitate future cleaning of the J-valve, a flanged connection was installed near the inlet to the lift pipe.

KT940317. This run was characterized by relatively trouble-free operation with the exception of some interruptions in solid recycle to the pyrolysis zone during heat up. These breaks in recycle were probably due to small slag particles that had not yet been purged from the system and that got temporarily hung up in the J-valve or lift pipe or both. The plenum temperature was maintained between 1100 and 1150°C throughout the heat-up process. Like run KT940222, raw shale was fed continuously to the pyrolyzer for over three hours and a

Table 2. Ash fusion analysis (ASTM D-1857) of the master oil shale sample.

Initial Deformation Temperature-	1168°C
Softening Temperature-	1206°C
Hemispherical Temperature-	1244°C
Fluid Temperature-	1485°C

steady-state period of operation was achieved during that time. Temperatures in the combustor and the gasifier were at least 100°C higher than the previous successful run (see Table 1). The temperature of the combustor was actually a little bit higher than what we would like to see because of the particle agglomeration problem. However, while the combustor bed temperature was above 900°C for over two hours, the plenum temperature was maintained at approximately 800°C so that there was no possibility of over heating the gas distributor. With the high end of the temperature range demonstrated by this run, it was determined that the system was ready for a steam-fluidized run to begin the parametric test matrix.

KT940329. The start-up period was riddled with solid-recycle interruptions to both the combustor and pyrolyzer. After attempting for several hours to heat up the system, it was determined that the J-valve or lift pipe to the combustor was clogged again and needed to be cleaned out. Indeed, shale agglomerates were found throughout the system and in the J-valve. As opposed to run KT940308, however, the agglomerates were few in number and small in size. In fact, no agglomerates were recovered from the combustor itself, but it is possible that they could have formed there and migrated throughout the rest of the system. The production of these agglomerates during the heat-up period is difficult to explain because the conditions were in all respects less severe than run KT940317. One possibility is that a thin layer of molten shale formed on the distributor plate of the combustor during KT940317 and remained there throughout the run without causing any problems. There was a four-hour-long period where the plenum temperature was held between 1100 and 1150°C which could have overheated the gas distributor and caused the thin layer of molten material to form. All of the agglomerates were 1/8" or less in thickness. The molten material could have cracked following solidification from cooling after run KT940317. The agglomerates would have then been present at the start of run KT940329. A detailed discussion of the characteristics of the agglomerates will follow in a separate section. This is an important matter because particle agglomeration can be a serious problem in this type of system. Only when over-sized particles have been in the system have the solids-recycle systems displayed any inconsistencies.

ASH AGGLOMERATION AND FUSION

The occurrence of ash agglomeration and fusion during shakedown tests was identified in the previous sections as a serious operational problem. Therefore, it is important that we understand the conditions under which these large masses of material form. There is no great mystery concerning the formation of the fused shale during KT940308 because of the extraordinarily high temperatures that were experienced. While no accurate measure of the temperature of the combustion distributor plate was recorded, it is quite certain that localized temperatures exceeding 1000°C were attained at least for a short period of time. The more disturbing occurrence of shale agglomerates was observed during the attempted heat up of run KT940329 because there were no obvious over-heating episodes or other disturbances which could definitely explain the formation of the fused particles. As noted previously, the fused particles from KT940329 were thin flakes. With the naked eye, one side of each flake had a greenish tint, was almost completely molten, and evidence of individual shale particles had nearly disappeared. The other side of each flake had a more granular texture consisting of imbedded, reddish particles which were approximately the size of the raw oil shale. In addition, the molten side had no obvious curvature that would indicate formation on the inside or outside surface of a pipe. From these observations, it appears that the flakes were formed on a flat surface which was hotter than the environment on the granular side of the flakes.

Scanning electron microscope-energy dispersive X-ray analyses (SEM-EDX) were performed using a Hitachi S-2700 SEM with $\times 10^4$ magnification. Materials included a glassy phase that is intergrown with residual shale particles and red and white mineral precipitates that formed preferentially on the surface of the flakes. Figure 3 illustrates how partial melting and cooling of mineral grains resulted in the formation of glassy regions that engulfed residual shale particles. Figure 4 is an enlargement of the previously viewed area and illustrates the glassy structures which include some fibrous networks. Mineral grains and shale particles are observed at higher magnification in the SEM as a matrix bounded by glassy structures (Figure 5a). EDX analyses further indicate that the mineral matrix is composed predominantly of Si, Al, K, and Ca, with smaller amounts of Fe (Figure 5b).

White precipitates were present in all samples and were identified as hexagonal calcium hydroxide ($\text{Ca}(\text{OH})_2$) and magnesium hydroxide ($\text{Mg}(\text{OH})_2$) crystals that were formed by hydration of CaO and MgO upon exposure to moisture after sampling. Calcination of limestone and dolomite impurities in the raw oil shale sample is the principal origin of the CaO and MgO. The primary crushing of the master shale sample was performed in a limestone processing facility so a small amount of contamination by limestone and dolomite was experienced. The presence of Ca in the SEM-EDX analyses, therefore, should not be interpreted as an indication of high levels of carbonate minerals in the shale, but rather, as an impurity introduced during crushing.

The reddish color of the granular surface is the result of the formation of oxidized iron phases (hematite, Fe_2O_3). Clusters of iron-rich mineral agglomerations are shown in the SEM microphotograph of Figure 6a. Almost all areas of the hardened crust are intergrown with the

Figure 3. SEM photograph of shale agglomerate at x70 magnification illustrating a glassy phase engulfing shale particles.

Figure 4. Enlarged view of the sample shown in Figure 3 at x900 magnification illustrating the fibrous nature of the glassy melt.

a)

b)

Figure 5. a) SEM photograph of the mineral clusters between the glassy phases of the agglomerated shale at x5000 magnification; b) EDX analyses of the mineral clusters.

glassy matrix. The EDX analyses reflect the presence of a Ca-Si rich glassy phase together with the Fe-rich precipitates (Figure 6b).

The clay minerals which dominate the composition of the shale (illite, kaolinite and chlorite) are most likely to dewater and to then melt first. The dehydration of the clays, which starts at approximately 600°C, will increase P_{H_2O} which lowers the melting point of various silicate phases, including clays, quartz, feldspars, etc. Therefore, the clays are believed to influence the agglomerating behavior of the shales the most. The glassy regions were characterized by compositions that are representative of the shale matrix as a whole. The formation of mineral agglomerates is, therefore, expected to be primarily influenced by temperature and to a lesser degree by P_{H_2O} . From our experiences to-date, we would suggest a maximum processing temperature of 950°C for these shales because of the potential for hotspots that can be hundreds of degrees hotter. For the KENTORT II process, combustor plenum temperatures of no more than 1100°C are now being employed because it appears that a thin layer of molten material can form on the distributor plate if higher temperatures are achieved.

a)

b)

Figure 6. a) SEM photograph of red deposits at x450 magnification; b) EDX analysis of the red deposits.

REFERENCES

1. Rubel, A.M., M.J. Margolis, J.K. Haley, and B.H. Davis, *1983 Eastern Oil Shale Symposium Proceedings*, 1983, IMMR83/089, University of Kentucky, Lexington, Ky.
2. Margolis, M.J., *1981 Eastern Oil Shale Symposium Proceedings*, 1981, University of Kentucky, IMMR82/066, Lexington, KY.
3. Richardson, J.H., E.B. Huss, L.L. Ott, J.E. Clarkson, M.O. Bishop, L.J. Gregory, and C.J. Morris, Lawrence Livermore National Laboratory, UCID-19548, 1982.
4. Ahmed, M.M., D.W. Parker, and D.H. Archer, *1982 Eastern Oil Shale Symposium Proceedings*, 1982, University of Kentucky, IMMR82/075, Lexington, KY.
5. Rubel, A.M. and S.D. Carter, *Preprints Div. Pet. Chem.*, ACS, 1984, 29, 202-208 (1).
6. Wallman, P.H., Tamm, P.W., and Spars, B.G., *ACS Symp. Ser. 163*, 1981, 93.
7. Bissel E.R., Burnham, A.K., and Braun, R.L., *I and EC Proc. Des. Dev.*, 1985, 24, 381.
8. Carter, S.D., Rubel, A.M., Robl, T.L., and Taulbee, D.N., 'The Development of the KENTORT II Process for Eastern U.S. Oil Shale,' 1990, Final Report for work performed under Contract No.: DE-FC21-86LC11086, DOE/LC/11086-2860.
9. Carter, S.D. and D.N. Taulbee, *Fuel Processing Technology*, 1985, 11, 251-272.
10. Robl, T.L., K. Cisler, G. Thomas, and D.W. Koppenaal, *1985 Eastern Oil Shale Symposium Proceedings*, 1985, University of Kentucky, KCERL/85-147, Lexington, Ky.
11. Carter, S., Stehn, J, and Vego, A., "The Development of an Integrated Multistage Fluid Bed Retorting Process," Quarterly Technical Progress Report for the Period: Oct. 1-Dec. 31, 1993, U.S. Department of Energy, DE-FC21-90MC27286.

DATE

FILMED

9 / 27 / 94

END