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Proceedings of the Fuels Technology Contractors Review Meeting

Rodney D. Malone

November 1993

U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
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Proceedings of the Fuels Technology Contractors Review Meeting

Editor
Rodney D. Malone

Sponsored by
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November 16-18, 1993

Foreword

The Fuels Technology Contractors Review Meeting was held November 16-18, 1993, at the Morgantown Energy Technology Center (METC) in Morgantown, West Virginia. This meeting was sponsored and hosted by METC, the Office of Fossil Energy, U.S. Department of Energy (DOE).

METC periodically provides an opportunity to bring together all of the R&D participants in a DOE-sponsored contractors review meeting to present key results of their research and to provide technology transfer to the active research community and to the interested public. This meeting was previously called the Natural Gas Technology Contractors Review Meeting. This year it was expanded to include DOE-sponsored research on oil shale and tar sands and so was retitled the Fuels Technology Contractors Review Meeting. Current research activities include efforts in both natural gas and liquid fuels. The natural gas portion of the meeting included discussions of results summarizing work being conducted in fracture systems, both natural and induced; drilling, completion, and stimulation research; resource characterization; delivery and storage; gas to liquids research; and environmental issues. The meeting also included project and technology summaries on research in oil shale, tar sands, and mild coal gasification, and summaries of work in natural-gas fuel cells and natural-gas turbines. The format included oral and poster session presentations.

This meeting contained 15 formal sessions and one informal session, and included 41 papers and 16 poster presentations.

- Keynote, Plenary and Opening Sessions (6 papers)
- Liquid Fuels Technology
  - Oil Shale (4 papers)
  - Tar Sands (1 paper)
  - Mild Gasification (2 papers)
  - Gas to Liquids (5 papers)
- Natural Gas Technology
  - Hydraulic Fracturing Technology (3 papers)
  - Natural Fractures (4 papers)
  - Resource Assessments and Modeling (2 papers)
  - Secondary Natural Gas Recovery (1 paper)
  - Coal Seam Gas (3 papers)
  - Drilling, Completion, and Stimulation (5 papers)
  - Natural Gas Atlases and Data Management (2 papers)
  - Low-Quality Natural Gas Upgrading (5 papers)

We gratefully acknowledge the participation of the Energen Corporation, the research contractors, and various offices of DOE for the presentations provided in this document. The papers printed in this document have been produced from camera-ready manuscripts provided by the authors. They have been neither refereed nor extensively edited.

Rodney D. Malone
Conference Coordinator

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Keynote Address

Managing Change

by

Rex J. Lysinger

Energen Corporation

Thank you, Hugh, for that fine introduction. It is a pleasure for me to be here today because it is like coming home. As Hugh told you, I was born in Pittsburgh and raised in a little town on the Ohio River, so I really enjoyed the scenery as I drove down here from Pittsburgh yesterday.

When I was growing up in Martins Ferry, Ohio, a small town across from Wheeling, West Virginia, we used to joke about the fact that in our school they taught the three R's: "Readin, Ritin, and Rithmetic", but in West Virginia, they taught the four R's: "Readin, Ritin, Rithmetic, and Route 21 to Ohio". A lot of things have changed since those days, and the title of my remarks today is managing change.

My perspective is both that of a businessman and a strong supporter of research and development. The major lines of business of Energen Corporation have undergone significant change over the last five to ten years. Likewise, the Gas Research Institute, which I chaired for two years and currently serve on the Executive Committee, is experiencing significant change.

My vision for the year 2000 for the energy industry is a very exciting, dynamic and positive one. This is especially true for the gas industry. And, just like my boyhood days had the three R's, I believe the very positive outlook for the gas industry is built on three E's: energy, environment and efficiency. To me, the first two E's, energy and environment, go together like "readin and ritin". They are hard to separate because they are so interdependent. On the other hand, the third E, efficiency, is like "Rithmetic" because it is where the numbers are and why our research efforts are concentrating on developing new technology. We also must concentrate on transferring that technology to the marketplace. If there is one message I can leave you with today, it is this: new technology does no good unless it is deployed in the marketplace, therefore, we must emphasize the transfer of technology to the marketplace.

The energy industry, especially the natural gas segment, has been undergoing restructuring for at least the last ten years. This restructuring culminated with the Federal Energy Regulatory Commission issuing Order 636 which basically separated the gas merchant functions of the interstate pipelines from the rest of their activities. The responsibility for buying, aggregating, and reselling of the gas was transferred from the pipelines to the distribution segment. With that transfer came significant increased risk to the distributors. The result is a much more dynamic and competitive marketplace. There are more players in the gas buying and selling commercial transaction chain. There is increased direct contact between end-users and supplier/aggregators. This greater risk in the competitive marketplace also includes the risk of economic bypass of traditional service. This fact makes the value of the service that is provided more important than ever.

What's the significance of all this? To me, it means that distributors interests will be moving up stream to the supply end. Therefore, distributors will have much more interest in activities such as fracturing, drilling and storage, and in related technology that historically they have not had direct involvement. In like fashion, producers will be moving down stream and should become more interested in end-use technology which addresses new and better ways to increase demand and improve efficiency of utilization.

The National Petroleum Council has issued a very positive report which establishes a new benchmark for the gas resource base of the lower 48. While we should all be pleased that this report was very positive, we must recognize that there were two issues identified as critical to success.

The first item was the necessity to increase drilling. We cannot continue the low level of drilling that has been conducted over the past several years and be successful in proving-up the resource base.

Second, we must continue developing new technology applicable to all phases of exploration and production activities so that we can continue to improve efficiency.

Environment - when I speak about environment, I am including our public policy environment with our natural environment.

Our President has identified energy, especially natural gas, as one of his top priorities. By now it is also very clear that this administration is going to be more active in deploying or commercializing new technology. The new Secretary of the Department of Energy, Hazel O'Leary, certainly understands the energy industry from a business perspective and also understands the opportunities and benefits of new technology. We also have a new comprehensive National Energy Policy that has identified the use of natural gas as "an environmentally enlightened activity". I am not really sure what that means, but I think it means natural gas is good. I have an old tee shirt that I use to jog in that has written on it "Natural gas, the environmental protection energy". I think that is what we are talking about.

However, one word of caution. Before we start off on a new path, whether it is a new political or technology path, let's have a reality check on present conditions and, most importantly, what we are trying to accomplish.

The reality of our national business environment is that it has been significantly impacted by the globalization of industry. Alabama Gas Corporation used to think that it was a local distributor that only had to be concerned about business activities in the state of Alabama. Then we found out that a lot of our industrial customers would produce their product in a different state if we could not provide them with competitively priced energy.

Next, we found that some of our customers had the ability to schedule their production in another country if we could not be price competitive. Today, Alabama Gas is a local distributor that is able to compete with alternate fuels and also assists its large commercial and industrial customers in competing regionally, nationally, and globally by providing competitively priced natural gas.

Sometime this evening, after another day of discussion on the Hill, we will vote on NAFTA. I certainly hope that there will be a positive outcome to the vote and that will add even greater emphasis to the global economy issue.

We are entering a new era in this country with regard to social economic policy. Important issues span the spectrum from health care reform to education reform. I believe we need to recognize and consider in our planning that this administration will be a more proactive administration with regard to public policy. I believe the result will be not only a more complicated business environment but also greater competition for research dollars and, with greater money coming out of the private and business sector to fund government activities in the form of increased taxes, I do not think it is reasonable to expect that business will be able to increase their allocation of funds for research. It will be a tough battle, however, I firmly believe that there is a great opportunity for natural gas because of several advantages.

One advantage of natural gas is that it is a domestic energy source. I had an opportunity yesterday to hear Lieutenant General Tom Kelly (retired) who most of us got to know during Desert Storm as he conducted a lot of the press briefings. The theme of his remarks was energy independence, an issue I think we will be hearing more of in the future, from both a national security and economic standpoint.

General Kelly made the observation that imported oil still accounts for about 70% of this country's balance of payments, so it just makes good policy to promote natural gas from both an economic and national security perspective.

I also think the natural gas industry will benefit in future years because of the formation of the Natural Gas Council. This new council demonstrated its worth in the debate over the energy or Btu tax as the various segments of the gas industry had a forum in which to discuss the impact of various proposals and reach a consensus. The council is an excellent way to demonstrate that people working together in a spirit of cooperation can accomplish much more than everyone acting independently and going their own way.

What about efficiency? Well, at the federal level we have the mandates of the Clean Air Act amendments and the Environmental Protection Act. We also have the new appliance efficiency standards that impact new appliance design and technology. On the state level, state Public Service Commissions are in the process of looking at integrated resource planning and demand side management to determine whether either or both of these programs could be a positive factor to improve efficiency and encourage customers to conserve energy. As distribution companies become more involved in the buying, aggregating and reselling of gas supplies, state commissions should also become more involved in supply side research and development. The opportunity is also present for state commissions to become more involved in research activities applicable to all industry activities and, managed properly, I think that can be a very positive development.

All of these activities and changes are going to be taking place at the same time that the industry must emphasize cost control, productivity and efficiency. As I have already stated, I believe that there is going to be more competition for R&D grants, and the significance of this to me is that I believe we are going to have to do a better job of demonstrating the value of research. Further, we are going to have to concentrate more on market-pull rather than management-push to transfer new technology to the marketplace.

GRI is a major force in the gas industry, managing in excessive of $200 million dollars in R&D funds for each of the last few years. We are just beginning the budget process for 1995, and I am hopeful that the budget will be increasing in the future. In many ways, GRI is a microcosm of the gas industry. It is managing change and doing a good job of it. It is meeting the needs of a dynamic industry by becoming more market-driven in response to industry changes. GRI has a modified funding mechanism in place that was achieved through a negotiated process, and I think this is another demonstration of increased unity in the gas industry.

I began my chairmanship with GRI in April of 1991. At that time, my vision for GRI encompassed three items: The first was that GRI should become more market driven and responsive to a dynamic industry. I believe this has been accomplished. Second, GRI should help improve industry unity. Again, I think GRI has been successful. The third item I wanted to accomplish was to push the limits of technology transfer by pushing deployment of new technology into the marketplace. GRI has made a good start on this objective, but it will take many months or several years before GRI can demonstrate success.

What other changes have been made at GRI? I get a lot of questions about the impact of the reorganization and changes that have been made and how they will impact the research projects of GRI. The first thing I would like to state is that GRI is a great organization that has served the industry well. It was formed in 1978, and through 1992 had done an excellent job of meeting the needs of the industry. But, the Board recognized that the successes of the past would not guarantee future success, primarily because of the dramatic new business conditions of a restructured industry and competitive marketplace. Therefore, the Board decided to undertake a complete review of programs and operations to ensure that GRI was properly organized and focused to meet the needs of the future.

In the spring of 1992, a Program Review Task Force made up of members of the Board of Directors was assembled. The first order of business was to conduct a member survey. Members were asked how they believed GRI was performing and also how they felt GRI could become a more focused, effective, and efficient organization. During the fall of 1992 and into March of 1993, a comprehensive study was conducted that covered mission and governance, technology transfer, program process, and operations. In March of 1993, the Board reduced its size from 40 to 25 members in order to become a more involved, active Board. It also added three large gas users to the Board.

At that same time, the Board directed GRI management to undertake to accomplish six goals:

- make technology transfer and deployment top priority;
- reemphasize results-driven performance;
- improve organizational efficiency and cost control;
- improve communications. It was emphasized that communications is a two-way street. Communication involves listening to your clients and other affected parties to ensure that you are getting proper input and not just providing output. Engineers and scientists have a habit, just like business people or doctors of going to meetings and talking to themselves;

- streamline the program development process. The objective is to reduce the cycle time for starting a project, developing the technology and/or information, and, finally, making it available in the marketplace and, at the same time, improve the flexibility in that process; and
- reemphasize and seek additional supplemental cofunding.

Dr. Ban and the GRI management team immediately grabbed the ball and started running. The first thing they did was to go through a benchmarking effort. They talked to the best there was in the research area to determine the best practices in R&D management. They also conducted some focus group interviews at the GRI 1993 Annual Meeting. Some of you may have been involved in those meetings.

A new GRI mission statement has been developed. That statement says that GRI's mission is to discover, develop and deploy technology and information that provides measurable benefits to gas customers and the gas industry. Further, GRI will enhance the value of gas energy service through planning and managing a consumer sensitive cooperative research program, emphasizing technology transfer. Many of you, I am sure, have received some communications from Dr. Ban and GRI discussing the program and emphasizing a more performance driven organization.

Performance will be measured by a combination of traditional performance measures plus some new or revised measures. We will keep measures such as:

- consumer cost/benefit ratio;
- financial performance;
- level of cofunding achieved;
- patents awarded;

Several new or revised performance measures include:

- customer satisfaction;
- impact of new technology in the marketplace;
- progress towards goals;
- transfer or use of information.

The GRI organization has been completely restructured into four major divisions including product development, technology development, business operations, and policy and regulatory affairs. The product development division is new and was formed by taking existing skills available within GRI in business management and development, and supplementing those with outside resources necessary to establish a state-of-the-art product development organization. The new organization emphasizes teamwork. Teams are assembled representing GRI staff from all areas of the organization plus contractors, members and manufacturers. These teams develop product plans which, once approved, are taken to completion.

The new organization also emphasizes customer satisfaction. Customer teams have been formed to address the specific needs of producers, pipelines and distribution companies. These client sector teams are a major factor in the emphasis on improved, two-way communications.

There is also a strategic collaboration program which promotes expanded cofunding.

Finally, there is a targeted communication strategy. GRI is establishing a new communication process to ensure that the right information can get to the right people at the right time.

GRI has also streamlined the contracting process. I would hope that some of you are already familiar with this improvement. As I mentioned previously, our objective is to shorten the cycle time and also increase flexibility.

GRI has already lowered operating costs and will continue this emphasis at the same time it is implementing all of the previously mentioned improvements.

A continuing challenge is program balance. How many dollars should be allocated to supply, transmission, distribution, end use, or the environment? How does GRI meet the needs and demands of each of these sectors. That is a continuing balancing problem for the Board. The second balancing problem is the allocation of funds to short-term versus long-term research. We must balance the short-term emphasis on technology transfer with the long-term needs of basic research.

On behalf of GRI, I certainly thank you for your continued support and understanding during this period of change. I would emphasize that this is not a completed program - it is a dynamic ongoing process that will continue to evolve and change to meet the changing needs of our customers and our industry.

In conclusion, I am really encouraged because of the outlook for the 3 E's of energy, efficiency, and environment in my vision for the year 2000 and beyond. But, I have to admit that just like there was a fourth R when I was a boy in Martins Ferry, I believe there is also a fourth E to future success. That fourth E that I would like to stress is ethics. I would like to see a renewed individual and corporate emphasis on standards and values that are built on a foundation of truth, honesty and integrity. It has served this world well since the beginning of time, and it will serve us well in the future. I would ask your support for a reemphasis of the fourth E, ethics.

Where does that leave us? Well, we have more players as well as new players in the research process. They have different roles and different interests. It is going to be more complicated and difficult in structuring research activities. There is going to be more competition for the R&D dollar. We're going to have pressures from social, economic, and political considerations. There is and will be a greater requirement to be performance-driven. The research industry is going to have to demonstrate value more so than they've ever done before, and will have to also focus more on market-pull rather than management-push. The emphasis in the near term will be on technology transfer because we must get that new technology into the market place, and we must do it in a manner that is not only effective but efficient.

Finally, we need a greater focus for our activities. We must be very specific about our objectives and our direction. And, as a part of that focus, we must have greater clarity of our communications. We must be able to explain why we are conducting certain research and make it understandable to those who will be paying the bill.

The outlook is good, but success will come the "old fashioned way", as that gentleman on TV says, "we'll have to earn it." The way that we do that is by managing change and concentrating on the four E's.

Thank you and I would be pleased to respond to questions

Questions and Responses

Question by Tom Bechtel of METC:
One of the issues that has surfaced as METC considers advanced power plant concepts using large gas fired turbines is increasing stress between some local distribution companies and the large volume users of gas for power generation, specifically as it relates to pipeline open access and potential bypass of the gas distributor. Some companies don't like the fact that we are in the large turbine business because they feel it supports their competitors. This issue is compounded by some companies being combination gas and electric. Would you give us your thoughts on how this issue may be resolved.

Response by Rex Lysinger:
First, with regard to the combination company issue, I believe that new competitive market conditions, combined with the restructuring of the gas industry, could promote an examination of whether such combinations are still in the public interest and should be continued. With regard to your primary question, I believe that it will take a greater understanding and acceptance of competitive market forces to ultimately settle the issue. For example, Alabama Gas Corporation recently entered into a contract with Alabama Power Company to construct a pipeline to provide gas for nine new combustion turbines currently approved to be installed in the western portion of Alabama. We did this in recognition of competitive market conditions and gas industry restructuring. Historically, large volume users have subsidized residential customers. This is no longer the case. It is only a matter of time before this is fully reflected in the marketplace. Large volume users of gas for power generation - and all other large volume users - will operate on a very slim margin, primarily a cost of service type margin. It will be extremely difficult for a distributor to maintain historical higher margins in view of current, and especially future, market conditions. Some distributors want to embrace the competitive market but cannot get regulatory support. In summary, this issue should take care of itself over time - which could be several years - and it will be very pipeline, state jurisdiction, and distributor specific.

Question by Elena Melchert, Department of Energy, Washington, DC
I serve as the new program manager for the natural gas supply R&D program. The other hat we wear is oil and gas technology transfer. You talked about the role of states and their contribution to upstream R&D, and I wonder if you can tell me if you believe a high tech role for states or potential contribution of states is a healthy transfer?

Response by Rex Lysinger:
This would be a dramatic change and certainly effected on a state-by-state basis. Historically, it has been easier for

states and local distribution companies to let research, demonstration, deployment, commercialization and technology transfer be handled at the federal level with dollars being collected and forwarded to the interstate pipelines who forward it to GRI who worked with outside entities, including the Department of Energy. It was all taken care of at the federal level. Several states already have programs which provide for specific research activities on the part of distribution companies. Some also have provisions which allow them to specifically approve demonstration or commercialization projects. Over the long term, I see local distribution companies working with state commissions to gain support for research and development, including technology transfer that they believe to be in the best long-term interest of their consumers. Second, I would hope that we will see some greater cooperation between the Department of Energy and state commissions in the form of people like yourself, as an objective third party, encouraging them to consider support for R&D. However, we must remember that Public Service Commissioners, whether elected or appointed, must be very sensitive to how they spend consumer dollars and will be very sensitive to complaints about spending dollars for things that may not work. So, it will be a tough sale and very state specific.

Question by Lou Salvador, Associate Director, METC
My question has to do with the ability of GRI to deal with its diversity of stakeholders. Can you comment on how GRI has been achieving a consensus on its research program given the variety of independent interests which they represent?

Response by Rex Lysinger:
I will try to respond from a Board perspective, but I would also recommend that you talk with one of the GRI employees who are here. I saw Mr. Chuck Brandenburg earlier and there may be some others that could provide you more specific detail. The GRI staff, with input from four major standing advisory groups plus specific project advisory groups made up representatives from all stakeholders, discuss and evaluate all potential projects. Potential projects are prioritized based on the performance measures that I mentioned, including cost/benefit ratio and financial impact. They are then arrayed for presentation in a budget. The budget is then evaluated and revised at each review level and then presented to the Board. The Board primarily involves itself with an allocation of funds between industry segments rather than with specific projects. For example, they will discuss the number of dollars that should go into supply research versus end-use research. The board must balance political, social, economic, and program interests. The new board is going through, at the present time, its first budget review and it needs to be understood that, historically, we have ended up with a very strong majority consensus, however rarely unanimity. The Board can exercise its judgment with regard to

valuing those benefits or technologies which have the highest priority at any given review time. Currently, technology transfer is certainly on the high priority list and will be given slightly higher weight than some of the other areas. However, in the final analysis, the full board votes on dollars allocated to various areas rather than on specific projects because the Board relies on the staff plus committees and other advisory groups to have already done their job of prioritizing specific projects.

Session LF -- Liquid Fuels Technology

Session LF-1

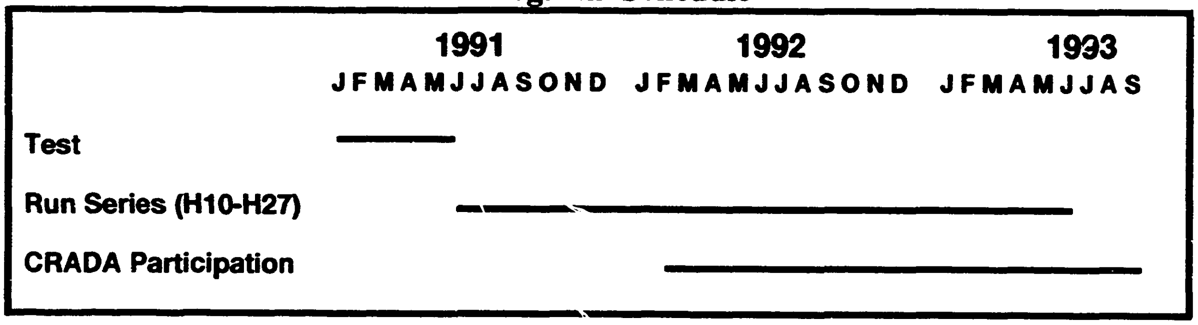
Oil Shale

LF-1.1 Status of LLNL Hot-Recycled-Solid Oil Shale Retort

CONTRACT INFORMATION

Contract Number	W-7405-ENG-48
Contractor	Lawrence Livermore National Laboratory 7000 East Avenue Livermore, CA 94550 (510) 422-7316
Contractor Project Manager	David E. Baldwin
Principal Investigators	Robert J. Cena
METC Project Manager	Hugh Guthrie
Period of Performance	January, 1991 to September 30, 1993
Schedule and Milestones	

Program Schedule



OBJECTIVES

The oil shale deposits in the Western US represent a massive liquid fuel resource, with over 600 billion barrels of recoverable deposits in the Piceance Basin alone. Our objective, together with our CRADA partners[1], is to demonstrate advanced technology that could lead to an economic and environmentally acceptable commercialization of oil shale.

We have investigated the technical and economic barriers facing the introduction of an oil shale industry and we have chosen Hot-Recycled-Solid (HRS) oil shale retorting as the primary advanced technology of interest. We are investigating this approach through fundamental research, operation of a 4 tonne-per-day HRS pilot plant and development of an Oil Shale Process (OSP) mathematical model.

Over the last three years, from June 1991 to June 1993, we completed a series of runs (H10 - H27) using the 4-TPD pilot plant to demonstrate the technical feasibility of the HRS process and

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[1] Cooperative Research and Development Agreement, established in February 1992 with Amoco, Chevron, Conoco and Unocal

answer key scale-up questions. With our CRADA partners, we seek to further develop the HRS technology, maintain and enhance the knowledge base gained over the past two decades through research and development by Government and industry and determine the follow on steps needed to advance the technology towards commercialization.

One of the crucial challenges in beginning a oil shale industry is how to overcome the high capital cost and long lead time needed to make process improvements which would enable shale oil to compete as a fuel feed stock. We have chosen to focus on an initial plant that converts a large fraction of its production into high-valued specialty products to gain an initial market entry.

We have determined the economics for a plant producing 10,000 Bbl/day of oil from shale. The plant converts the raw shale oil into a slate of high valued products including specialty chemicals, a shale oil modified asphalt binder and transportation fuels[2], while co-producing electric power. This small scale venture is shown to be competitive in today's market with a fifteen percent internal rate of return on a capital investment of $725 million dollars. Once in operation, expansion to 50,000 Bbl/day has the potential to become economic through economies-of-scale and cost reductions based on operating experience and plant innovation. This small beginning would provide the operating experience prerequisite for a larger industry, if and when appropriate, that could supply a significant fraction of the US liquid transportation fuel needs.

BACKGROUND INFORMATION

The LLNL 4-tonne-per-day pilot plant was constructed in 1990 and began operating late that year. Preliminary runs were conducted to shake down the system and in June 1991, we executed H10, which is the first run reported herein.

The pilot plant, which features no moving parts in critical areas, has been successfully operated for over 100 hours, allowing development of control algorithms and operating strategies while demonstrating process reliability. In the process, efficiency is obtained through the high solids throughput, complete carbon utilization, waste shale heat recovery, improved oil yield and one hundred percent utilization of mined material, including shale fines. We have demonstrated the ability to work with both lean and rich shales (22 - 38 gallons-per-ton), and the process has been shown to be environmentally superior, producing non-hazardous waste shale, minimal sulfur emissions, lower NO_x emissions and minimum CO_2 production.

Fundamental laboratory experiments support the pilot plant efforts. We have determined kinetics for pyrolysis, combustion and carbonate decomposition and have incorporated these into an Oil Shale Process (OSP) mathematical model which we use as an aid in critical thinking and scale up of the HRS process.

We have put forth a commercial plant concept at 10,000 Bbl/day which combines the production of shale oil and electric power. This plant concept would fully utilize available thermal energy, would filter contaminates from the oil prior to condensation, would co-produce electric power for on-site use and off-site sale, would solve the waste shale cooling problem and would produce a spent shale meeting Federal standards as a non-hazardous mining waste. The plant would produce a slate of products, including feed stock for specialty chemicals, a proprietary shale oil modified asphalt (SOMAT) binder and refined products including motor gasoline, aviation gasoline and diesel fuel.

PROJECT DESCRIPTION

The LLNL 4-tonne-per-day pilot plant consists of a circulating loop and peripheral equipment for the production of oil from shale. Major units, shown in Figure 1, include a fluidized bed mixer (FBM), a moving packed bed pyrolyzer (PYR), a pneumatic lift pipe (LFT), and a fluidized bed combustor (FBC). Solids are circulated around the loop at 10 kg/min. Fresh shale, crushed to a top size of 7mm, is mixed with hot circulating solids in the FBM.

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[2] A mixture of fuels, thirty percent each motor and aviation gasoline and forty percent diesel fuel.

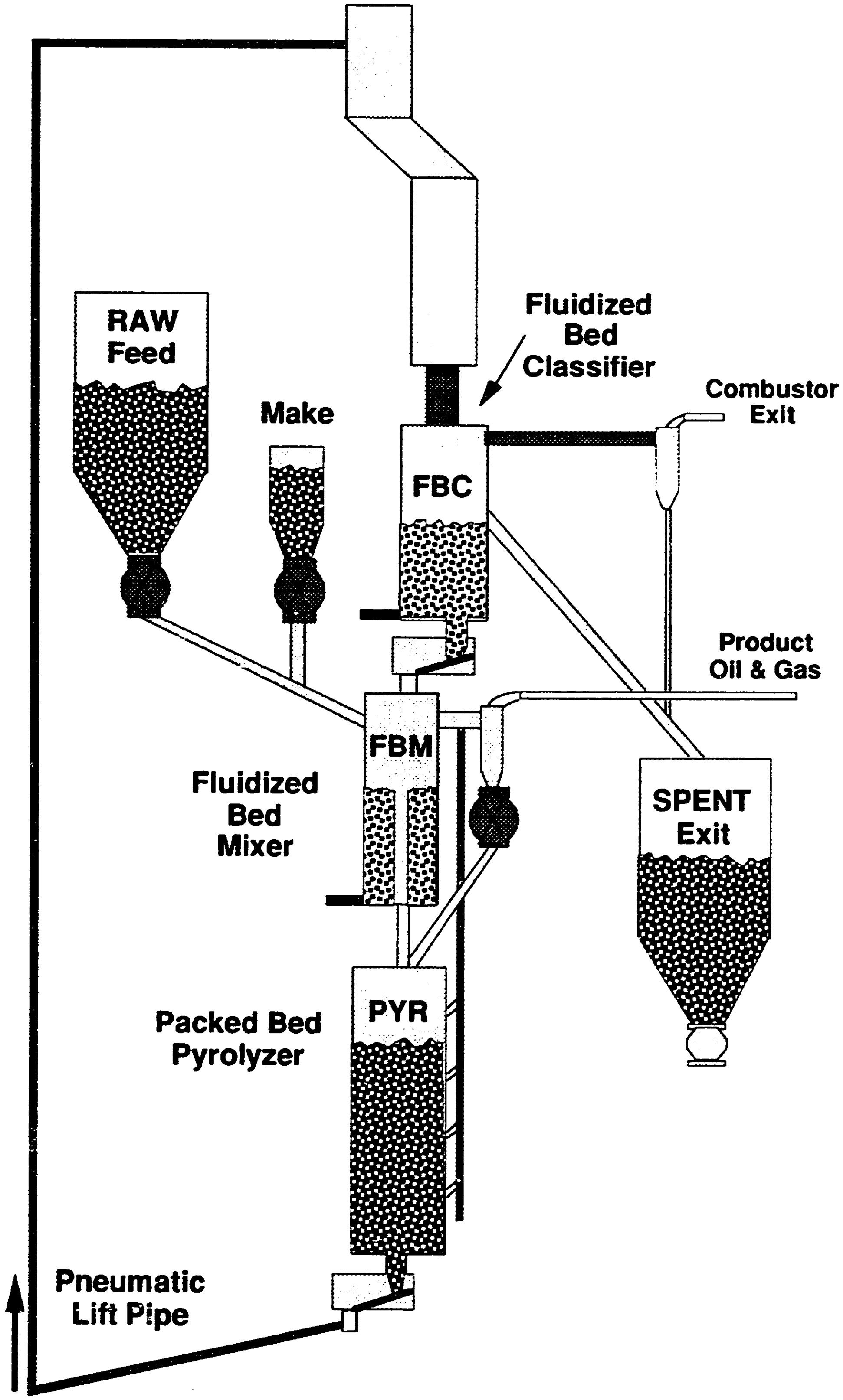

Figure 1. Schematic of the LLNL Hot-Recycled-Sold (HRS) Oil Shale Retort

Rapid pyrolysis occurs in 2-3 minutes in the FBM and PYR and the oil vapor, containing water and dust pass through cyclones and filters prior to staged cooling for product recovery. Residual carbon on the spent shale, after pyrolysis, is combusted in the LFT and FBC, providing the process heat, completing the circulation loop.

Solid flow and bed levels within the circulating loop are maintained using a pair of L-valves, one located below the PYR and one located below the FBC. Each valve is equipped with a horizontal skid separating inlet and exit by approximately 10 inches. Solids are transported from inlet to exit using gas jets which are pulsed at a frequency of once every 1 to 2.5 seconds. Each pulse moves approximately 250 grams of material. By adjusting the pulse rate and local pressure in the vicinity of the L-valve we achieve a balanced loop at the designed circulation rate, processing 2.5 kg/min of raw shale.

Concurrent to our pilot plant studies is the development of a steady state OSP mathematical model. OSP models each of the major components, shown in Figure 1, allowing us to compute properties and phenomena not readily determined experimentally. The model serves as a critical judge of the experiments and an aid in process scale up.

One of the major discrepancies early on between model and experiment was the degree of carbonate decomposition which occurred. To resolve this discrepancy, we have, in the laboratory, reexamined carbonate decomposition kinetics, focusing on the lower temperature ranges typical of our retorting conditions.

RESULTS

Reported herein are results from six pilot plant runs conducted between June 1991 and January 1992, prior to the formation of our industrial consortium. (Runs conducted after February 1992 fall under our contract as CRADA protected data and are not discussed).

Pilot Plant Results

Two of the runs processed a lean, 22 gallon-per-ton shale from one master batch and four of the runs processed rich shale from two master batches ranging from 34 to 38 gallons-per-ton. Information concerning the three master batches are given in Table 1.

Table 1. Raw Shale Feed Composition

	MB 2	MB 4	MB 5
Total C (%)	15.14	20.20	22.53
Total H (%)	1.54	2.16	2.41
Total N (%)	0.63	0.83	0.85
Total S (%)	0.53	0.96	0.91
Mineral C (%)	4.72	4.75	3.94
Organic C (%)	10.42	15.45	18.59
Fischer assay			
Gallons/ton	21.62	34.23	38.57
C4+ Assay (gm/kg raw)	83.5	131.5	149.2

Reported in Table 2 are the process conditions for the six runs. The two lean runs H10 and H14 are reported first, followed by the four rich shale runs. Runs H14 and H15 used air in the FBC, the others used nitrogen. Of the two lean shale runs, H10 is the more typical, since the purpose of H14 was to examine the effect of high recycle and high carbon burnout on yield loss via oil coking. The first three rich shale runs are vary similar in conditions giving an indication of repeatability. The final run, H15 used excess air in the LFT and air in the FBC to achieve high carbon burnout to explore it's effects on results.

Temperatures for all of the runs are very similar except for run H15. PYR temperatures ranges from 500°C to 509 °C for the first five runs and 535°C to 556 °C for H15. Temperatures in the FBC ranged from 644°C to 684 °C for the first five runs and 787 °C for run H15. The raw shale was preheated prior to each run. However, for two of the runs, H14 and H15, the shale was allowed to cool following preheating to achieve higher carbon burnout while maintaining a recycle temperature below 800 °C.

Table 2. Process Data

Run	**H10**	**H14**	**H11**	**H12**	**H13**	**H15**
Run Date	12-Jun-91	16-Dec-91	29-Aug-91	24-Sep-91	14-Nov-91	16-Jan-92
Master Batch Number	2	2	4	4	5	5
Process Flows						
Gas Flows (mol/s)						
LFT	.528	.504	.500	.503	.542	.639
FBC Nitrogen	.352		.351	.346	.348	NA
FBC-ALT Air		.344	NA		NA	.355
FBM	.701	.674	.705	.692	.654	.720
PYR	.084	.071	.074	.068	.060	.073
BLD	.012	.018	.018	.018	.015	.015
LVP	.053	.069	.046	.049	.062	.052
LVC	.056	.050	.042	.051	.046	.045
PRD	.904	.878	.126	.090	.110	.132
Solid Flow (kg/min)						
Raw feed SV	2.50	1.68	2.51	2.51	2.51	2.50
Raw feed WT	2.39	1.82	2.43	2.41	2.06	2.08
Spent Hopper	1.95	1.51	1.63	1.73	1.37	1.16
LFT Solid	10.16	11.10	8.88	10.20	9.53	10.40
DFC SV	9.61	9.98	8.96	9.71		9.26
Temperatures						
At LFT L-valve	494	489	499	493	486	540
LFT Gas at 3.6 m		535			572	626
LFT Gas at 6.5 m		561			691	765
LFT Gas at 9.6 m		581			711	770
Into CLS	622	634	716	698	752	783
FBCBed	644	684	678	665	681	787
FBC to FBM	628	640	653	645	638	757
FBM Baffle Plate	472	330	490	479	500	566
FBM to PYR	509	509	512	507	515	560
PYR Bed at 1.06 m	507	506	507	501	504	556
PYR Bed at 0.88 m	507	506	507	502	509	556
PYR Bed at 0.71 m	504	505	506	500	508	549
PYR Bed at 0.53 m	503	503	504	500	507	548
PYR Bed at 0.35 m	504	504	504	500	506	534
Raw Temperature	126	10	136	127	149	11

Table 2. Process Data (Continued)

Run	H10	H14	H11	H12	H13	H15
Process Pressures (kPa)						
Average	147	144	160	152	155	158
Differential						
FBC Bed	10.30	3.38	2.58	2.92	3.60	0.40
FBM Bed	1.94	0.12	2.71	2.50	2.48	2.44
PYR Bed	0.11	0.06	0.31	0.55	0.15	1.26
LFT	2.77	3.09	2.59	2.66	2.49	2.90
FBC L-valve	3.81	0.01	1.33	1.48	1.20	0.22
PYR L-Valve	-1.02	-0.29	-1.95	-1.59	-1.06	-2.55
DFC	-0.33	-0.30	-0.31	-0.39	-0.38	-0.53
Bed Level Sensors (cm)						
FBC	57	78	78	77	103	43
PYR	87	93	92	94	93	92
Material Balances (%)						
Mass Balance	100	97	97	98	97	98
Oxygen Balance	103	95	99	100	101	98
Total Carbon Balance	100	98	97	95	98	106
Organic Carbon Balance	100	97	97	94	97	107
Mineral Carbon Decomposed (%)	14	22	22	20	22	45
Organic Carbon Distribution (%)						
Pyrolysis gas CO & CO2	3.0	2.5	1.6	1.1	0.7	3.1
Pyrolysis gas C3-	3.8	3.7	4.6	3.5	3.7	9.5
Pyrlolysis gas C4+	5.6	5.2	2.5	2.1	2.5	4.2
Combustion gas	21.0	27.4	14.3	14.8	17.2	21.1
Spent Solids	6.4	2.0	3.1	2.9	3.0	0.4
Liquid Oil	58.6	56.0	70.0	68.6	69.8	66.2
Liquid Oil & C4+ (% of Fischer Assay)	95	89	102	101	103	100

Operating pressures varied little, ranging from 144 to 158 kPa. Differential pressures were maintained to balance the loop, with only a few kPa differential between the pyrolysis and combustion sides of the system. The most sensitive pressures were those in the vicinity of the L-valves, which were generally maintained below a 2 kPa differential pressure.

Solid sampling and analyses coupled with integration of the on-line data allowed component balances to be made for each of the runs. A mass balance for all runs obtained closure of 97 percent or better, with component balances for oxygen, organic and total carbon at 95 percent or better. Decomposition of the mineral carbon is reported for each of the runs. The amount of decomposition correlates with the temperature of the FBC, as shown with H15, where a one hundred degree higher shale temperature resulted in a doubling of the measured amount of carbonate decomposition. The organic carbon distribution for each of the runs is reported. As shown, the amount of organic carbon left on the exiting solids in all cases less than 7 percent of the original and for the high carbon burnout case is less than one half of one percent.

Oil yield for the six runs is reported on a liquid oil plus C4+ gas basis. Run H10 most typifies the lean shale case, with 95 percent of assay obtained. For the rich runs, there is little difference in yields, ranging from 100 to 103 percent of assay. Although the difference is small, there appears to be a definite yield penalty of five to ten percent for lean shales.

Oil Shale Process Model (OSP) Results

We continue to develop our Oil Shale Process model (OSP) as a aid toward process scale up and critical thinking concerning our pilot plant results[1]. OSP is a steady state model, written in FORTRAN, which allows a variety of modules to be coupled together to simulate some overall process. The model consists of three interacting parts: a control portion which handles overall direction of computation and is responsible for coupling process units together through the use of stream variables; a service routine portion which allows common properties to be computed; and any number of modules which do the actual computations associated with a given unit operation. The model defines three types of streams: solid, gas and liquid. All streams have associated with them values for composition, temperature and flow rate. Solid streams are treated as a homogeneous collection of a single specified particle size. Multiple particle sizes are handled by specifying multiple solid streams.

OSP currently contains 13 computational modules. These modules have been kept relatively simple but allow many of the important oil shale physical and chemical processes to be modeled. The modules rely on one of two simplifying assumptions, either one-dimensional co-current flow or complete mixing. The one-dimensional co-current flow construct allows particle/gas systems to be modeled, such as a dense phase moving packed bed, or a dilute phase lift-pipe. The complete mixing construct has utility in modeling fluidized bed systems. Using some combination of these two module types, a variety of unit operations can be simulated.

The moving packed bed pyrolyzer provides a good example of how OSP operates. In this unit, the solids travel from top to bottom in plug flow, while a sweep gas and vapors produced in the bed travel radially from centerline to wall, where vapor removal ports are located. This non co-current gas solid contact is modeled within OSP as a series of well mixed modules coupled from top to bottom to simulate the solid motion.

Under most circumstances, pilot plant results are uses as a guide in verifying modeling assumptions. However, in one case, the discrepancy between model and pilot plant could not be rectified by altering model constructs. This was the case for the measured amount of carbonate decomposition observed from the pilot plant.

Laboratory Experimental Results

We have recently published retorts of fundamental laboratory experiments in oil coking kinetics[2], char combustion kinetics[3] and flue gas NOx reduction with ammonia addition[4]. Our latest laboratory study focused on carbonate decomposition kinetics.

Decomposition kinetics were measured in the laboratory as an aid in resolving the discrepancy between model and experiment. In the experiments, raw shale was first prepared via slow combustion at low temperature (200 to 350 °C) to remove all of the kerogen while not affecting the initial mineral carbonate concentrations. The prepared sample was then dropped into a fluidized bed and the temperature was ramped from initially 500 °C to 850 °C at 5 deg/min. The evolved CO_2 was measured on a mass spectrometer as a determinate of the rate of carbonate decomposition. Analysis of the dropped sample showed 96% of the carbon to be inorganic. A first order kinetic expression was fit to the experimental data. The kinetics were faster, particularly at low temperatures, compared to previously reported results used in the OSP model. Incorporating these kinetics into OSP has eliminated the large discrepancy between model and experiment.

Economic and Commercialization Results

Our commercial concept for the HRS process combines reliability and efficiency with the production of high valued products and minimum environmental disruption. Economics for a 10,000 Bbl/day plant producing a slate of high valued products and co-producing electric power is discussed below.

Development of an efficient, reliable retorting process coupled with pioneering efforts by others in using shale oil as a chemical feed stock for the manufacture of high valued specialty chemicals and for use as an asphalt binder, using the Shale Oil Modified Asphalt (SOMAT)[3] process combine to make for a small scale venture potentially profitable in today's market.

The heart of the 10,000 Bbl/day commercial HRS process is depicted in Figure 2. This plant produces shale oil combined with generation of electricity for on-site use and off-site sale. The power cycle provides a means for spent shale cooling and fuel gas utilization while providing enough revenue to offset the cost of mining the raw shale.

The produced shale oil is split into three fractions. Ten percent is converted into specialty chemicals, unique to shale oil, which could command a sale price of $100/Bbl. The heaviest forty percent is converted into an asphalt binder (SOMAT) for road paving, with a projected sale price of $100/Bbl. The lightest fifty percent is then hydrotreated/refined producing a slate of transportation fuel products ranging from diesel to aviation fuel. The wholesale market price for this transportation fuel mix, averaged in 1993, $.73/gallon or $31/Bbl.

The economics of this 10,000 Bbl/day plant are shown in Table 3. Cost and revenue items are reported on per capacity basis, assuming a 330 day operating year. The capital cost on the $725 million dollar plant with a 15 percent internal rate of return (IRR) on investment equals a capital charge of $37/Bbl. Operating costs including mining, disposal, plant operations and maintenance are estimated by direct comparison with Unocal's operating experience at Parachute Creek. These costs are estimated at $23/Bbl. Hydrotreating/refining costs of $10/Bbl are also based on Unocal's experience, with fifty percent of the product needing hydrotreating in the current plant configuration, this equates to a $5/Bbl cost. The next two operating costs involve conversion of forty percent of the product into a shale oil modified asphalt binder SOMAT and ten percent into specialty chemicals.

Next in the table are the four products from the plant. The first is excess electrical production capacity obtained from the cooling the waste shale and on-site combusting of produced fuel gas. Off-site electrical sales amount to a $5/Bbl credit. The sale of SOMAT and specialty chemicals, each assumed to have a value of $100/Bbl bring in an additional $50/Bbl revenue, leaving a $15/Bbl gap between costs and revenues, with fifty percent of the product left. Here the table deviates from the heading by reporting the required price of the transportation fuel products needed to achieve the fifteen percent rate of return desired. As shown, the required price is about equal to the wholesale price of these fuels during 1993. Thus, the economics for a 10,000 Bbl/day plant have been shown to provide a fifteen percent rate of return on investment in today's market.

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[3] The New Paraho Corporation, Aurora, Colorado.

Figure 2. Commercial Oil Shale Plant Concept

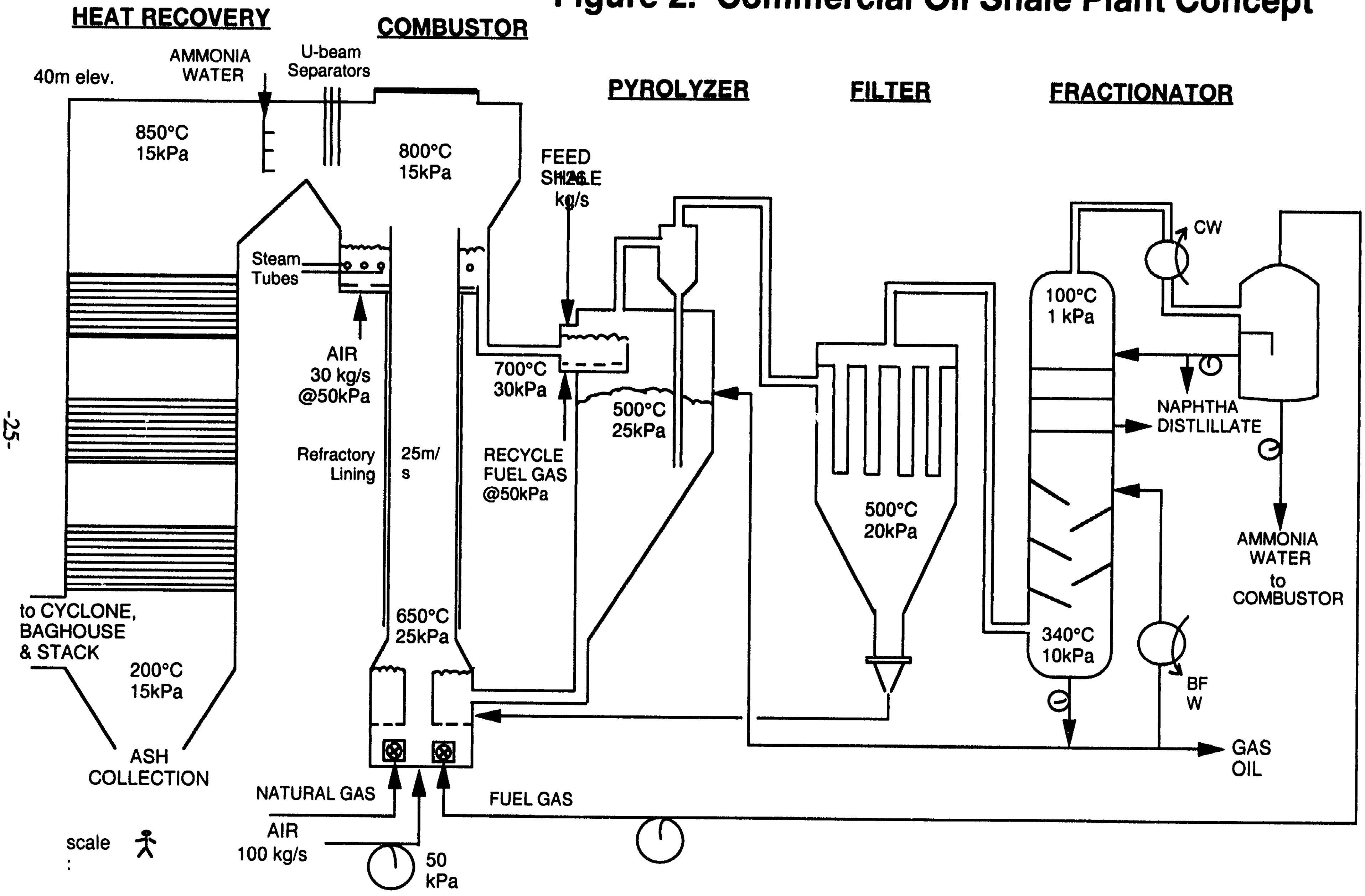

Table 3. Economics of a 10,000 Bbl/day Plant

Description	Cost & Revenue $/Bbl
Capital cost @ 15% IRR - 725 Million	$37
Unocal's projected operating costs (full production excluding hydrotreating)	$23
Hydrotreat/refine 50% into transportation fuel (cost $10/Bbl)	$5
Convert 40% to SOMAT (seasonal average - cost $10/Bbl)	$2
Convert 10% to specialty chemicals (cost $10/Bbl)	$3
Subtotal - Capital & Operating Costs	**$70**
Off-site electricity sales @ $.03/kWh	($5)
SOMAT asphalt additive @ $100/Bbl	($40)
Specialty chemicals @ $100/Bbl	($10)
Required transportation fuel price for 15% rate of return	**$30**
Transportation fuel wholesale price in 1993	**$31**

Table 4 shows the impact of scale up on economics. As more capacity is added, the capital and operating costs per barrel decline, while revenues from the production of high valued specialty products decline. The required motor fuel price increases to $39/Bbl or $.93/gallon to achieve the desired fifteen percent rate of return, which is a foreseeable rise in fuel price over the next 1-2 decades. In addition, process improvements and innovation based on experience will aid in lowering the overall cost projections for this plant.

Table 4. Economics of a 50,000 Bbl/day Plant

Description	Cost & Revenue $/Bbl
Capital cost @ 15% IRR - 2,225 Million	$23
Operating costs including hydrotreating/refining	$25
Subtotal - Capital & Operating Costs	**$48**
Off-site electricity sales @ $.03/kWh	($5)
SOMAT asphalt additive 15% @ $60/Bbl	($9)
Specialty chemicals 5% @ $60/Bbl	($3)
Required transportation fuel price for 15% rate of return	**$39**

CONCLUSIONS

Oil shale is one of the most promising alternatives to dwindling petroleum supplies in the US, with over 600 billion barrels of recoverable deposits in the Piceance Basin of Colorado alone. A commercial industry would provide domestic feed stock for specialty chemicals, asphalt binders for longer lasting roads, alternative transportation fuel and electric power at a cost competitive in today's market. A demonstrated technology would provide domestic jobs, aid the US balance-of-payments and give a measure of energy security by serving to cap the price of imported oil and provide an option to partially replace foreign oil in an extended national emergency.

A small-scale industry, today, exploiting high valued products would provide the framework for technological advancement to bringing down the cost for a potential large-scale fuels industry tomorrow.

The Government owns most of the resource, and stands to benefit from a commercial oil shale industry through lease and tax revenues. Technical development, however, has been left to industry, with the cost of development proving to be too large for any single company to bear. A small investment by Government, now, could bring into being a small oil shale industry which would pave the way for further development, revenues and jobs in the future.

The LLNL Hot-Recycled-Solid process has the potential to improve existing oil shale technology. It processes oil shale in minutes instead of hours, reducing plant size. It processes all oil shale, including fines rejected by other processes. It provides controls to optimize product quality for different applications. It co-generates electricity to maximize useful energy output. And, it produces negligible SO_2 and NO_x emissions, a non-hazardous waste shale and uses minimal water.

FUTURE WORK

Dust Removal

One of the major obstacles to successful operation of a shale oil plant is the removal of fine dust from the produced oil. We have explored two methods for dust removal: 1) using hot-vapor filters and 2) using heavy oil recycle.

In the first method, a filter is placed between the retort and condensers to trap the dust while the oil is still in the vapor phase. We have tested both metal mesh and ceramic filters in our pilot plant.

In the second method, the shale oil is fractionated and the heaviest fraction, containing the dust is recycled back to the pyrolyzer where the dust is deposited and the heavy oil is cracked into lighter boiling oil fractions.

Although we have tested both methods using our pilot plant. additional testing is required to quantify performance. Results from both of these tests are being held as CRADA protected data.

Scale Up

We have proposed a scale up of the HRS process to begin answering major question which cannot be addressed at the present scale. Our first proposal is to build and test an HRS module at the 100 tonne-per-day scale in cold-flow at LLNL. Following successful of cold-flow operations, we would then propose to build and operate a hot facility in Colorado, making enough raw shale oil for continued testing of the SOMAT process by The New Paraho Corporation.

As stated, our ultimate goal is commercialization of the process. We believe that commercialization is possible by taking advantage of high-valued products early on in order to build and test the process allowing innovation and improvements to further bring down the cost of future plants. Through the identification of high valued products, such as SOMAT and specialty chemicals, commercialization may become a reality in the near future.

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LF-1.2

Shale Oil from the LLNL Pilot Retort: Metal Ions as Markers for Water and Dust

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CONTRACT INFORMATION

Contract Number	W-7405-ENG-48
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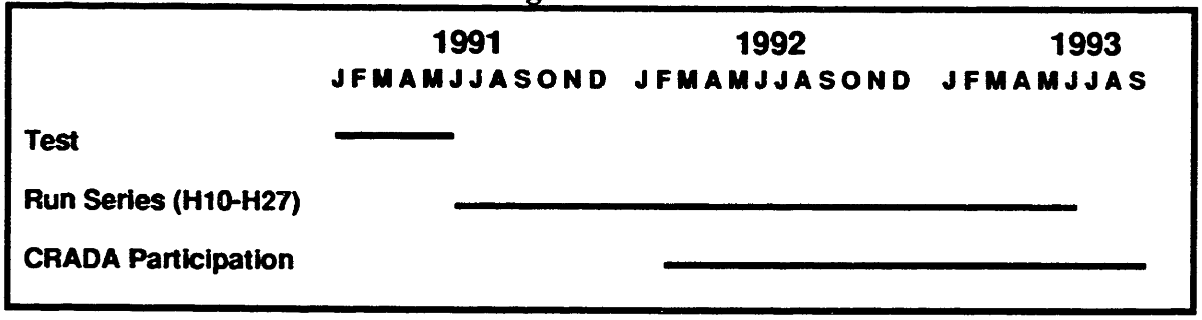
METC Project Manager	Hugh Guthrie
Period of Performance	January, 1991 to September 30, 1993
Schedule and Milestones	

Program Schedule



Abstract

A metal ion found primarily in one of the three phases (oil, water, or dust) can serve as a marker for that phase. Emulsified water contains most of the magnesium detected in a shale oil. Extraction with saturated salt solution removes most of that Mg. The Mg content of retort water and the percentage of water in the oil (by ASTM D-4006) provides a good estimate of an oil's Mg content. Mineral matter elements with poorly water soluble carbonates (or oxides) at pH 8 (calcium, for example) serve as markers for dust. When the water is separated from the main and light oil fractions before adding the heavy fraction containing dust, a much drier oil can be obtained. However, when done in this way, a powder containing Ca and Si remains in the oil; it cannot be completely removed even by filtering through a 0.24-μ frit. Iron, and certain other transition metal ions, is quite oil soluble. Extraction with dilute nitric acid to remove basic amines reduces the Fe content of shale oil. Unlike carboxylate-complexed metal ions in crude oils, the iron in shale oil does not extract efficiently into an aqueous EDTA solution (pH 5.9). Distillation of shale oil leaves most of the iron and other metals behind in the vacuum residuum. Shale oil corrodes the hottest condenser's steel interior; this is the chief source of iron in the oil.

Introduction

The Lawrence Livermore National Laboratory's (LLNL) Oil Shale Project produces shale oil in a hot-recycled-solids (HRS) pilot retort.[1] The goals of the Project are to develop this retorting methodology while gaining a better understanding of oil shale pyrolysis and shale oil chemistry. Increasingly, oil characterization has become the focus of the chemistry effort.

Shale oil from the LLNL retort, like most shale oils, ordinarily comes well mixed with water and dust. A representative oil must be obtained quickly for characterization, while avoiding air contact and volatile loss. Requiring quick turn-around forces a compromise, and some water and dust remain with the oil. These substances in oil influence analytical data, impart inhomogeneity with associated sampling problems, and possibly, speed aging. With dust and water slowly separating, metal analysis by inductively coupled plasma, atomic emission spectroscopy (ICP-AES), in particular, shows poor repeatability.

Analytical data collected to date force the conclusion that HRS shale oils produced in a standard way are very similar to Colorado shale oils produced by other heat-and-collect processes. Table 1 compares an LLNL shale oil (shale oil *A*) with bulk shale oils analyzed at Gulf by Stauffer and Yanik 15 years ago.[2] Figure 1 shows D-2887 simulated distillations of some recently prepared oils, including shale oil *A*. The remarkable similarity of these oils is testimony to the uniformity of Green River Formation kerogen. Yet, the data hide important details of the oils, such as unsaturation and aromaticity. The simulated distillation curves need to be adjusted for residuum content and relative response factors of compounds eluting at each temperature if they are to provide an accurate comparison. Nevertheless, the generalization that all simple thermal processes produce the same Colorado shale oil seems correct.

Table 1. Whole Shale Oil Properties.

Source: Retort:	Dow[2] Tosco	Paraho[2] Paraho	LLNL HRS *A*
Gravity, °API	20.7	20.1	20.5
Viscosity, SUS: @130°F	85.7	121.4	87.0
Pour Point, °F	+75	+85	+15
Carbon, wt%	84.52	84.83	84.78
Hydrogen, wt%	11.14	11.51	11.36
Sulfur, wt%	0.70	0.58	0.69
Nitrogen, wt%	1.99	2.04	2.36
Oxygen, wt%	1.32	1.24	1.63
Arsenic, ppm	13.9	20.9	24.8
Ash, wt%	0.20	0.03	0.05
Vac Resid, vol% 960°F+	26.84	30.97	30.5

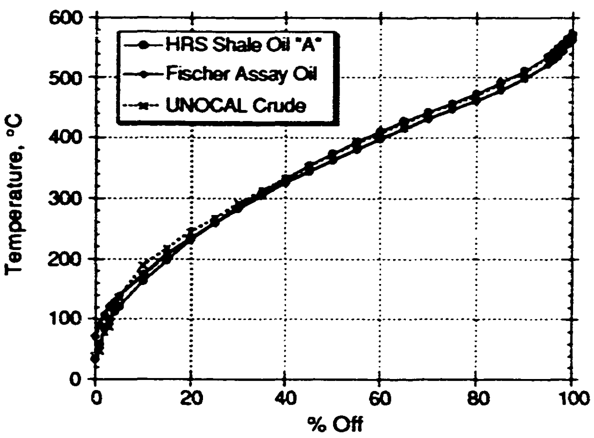


Figure 1. ASTM D-2887 simulated distillations.

For a series of HRS retorting experiments, certain oil properties reflected processing variables such as condenser efficiencies, yield loss by coking or cracking, and introduction of chemically active reagents (including steam and burnt shale).[3] However, trace metal analyses of HRS shale oils did not vary in a logical way with processing changes but wandered widely and unpredictably. This is not a unique observation. For at least 25 years, unpredictable metal analyses have been a recurring complaint.[4] The most notable feature of an extensive shale-oil metal-content data base is the wide range of analysis data.[5] This report addresses factors that influence the metal content of shale oil with the goal of better understanding the chemistry.

Experimental

Samples

Shale oil was prepared in the HRS pilot retort.[1] Dust was filtered off and water separated after freeze-warm cycles. An 8-gal sample of each oil was obtained for characterization. Homogeneous shale oil samples were prepared by mixing on a shaking tray for 0.5 hour. A valved spigot extending to the midpoint of the oil was used for transfers; oil was driven out of the brown glass bottle via the spigot by applying an argon head pressure. Dried shale oils were obtained by adding 10 wt% activated 4Å molecular sieve. After intermittent shaking for one day and then standing over the sieve for a week or more, the dried oil was decanted.

Certain shale oils were extracted with the following aqueous solutions (1:1 v/v): a) saturated NaCl, b) half-saturated dibasic ethylenediaminetetraacetic acid (EDTA), c) 0.35% HNO_3, and d) 1.4% HNO_3. Acid extractions were carried out in centrifuge tubes under argon. After warm centrifuging, the oil was separated, dried over a K_2CO_3/Na_2SO_4 mixture, and filtered. Extractions with salt solutions were carried out in separatory funnels; after shaking for 0.5 hour, the mixtures were warmed to 50°C to speed separation and were allowed to stand overnight.

Inductively Coupled Plasma/Atomic Emission Spectroscopy (ICP-AES)

Following a recommended method,[6] 2 g of shale oil (or the 1050°F$^+$ vacuum residuum) was ashed in an open Pt crucible at 500°C for 2 hours. After ashing, HCl (5 ml, conc.) was added. The solution was heated to 150°C on a hot plate and held for 20 min. ICP-AES metal determinations were made after transferring the solution to a 50-ml Teflon volumetric flask with deionized water. A xylenes solution containing acetonylacetate complexes of Co, Cu, Fe, Ni, V, and Zn mixed with NIST metal-in-oil standards for Ca, Mg, and Na was prepared so each element was present at near its concentration in shale oil. This and NIST's standard fuel oil #1634b were ashed and run as controls (both neat and spiked into shale oil). Sc was always added as an internal standard. A Fison (formerly ARL) model 3560 simultaneous ICP-AES measured Al, Ca, Fe, Mg, Na, and Si. Other elements (Co, Cu, Ni, V, and Zn) were determined with a Jobin Yvon Instruments sequential ICP-AES, model JY-38. Shale oil samples also were sent to commercial laboratories for ICP-AES analysis where they were diluted with *o*-xylene or kerosene and were aspirated into the instrument.

Retort water was separated from shale oil and filtered. The water always contained a few percent of the more water-soluble oil components. It was diluted 5:1 and 25:1 to adjust the ion concentrations for best accuracy and to prevent extinguishing the plasma flame.

Water Analyses

Water in oil was determined by a Karl Fischer procedure, by an ^{17}O-nmr method, and by azeotropic distillation following ASTM D-4006 with certain modifications. Results by the last two methods agreed well, and the D-4006 procedure with toluene as solvent proved to be the most reliable and convenient technique, provided the sample size was large (i.e., 250 g of oil). Generally, shale oil was sampled for water and ICP-AES metal analysis during the same transfer operation. Certain samplings and water analyses were done after an oil had stood for a time following shaking.

Oil Inspection Data

A LECO SC132 Sulfur Determinator was used for sulfur analysis. Organic elemental analysis (C,H,N,O) was provided by Midwest MicroLab and verified in-house using a LECO CHN-600 Micro-CHN Determinator. A Mettler model DA-300 density meter measured specific gravity. The ASTM D-4530 method was used to determine viscosity. Simulated distillation followed the ASTM D-2887 method. The National Institute of Petroleum and Energy Research (NIPER) provided petroleum tests to ASTM specifications or by other standard methods. These included the following: pour point (D-97), distillation (D-2892), vacuum distillation (D-1160), total nitrogen (D-4629 Mod.), basic nitrogen (UOP 269), ash content (D-482), wax (UOP 46), and arsenic (ICP-AES in kerosene).

Results and Discussion

HRS shale oils had a higher metal content than typical crude oils. Iron, in particular, was present at high levels—often 300-400 ppm. Only a few other shale oils (for example, that from the gas combustion retort[3]) have had iron in this range. High Fe content has a negative impact on oil quality. Metals poison catalysts and complicate water disposal. Thus, the metal ions in HRS shale oil were of immediate interest and concern. Goals of this study were to provide definitive answers to questions such as the following:

- If metals in the oil come from retort corrosion, can this be avoided?
- If metals are extracted from dust that collects with the condensate, can oil-dust contact be minimized?
- If metals distill as complexes, can they be de-metallated or destroyed in a simple way?

Understanding the nature of metal ion association with shale oil components was necessary information and a first step toward addressing these questions.

ICP-AES analyses of shale oils initially generated by the HRS process agreed poorly from laboratory to laboratory (see results of shale oil *A* analyses in Table 2).

Table 2. The Effect of Dust and Water Present in Shale Oil *A* on ICP-AES Reproducibility.

Element	LLNL	Lab I	Lab II
Al	5.6	<0.4	<0.2
Ca	4.4	1.1	<0.1
Mg	5.8	2.2	<0.2
Na	13	10.9	<0.2
Cu	5.4	5.0	3.1
Fe	340	304	435
Ni	16.4	15.1	21.1
V	1.8	2.1	2.4
Zn	8.6	6.6	6.9
Co	6.9	6.5	7.2
Cr	<2	0.24	

units: ppm

Problems with ICP-AES methods were ruled out because controls analyzed correctly in our Laboratory. Typically a xylenes solution containing Ca, Co, Cu, Fe, Mg, Na, Ni, V, and Zn at the level found in shale oil gave results within ±20% of the known concentration for all ions (when concentrations were at least 10 times the detection limit). Sodium often proved most difficult to analyze accurately since its concentration was seldom much above its 3-ppm limit of detection. The spread of results for certain Table 2 metals suggested difficulties in sampling heterogeneous oil-water-dust mixtures. Those elements that showed the worst scatter (Al, Ca, Mg, Na, and Cu) were likely candidates as water and dust markers.

How the oil is prepared and handled can contribute to difficulties in sampling. Shale oils from the LLNL pilot retort condensed in three fractions: i) a heavy cut containing dust but no water, ii) a main oil fraction with most of the water and about half the dust in it, and iii) a light oil cut plus water. Table 3 lists differences in how these three fractions were generated and treated to obtain oils for this study. These differences relate directly to water and dust content and indirectly to sampling difficulties.

Table 3. Work-up Procedures for those HRS Shale Oils Studied.

Oil	Conditions
A	**Water distillation:** Water distilled from heavy and main cuts during 2 days; then filtered and lights added.
B	**Standard method:** Mix of heavy and main cuts filtered; freeze/warm cycles to drop off water; lights added.
C	**Double filtration:** Main cut filtered; water dropped out; heavy cut added and re-filtered; lights added.
D	**Heavy cut omitted:** Main cut filtered with no heavy oil cut added; otherwise, like ***B***.
E	**Heavy cut coked to extinction:** Main cut filtered (no heavy fraction obtained); work-up like ***B*** and ***D***.
F	**Hot vapor filtering experiment**: Water removed from main fraction (<0.02% dust in oil); combined with heavies; filtered and again separated water; lights added.

Magnesium as a Marker for Water in Shale Oil

Shale oils were shaken, sampled, and analyzed for water content by an azeotropic distillation with toluene, a modified ASTM D-4006 procedure. During the same transfer, a sample was taken for metal analysis by ICP-AES. Those oils with appreciable water content generally contained more Mg, Na, and Cu than did dry oils. Table 4 lists metal ions of interest in two shale oils (*B* and *C*) and the respective retort waters. Ions added to oil by water are calculated and included in the table. Retort water from the main condenser fraction is used for the water metals analysis. This water is not an exact match to the emulsified water, but its ion content should be close. Magnesium in emulsified or dispersed retort water accounts for all the Mg in the oil. Sodium also is largely in water, but as noted, errors in Na analysis make it a poorer marker for water. Copper apparently results primarily from corrosion of new copper gaskets in the condenser train. Copper has both water and oil solubility. Retort waters varied wildly in Cu content, and occasionally water that condensed with lights accounted for most of the copper. Cu does not serve as a useful water tag.

Table 4. Retort Water as a Source of Magnesium in Shale Oils.

I. Element	Retort Water *B*	Oil *B* (3.26% H_2O)	Ions from H_2O in Oil, Calc'd	Dry Oil *B* (0.1% H_20)
Na	269	5.4	8.8	6.5
Mg	689	21.3	22.4	5.1
Ca	18.4	19.2	0.6	6.8
Fe	49	363	1.6	376
Cu	8.3	7.7	0.3	4.1

II. Element	Retort Water *C*	Oil *C* (0.39% H_2O)	Ions from H_2O in Oil, Calc'd
Na	194	2.9	0.8
Mg	688	2.8	2.7
Ca	18.9	128	0.1
Fe	52	301	0.2
Cu	57	5.3	0.2

units: ppm

Emulsified water separates from shale oil over a few weeks time. Figure 2 shows water separation kinetics (room temperature) for a shaken sample of shale oil *B* that had previously separated. Shaking disperses water, but does not cause all the separated water to again form the stubborn emulsion that was present initially—although, ultrasonic methods were not tried. Dust may well play an important role in making the original water-oil emulsion so stable. Distinct differences in original and subsequent oil-water mixtures have made it difficult to study appropriate methods for solving the emulsion problem. Others have encountered similar difficulties and have been plagued by the availability of only old samples unsuited for emulsion-breaking tests.[7] HRS shale oils differed in their tendency to emulsify water, both initially and later. Figure 2 cannot be generalized.

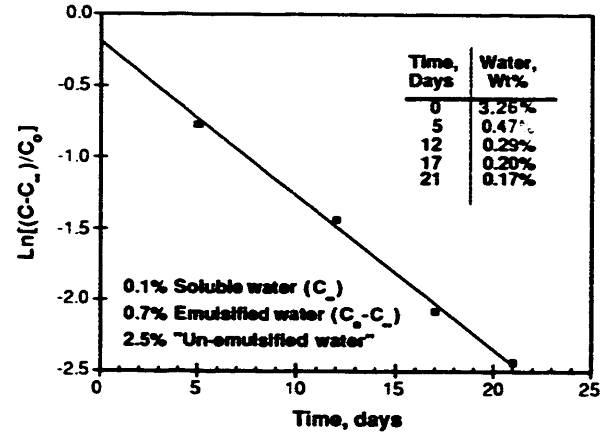


Figure 2. Separation of water from shale oil *B* according to a first-order rate law.

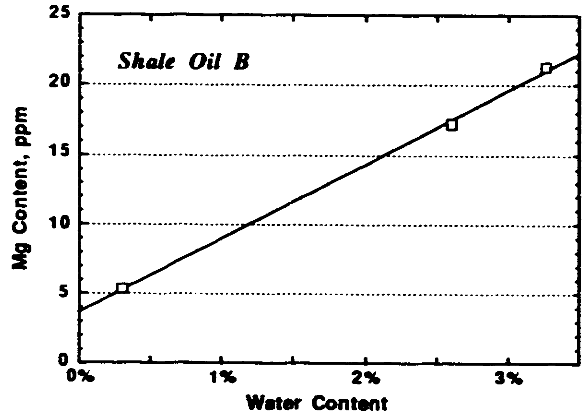


Figure 3. Evidence for water-phase Mg: the good correlation of an oil's Mg and water content.

The rate that water separates seems to depend on dust loading, nitrogen content, temperature, viscosity, and a variety of other factors. However, water content correlates with Mg content for each shale oil (see Figure 3 for oil *B* results). The tendency of water to slowly separate from shale oils and resist re-emulsification presents continual sampling problems. Two of the Figure 3 data points (3.26% and 2.67% water) are from analyzing "initial" samplings of a well-shaken shale oil (*B*). In one case, water was determined by ASTM D-4006 and in the other, by ASTM D-2892/1160 distillation (in which case, Mg was determined in the vacuum residue). The difference in water content is typical of the sampling error.

Table 5 shows water solubility data for carbonate mineral cations present in oil shale. Ca, Mg, and Fe carbonates have relative solubilities remarkably similar to their ratio in retort waters (see Table 4). HRS process water proves to be a dilute ammonium carbonate/bicarbonate solution buffered with a variety of salts to pH 8.5±1, and it contains water-soluble (polar) oil components. Since $MgCO_3$ solubility is influenced by pH and enhanced by both CO_2 and NH_4^+, it (and other carbonates) should have a somewhat higher solubility in retort water than in pure water. Over time, aging and air exposure have an effect on the water. The buffer loses CO_2 and NH_3, dust contact (and so carbonate mineral saturation) is not maintained, and sulfates with their greater solubilities become increasingly significant. Once dust-free, the oils soon fail to give plots such as Figure 3. Of course, if there is insufficient water, some Mg will remain as part of the dust.

Table 5. Carbonate Salt Solubilities in Water.

Cation	Salt	Solubility @25°C in g/100 cc	Solubility @25°C in ppm
Ca	Calcite	0.0014	6
Mg	Nesquehonite	0.1790	314
Fe	Siderite	0.0067	32

As a wet oil stood and separated, dust also slowly settled. Consequently, several metals that fail to track water decrease just as do the water markers. This makes the results of drying studies ambiguous. A shale oil's Mg content changes insignificantly during the early stages of drying with 4Å molecular sieve. Apparently a supersaturated solution is generated, or perhaps, precipitated salts remain suspended in the oil for some time. Dust from molecular sieve increases the oil's Na, Al, and Si content. Eventually much of this dust and salt settle from the oil. A dry oil analysis (*B* with <2 ppm Al remaining suspended) has been included in Table 4. Problems associated with heterogeneity leave some uncertainty as to the form of Mg in dried shale oil.

Calcium as a Marker for Solids in Shale Oil

Magnesium is transported into the product collection region as dust. Solubility of its carbonate salt makes it a water marker. Salts with poor water and oil solubility are good candidates for dust markers. Major mineral elements of insoluble rock grains are the best choice. High solid-phase dilution complicates the use of trace elements (Ba, for example) as markers. Calcium should be a particularly good indicator of solids, and it has the characteristics expected of a dust marker. Given the low water solubility of its carbonate salt (see Table 5), less than 10 ppm Ca is found in retort water. The large scatter of results, when oils containing very little Ca (~1 ppm) were analyzed in kerosene (no ashing), could be attributed to dust's granular nature. Ashed dissolved samples gave better short-term repeatability.

Association of calcium with the water phase is ruled out, since for a set of HRS shale oils, Ca content fails to correlate with water (see Table 4). Shale oil *C*, with quite a low water content (0.23%), has a particularly high Ca and Si content (93 ppm), for example (see Table 6). Oil *C* was prepared by first filtering the main condenser fraction and separating away water. Then this main oil fraction was mixed with the heavy oil and re-filtered through a 0.24-μ frit. It was intended that dust in the heavy fraction function as a drying agent, but it is possible that water simply separates more easily from the main cut than from the main-plus-heavy cut Nevertheless, the resultant oil was low in water but high in Ca. The Ca content of this oil failed to decrease on standing 6 months—when sampled without shaking. Remaining calcium-compounds either are exceedingly fine, or have some oil solubility.

Table 6. An Elevated Ca Content of Shale Oil *C*, a Relatively Dry Oil Prepared by Double Filtration.

Element	Metal Content
Ni	8.0
V	1.4
Fe	187
Ca	76.7
Mg	1.6
Cu	3.5
Zn	2.8
Co	3.3
Na	3.5
Si	94

units: ppm

Si and Al also are expected to be good markers for solids in shale oil (see Table 6). However, our study of these elements was less extensive and is incomplete.

Iron as an Oil Component

Transition metal ions were chiefly oil soluble, apparently complexed by organic ligands native to shale oil. Iron is representative of this group of metal ions, and as the metal present at the highest level in most HRS shale oils, it is of major interest. Good repeatability and reproducibility of analyses provide evidence that iron is primarily an oil component and is not associated with dust or water phases. Iron content of shale oil is affected very little by filtration, settling, aqueous extraction, or sample preparation for ICP-AES (ashed/aqueous or in an organic matrix, not ashed).

Table 7 shows ICP-AES data obtained after extracting shale oil *D* with a saturated salt solution or half-saturated disodium EDTA. Saturated aqueous NaCl partially dries oil. The original crude shale oil contained 1.1% emulsified water; after washing with the brine, 0.6% water is left (based on the Na content of the brine and assuming the oil sodium was all from emulsified salt solution). Saturated NaCl replaces the water that was originally present and removes water soluble ions (Mg and Cu) in the oil; it partially eliminates solids (and hence, Ca) as an emulsion at the oil-water interface. Polar ligands have some slight water solubility (pH of the salt solution was 8.2 after oil contact), and removal of these ligands may have decreased the oil's Fe content very slightly. Aqueous EDTA competes for carboxylate-complexed metals and removes them from crude oil at pH 5.9.[8] However, EDTA captures Fe (and Ca) from HRS shale oil inefficiently (only a bit better than brine). Apparently few metal ions in this shale oil are carboxylate-complexed, as they often are in crude oils.

Table 7. Shale Oil *D* Extracted with Salt Solutions (1:1 v/v).

Element	Raw Shale Oil	*pH = 8.2* Sat. NaCl Extracted	*pH = 5.9* EDTA Extracted
Ni	5.5	5.5	5.6
V	<0.7	<0.7	<0.7
Fe	61.5	56.	49.
Ca	14.9	6.4	5.8
Mg	9.4	2.7	3.1
Cu	9.0	3.4	4.4
Zn	5.7	5.1	4.0
Co	1.8	1.8	1.8
Na	<1	884.	44.

units: ppm

Table 8. Shale Oil *E* Extracted with HNO_3 (1:1 v/v).

Element	Raw Shale Oil	0.35% Acid Extracted	1.4% Acid Extracted
Ni	2.7	2.9	1.7
Fe	42.5	22.1	7.1
Ca	2.5	3.1	2.5
Mg	3.0	1.2	0.6
Co	0.9	1.3	<0.8

units: ppm

Table 8 shows the effect of extracting shale oil *E* with aqueous acid. This shale oil had a base number of 42 mg KOH/g (or 1.1% basic nitrogen). Basic nitrogen compounds, including some capable of complexing iron, can be removed by strong acid extraction. Incomplete extraction

(0.35% HNO_3, 1:1 v/v) removes some iron; even more is extracted when sufficient acid is available to protonate all shale oil bases (1.4% HNO_3, 1:1 v/v). Since a volume reduction of about 25% accompanied acid extraction, the decrease in an oil's total Fe content was 25% greater than the Table 7 data might suggest.

The perception that heavy polar compounds act as emulsifying agents may well have merit.[9] Coincidentally, some of these polar compounds are excellent ligands. The somewhat lower iron content of oil *C* might have been due to activated solid acting as an adsorbant for polar compounds. Certainly, the data in Tables 7 and 8 implicate nitrogen heterocycles as iron complexing agents. Zn was similar to Fe in its response to brine, EDTA, and acid.

The behavior of iron can be contrasted with that of nickel. Nickel in crude oils associates strongly with heterocycles (including petroporphyrins) and is unaffected by an aqueous EDTA or acid treatment.[8] In shale oil, Ni, and also Co, seem to form tight complexes that decrease ligand basicity (and aqueous solubility) to a greater extent than Fe and Zn. As a result, Ni and Co are particularly difficult to remove from shale oil by acid washing. Iron seems to complex more loosely, at least in part, so it can be largely acid extracted.

Table 9. Characterization Data for Shale Oil *E* and Other HRS Shale Oils, Showing the Beneficial Impact of Secondary Processing Conditions.

Test	Shale Oil *E*	Shale Oil *D*	Average Oils *A*,*B*,*C*	St.Dev.
Gravity, °API	26.4	21.8	20.7	±0.8
H/C Ratio	1.57	1.62	1.60	±0.01
% Water	0.42	1.09		
1050°F+ Resid	7.9	14.5	22.3	±0.7
Wax, wt%	0.02	0.60	2.11	±1.27
%N	2.00	2.10	2.85	±0.72
%N(tot)	1.75	1.66	2.12	±0.19
Basic N	0.95	1.09	1.16	±0.19
As, ppm	22.9	23.6	30.7	±5.3

When the metal content of crude HRS shale oils *A* to *E* (see Tables 2, 4, 7, 8) are compared, shale oil *E* stands out as the highest quality oil. Acid extraction of metal and nitrogen compounds result in a further improvement. Table 9 collects some crude shale oil inspection data for the series of oils analyzed here. HRS shale oils *A*, *B*, and *C* were prepared in the pilot retort under slightly different conditions, but they are similar. Shale oil *E* has excellent API gravity, low wax and 1050°F+ vacuum residuum content, and somewhat reduced arsenic and nitrogen as compared with other shale oils. This oil (*E*) was prepared by selectively coking heavy ends during the retorting process (see Table 3). There was a penalty in terms of coking loss, but most lost product would have been consigned to the residuum fraction anyway.

Shale oil *D* was prepared as a standard oil for judging the quality of *E*. It consisted only of main and light fractions from the HRS retort. Heavy oil that condensed in the hot condenser was rejected. Wasting this fraction lowered the effective yield. Yet, oil *E* is superior even to *D* by most measures (see Table 9, and also compare Tables 7 and 8). By selectively coking the heavy cut, the metal content of the shale oil is reduced substantially (the oil *E* case). Attempted condensation to remove chelating agents present in the heavy fraction is less effective due to hot condenser inefficiencies (mist formation results in some dust and heavy oil blow-by; the oil *D* case).

Whence Metals in Shale Oil?

With specific markers for oil (Fe), water (Mg), and dust (Ca), it should be possible to draw conclusions concerning sources of metal ions in shale oil. For instance, since retort water becomes saturated with carbonate salts as it stands in contact with dust, those oils high in Mg content contain water (saturated with $MgCO_3$). Furthermore, a high Ca:Mg ratio usually indicates a relatively dry oil containing dust. When an oil's calcium analysis is quite high, there is a lot of dust present. Finally, with oil-soluble iron as a tag for inorganic oil impurities, experiments can be now devised to answer the significant questions concerning the origin of oil-soluble metals posed earlier.

If dust were entirely prevented from entering the condenser system during retorting, the importance of spent shale dust as a source of metal ions would be defined. Shale oil *F* was produced in the HRS pilot retort with the exclusion of down-stream dust. Only completely vaporized pyrolysis products, free of solids (<0.02%) and oil mist, were allowed to pass from the retort into the condensation train. Table 10 shows the metal content of this oil. Ca and Mg content are very low as a result of the near absence of dust. This retort water was not the usual saturated solution of carbonate minerals. However, the transition metals (Fe, Co, Ni, V, and Zn) were in the oil at a level typical of those HRS shale oils condensed with dust present (compare Table 10 with Tables 4 and 7). Thus, the large quantity of oil-soluble metal ions in this particular oil must have either distilled from the retort as organic complexes or formed after the vaporized oil entered the condensers.

Vacuum distillation of shale oil *F* by the ASTM D-1160 procedure, showed that less than 3% of the iron was in compounds sufficiently volatile to distill at 550°C (see Table 10). Consequently, neither dust nor volatile metal complexes contributed much iron to the oil, and condenser corrosion is implied. This is consistent with a very low Fe content (<1.5 ppm) for shale oil generated in an aluminum/glass system (i.e., under Fischer Assay conditions).[10] While others have not reported corrosion of this type, prior work has been done using other methods. These focused on other parts of the retort, or stressed oxidation, embrittlement, and acid attack.[11,12]

Table 10. A Lower Mg and Ca Content, But No Less Fe, for Shale oil *F*, Condensed Dust-Free.

Element	Shale Oil *F*	650-1050, VGO Cut	1050°F+ Vac Resid	Residuum's contribution
Ni	15.3	<0.6	51.0	11.9
V	2.0	<1	7.9	1.8
Fe	329	15	1330	310
Ca	1.25	0.23	6.4	1.49
Mg	0.25	0.01	1.1	0.24
Cu	20.5	<1	84.1	19.6
Zn	4.1	1.0	15.5	3.6
Co	6.5	<1	25.9	6.0
Na	2.15	0.95	7.9	1.9
Al	0.7	0.36	3.0	0.7

units: ppm

The low Fe content of shale oil *E* (with heavy ends recycled to extinction) would suggest that corrosion responsible for iron in HRS shale oils occurs predominantly in the hot condenser where the heavy fraction begins to condense. If corrosion is estimated from the Fe content of the oil, about one-third pound of iron per day was lost from the pilot retort's condenser. The 304 stainless steel of the hot condenser may have been the source of some nickel as well as iron in the oil. Unless corrected for nickel contributed by steel, Ni:V ratios of shale oils could be misleading. A need exists to better assess shale oil's corrosive properties toward all metals present in 304 stainless steel. Solubility of various metals in shale oil at condensation temperatures would be valuable information. Chromium, while a significant component of 304 stainless steel, is baredly detected in HRS shale oils (see Table 2).

One cannot totally rule out the possibility that metal ions distill as unstable compounds, short-lived complexes, or transient intermediates. Certain transition metal elements present at the few-ppm level probably come over during retorting. The oil-soluble organometallics (Co, Zn, and V) are in this group. They are unlikely corrosion products since they are unimportant components of 304 stainless steel. Yet, caution must be exercised in defining the source of any ppm-level metal. As noted earlier, gasket corrosion contributes some copper to the oil and retort water. A variety of metals are present as trace impurities in steel, and a small retort always has gaskets, welds, and connectors of various compositions susceptible to corrosion.

Cold shale oil in contact with metals, dust, and salts has some capacity for leaching surface elements. Additional ions from oil shale dust are taken up by an oil when the work-up includes heating to distill away water. In one instance, a sample prepared according to the procedure for shale oil *A* contained 580-ppm Fe. Refluxing several days with dust present apparently increased the amount of oil soluble metal. Since the surface-to-volume ratio decreases as retort size increases, corrosive action of the oil might be somewhat less at larger scale. Attention to making surfaces in contact with the hottest shale oil inert will be the practical solution to obtaining a product of low metal content. Modern inert materials are available for lining or coating surfaces of a hot condenser. Heat conducting, corrosion resistant materials used in the chemical process industry—including glasses and ceramics—should be well suited for this application. Monitoring tags for oil, water, and dust will prove valuable as new materials are evaluated and as processing methods to improve oil quality are tested.

Acknowledgments

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LF-1.3 Shale Oil Value Enhancement Research--Separation Characterization of Shale Oil

CONTRACT INFORMATION

Contract Number	DE-AC21-93MC29240
Contractor	James W. Bunger and Associates, Inc. P. O. Box 520037 2207 West Alexander St. (801) 975-1456
Contractor Project Manager	James W. Bunger
Principal Investigators	James W. Bunger
METC Project Manager	James D. Westhoff
Period of Performance	Phase-I: March 1, 1993 to October 31, 1994 Phase-II: October 1, 1994 to April 31, 1996 Phase-III: April 1, 1996 to April 30, 1997

OBJECTIVES

The overall objective is to develop a new technology for manufacturing valuable marketable products from shale oil.

Phase-I objectives are to identify desirable components in shale oil, develop separations techniques for those components, identify market needs and to identify plausible products manufacturable from raw shale oil to meet those needs. Another objective is to conduct preliminary process modeling and economic analysis of selected process sequences and product slates, including an estimation of prices, costs and profitability. The end objective of Phase-I is to propose technically and economically attractive separations and conversion processes for small-scale piloting in the optional Phase-II.

Optional Phase-II activities include the pilot-scale test of the Shale Oil Native Products Extraction (SO-NPX) technology and to produce specification products. Specific objectives are to develop the engineering data on separations processing, particularly those in which mixtures behave non-ideally, and to develop the conversion processes for finishing the separations concentrates into specification products. The desired process scenarios will be developed and economic analysis will be performed on the process scenarios. As a result of the process simulation and economic analysis tasks, a product manufacture and test marketing program shall be recommended for the optional Phase-III.

Optional Phase-III activities are to manufacture specification products and to test market those products in order to ensure market acceptability. The activities involve the assembling of the technical, market and economic data needed for venture evaluation. The end objective is to develop the private sector interest to carry this technology forward toward commercialization.

BACKGROUND INFORMATION

In prior research, James W. Bunger and Associates, Inc. (JWBA) examined the potential for manufacturing high-value commodity and specialty products from Western U. S. Green River shale oil. Based on this research, a product slate averaging $90/bbl value was projected as a feasible objective of a technology development effort. If such an objective could be achieved at reasonable costs, a basis for a profitable shale oil venture would be established. Further, because the feedstock would be a raw shale oil rather than an upgraded syncrude, the economics would be largely uncoupled from the price of crude, which has historically limited the price of the traditional product, syncrude, to unprofitable levels. **By processing a portion of raw shale oil for higher value products, it may be possible to develop a profitable first-generation facility, paving the way for larger facilities in the future.**

When developing technology for manufacture of high-value products from raw shale oil, the main questions that need to be addressed are:

1. What chemical types or functionalities are present in raw shale oil in greater concentrations then can be found in competing sources.
2. Which of these types promise the greatest market value.
3. What are the effective steps for isolating and manufacturing these products.
4. How well will the market accept these products.

Raw Green River shale oil contains high concentrations of both pyridinic and pyrrolic nitrogen types, which promise high market value. Approximately 50% of the molecules in raw shale oil contain a nitrogen atom and we have estimated that about 10% of the total barrel may be manufacturable into nitrogen-based products valued in excess of $1,000/bbl. Some of these products are 100% imported, there being no current domestic production. Other possible products include oxygenates (phenols, ketones, etc.), olefinic monomers, resins, waxes, sulfonate aromatics and others yet to be identified.

The 50-month Project was initiated in March 1993. This paper reports progress of the first six months of the project.

PROJECT DESCRIPTION

The overall project connectivity is shown in Figure-1. The final result, an experimentally verified process sequence and product slate, is developed through a detailed study of composition, product specifications, market needs, process research and modeling, and cost and profitability analysis. The program consists of three phases and 13 tasks.

Phase-I Identification of Desirable Shale Oil Components and Development of Separation Techniques for these Components

Task 1, NEPA Requirements

Completed as per regulations.

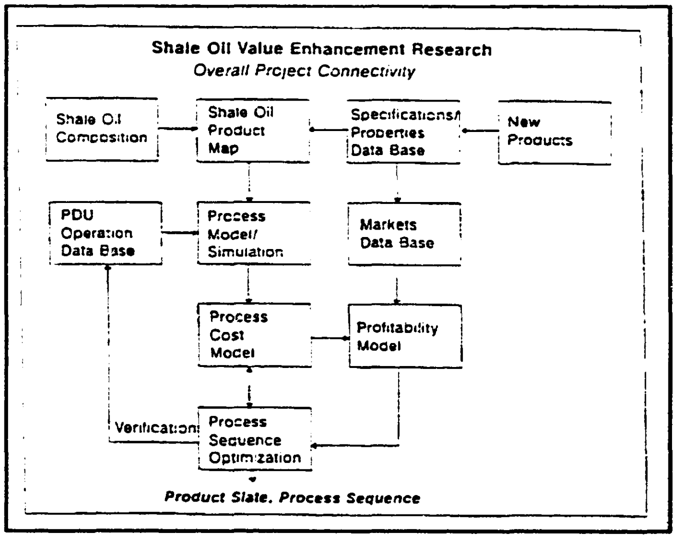

Figure 1

Task 2, Separation Characterization
Shale oil behavior will be determined in a thermodynamically logical separation sequence. Such a sequence involves distillation, liquid-liquid extraction, liquid-solid adsorption, and auxiliary finishing.

Task 3, Analytical Procedures and Characterization
A Z-BASIC (Z-Based Structural Index Correlation) method for rapid characterization of compound types has been developed by JWBA. Development of the instruments/methods for measuring the structural parameter values are being used for: a) rapid identification of target structures, b) measurement of partition functions at the molecular species level, c) process modeling at the compound-type level.

Task 4, Market Research and Product Identification
This key task will assess markets for products derivable from shale oil and will determine how shale oil can be processed to address emerging market needs. The optimum product slate will be determined based on the fit to markets identified.

Task 5, Separations Exploration
Exploratory studies will determine the best means for concentrating the target species.

Task 6, Conversion Exploration
Exploratory studies will determine commercially realistic means for converting concentrates into compounds of market interest.

Task 7, Process Modeling and Preliminary Economics
Results will be used to develop conceptual flow diagrams from which a preliminary assessment of costs and profitability will be made. Economics sensitivity analysis will be used to assess the effect of varying engineering and economic assumptions on profitability. Results will be used to project the likely outcome of Phase-II research and development of the conceptual processes.

Phase-II Technology and Product Development

Four specific tasks involving separations and conversion process development, product and process integration and economic analysis are to be completed. This work will provide engineering data, on small scale continuous units, for process optimization, and as a basis for venture development (Phase-III).

Phase-III Specification Product Development and Test Marketing

Three tasks will be conducted to manufacture specification products, introduce these products to the marketplace for market assurances, and to prepare a venture development plan designed to attract private sector funding.

RESULTS

Distillation

Raw shale oil was fractionated into four major cuts according to the scheme shown in Figure-2. The four cut points were chosen with the following rationale: <200°C restricts the compound types to monocyclics and is commensurate with the traditional refinery naphtha cut; 200-275°C restricts the compound types to dicyclics or less; 275-400°C is roughly equivalent to an atmospheric gas oil; >400°C is roughly equivalent to the atmospheric resid. The high initial point of the resid was chosen to enhance the quality of any lube oil base stock or wax product as well as to increase the volume of the 275-400°C cut.

Distillation is the first step in a thermodynamically-logical separation sequence. Distillation separates molecules on the basis of boiling point ($\Delta H_V/\Delta S_V$) which, in turn, is a strong function of molecular weight. Within a specified boiling range, the differences between polar and non-polar compounds are magnified. The narrower the distillation range, the more effective will be polar/non-polar

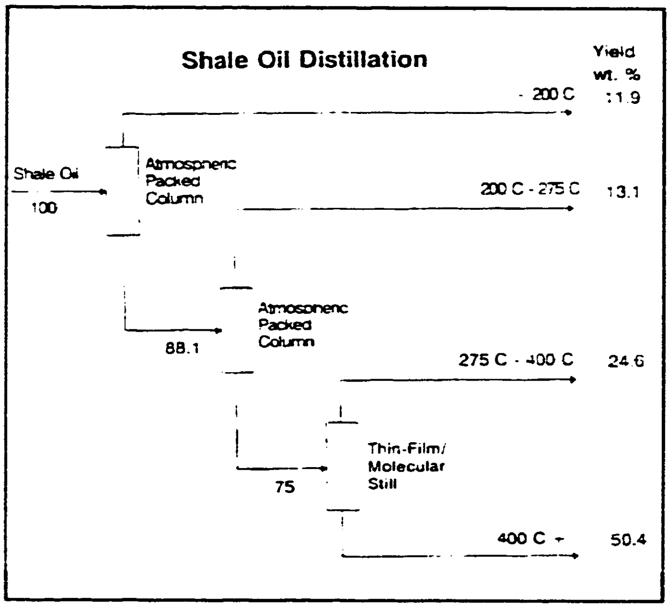

Figure 2.

separation by liquid-liquid extraction or liquid-solid adsorption. The number of distillation ranges selected (four) is sufficient to model variations in type and process behavior as a function of molecular weight, but not so many that the experimental work becomes unwieldy. The optimized process sequence (Phases-II and -III) may call for different cut points which will be performed at that time as indicated by the process modeling and economic analysis results.

Liquid-Liquid Extraction

A thermodynamically-logical second step is the liquid-liquid partitioning of a distillation fraction. In general, two immiscible phases consist of one predominantly polar phase and another predominately non-polar phase. When performing a liquid-liquid extraction, the partition function of individual species governs the proportion of that species appearing in the raffinate or extract. Ideally, one desires to extract a high percentage of polar types in the polar fraction and to leave a high percentage of the non-polar types in the non-polar fraction. (Free energy considerations tell us that 100% partitioning is not thermodynamically possible). In practice, the issue involves defining one or more objective functions which can be used to measure the quality of the separations.

Because a major part of the success of the project will hinge on the effectiveness of the liquid-liquid extraction steps, we are paying particular attention to: a) the selection of the solvent systems to employ, b) the effectiveness of the selected systems to perform the desired partitioning, and c) the ability to measure the thermodynamic behavior of target species so as to develop meaningful process models.

It should be emphasized that **if a liquid-liquid extraction model is well characterized by thermodynamic functions, process scale-up, on the order of 1,000 to 1, is feasible.** Thus, from a practical standpoint, the emphasis on liquid-liquid extraction as a technically and economically viable process step is justified.

Screening Studies of Liquid-Liquid Extraction

Selection of extraction solvents is an important task in discovering a desirable system. Initial emphasis has been placed on solvent matrix selection and screening. The primary criteria for solvent selection is process selectivity. In addition, solvent availability, cost, ease of recovery and handling are important considerations. A wide spectrum solvent types believed to be effective from a thermodynamic viewpoint were considered. Table 1 shows the solvent systems considered.

For purposes of screening, we initially conduct test-tube experiments observing whether or not phase separation occurs and what the relative volumes of the phases are in relation to the volume of oil and solvent added. For those systems showing promise, a series of larger scale "shake tests" using separatory funnels are completed. Samples recovered from the shake tests are subjected to simple analysis (density, elemental composition, etc.) to assess relative selectivity.

Table 1. Solvent Matrix

Solvent Type	Solvent Systems
1. Mineral Acids	H_2SO_4, HCl
2. Mineral Bases	KOH, NaOH
3. Organic Acids	Acetic Acid, Formic Acid
4. Organic Bases	Isopropylamine
5. Polar Hydrocarbon	N-methyl-2-pyrrolidone, Furfural, Phenol, MeOH, Isopropanol
6. Non-polar Hydrocarbon	Pentane, Hexane
7. Antisolvent	Water

Shake Tests

In managing the separations task, two considerations must be accounted for. First, we know that the extremely valuable components, i.e., >$1000/bbl, will likely be nitrogen compounds. Therefore, one simple objective is to optimize the separation of nitrogen compounds from non-nitrogen compounds.

Second, it becomes important that the systems selected promise reasonable commercial viability; one objective of the program being to develop the data needed to interest the private sector in the profit potential of pursuing subsequent development. As a result, we are concentrating our search on those solvents which are readily available and of reasonable cost.

In our screening work, we have adopted a simple method to assist in our screening by defining a parameter known as a coefficient-of-separation (CS). The coefficient-of- separation is a parameter commonly used in the extractive metallurgy industry and represents the degree to which an ideal separation of the target product is made. There are several definitions but the simplest one for our purposes is:

$$CS = \%N - \%\ non\text{-}N$$

where % N is the mole percent of all nitrogen compounds which are concentrated in the extract.

% non-N is the mole percent of all non-nitrogen compounds which are concentrated in the extract.

This definition accounts both for the % recovery (the first term) but also penalizes the quality of separation for non-nitrogen compounds that are extracted as well. It is believed that for a given system that the coefficient of separation will be inversely related to cost.

To illustrate, consider the data in Table 2 which are actual data for a polar/non-polar extraction using differing oil/solvent ratios. As the solvent ratio goes up, the amount of extract goes up and so does the % N recovery. However, the amount of non-nitrogen compounds extracted also goes up and the CS goes down. For this set of data, the maximum recovery of nitrogen with the least inclusion of non-nitrogen compounds occurs at an oil/solvent ratio of 1.0.

Separation of oxygen compounds will also be evaluated by this approach. The most attractive systems and oil/solvent ratios will be subjected to continuous counter-current extraction.

Continuous Liquid-Liquid Extraction

We have modified our continuous counter-current liquid extractor to handle smaller volumes of sample. The system is a 1" diameter, pulsed perforated tray (6 trays) column designed to operate at an oil feed rate of about 0.5 liter/hour.

Based on the shake tests results, we have conducted a continuous extraction at an oil-to-solvent ratio of 1:1. The coefficient of separation (CS) for nitrogen compounds was 0.68 and 94% of the nitrogen was recovered in the extract. Considering that there are non-nitrogen polar compounds present in the extract, this CS is quite high and establishes a promising benchmark by which to compare the effectiveness of other systems.

Analysis and Modeling

Boiling Point Correlations

One requirement of analysis is to develop algorithms for routine Z-BASIC characterization of shale oil fractions. The purpose is to use the GC-MS data to identify structures of commercial importance from complex shale oil fractions. The first step in this development is to predict boiling points of heteroatom containing compounds for which little or no data are available.

According to the Z-BASIC method, any molecule can be represented by the formula $C_nH_{2n+z}N_uO_vS_w$, where 'z' is a classification parameter. For a given homologous series, 'z' is constant and the addition of $-CH_2-$ groups increases the

Table 2
Illustration of Selectivity Criteria
% N in feed = 0.53 (8.33 mole % nitrogen compounds)

Oil/Solvent (single stage)	Fraction (% of feed)*	%N	% N Recovery	CS
1.68	R(67)	.25		
	E(33)	1.09	68	35
1.00	R(67)	.09		
	E(33)	1.40	87	60
0.50	R(47)	.07		
	E(53)	0.94	94	44
0.33	R(41)	.04		
	E(59)	.88	98	42
0.25	R(19)	.03		
	E(81)	.65	99	20

*E = Extract
R = Raffinate

value of 'n'. The prediction methodology is based on previously developed correlations between boiling point and molecular weight for paraffins($z=+2$), alkylmonocycloparaffins($z = 0$), alkylbenzenes($z = -6$) and alkylnaphthalenes($z = -12$).

For a parent compound, we obtain from the literature its boiling point and as many of its paraffinic substituted compounds as are available. According to the location of the compound, the two neighboring curves are chosen. That point lies at some fraction 'f', of the distance between the two selected curves, as do any additional points that data provide.

Using this approach, we generated curves of estimated boiling point vs molecular weight for parent compounds with from one to four condensed rings of varying degrees of saturation and functionalities. Table 3 shows various heteroatom containing compounds that have been correlated for boiling points from molecular weight using Z-BASIC methodology and prediction routines. The corresponding number of homologous curves generated is also given.

Figures-3 to 4 illustrate the nature of the homologous series curves for these heteroatom containing compounds. The legend for plots is shown in molecular structure for illustration purposes.

This procedure will assist us in identifying functional types seen in GC analysis of fractions obtained in Tasks 2, 3, 5 and 6. For a given peak from the GC, retention time approximates boiling point. From elemental analysis and mass spectroscopic data, the most probable 'z' and 'n' are calculated. These boiling point curves then tell us which among the possibilities is the one with the appropriate boiling point.

ΔH, ΔS and C_p from GC Runs

The objective of this methodology is to obtain thermodynamic properties such as enthalpy, entropy and heat capacities for components of a given GC peak. From thermodynamic properties, a host of other physical properties can, in principle, be calculated or estimated. Additionally, knowing the thermodynamic properties greatly assists the structural interpretation using Z-BASIC correlations.

The thermodynamic properties of adsorption and solution depend upon the column configuration, i. e., either packed or capillary column.

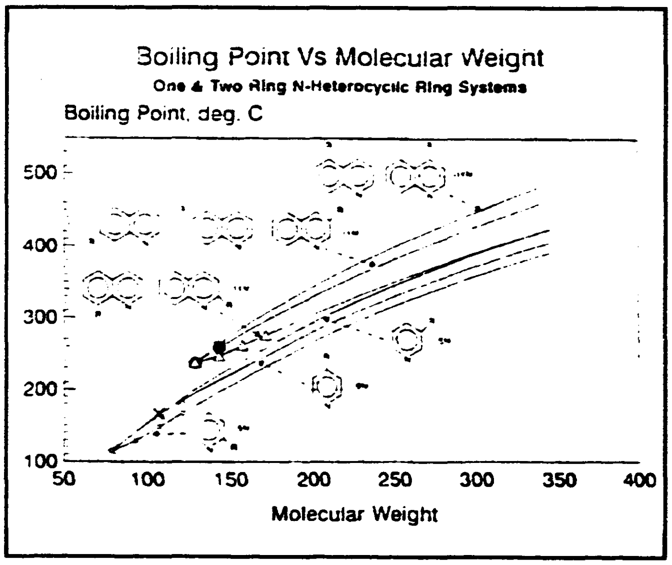

Figure 3.

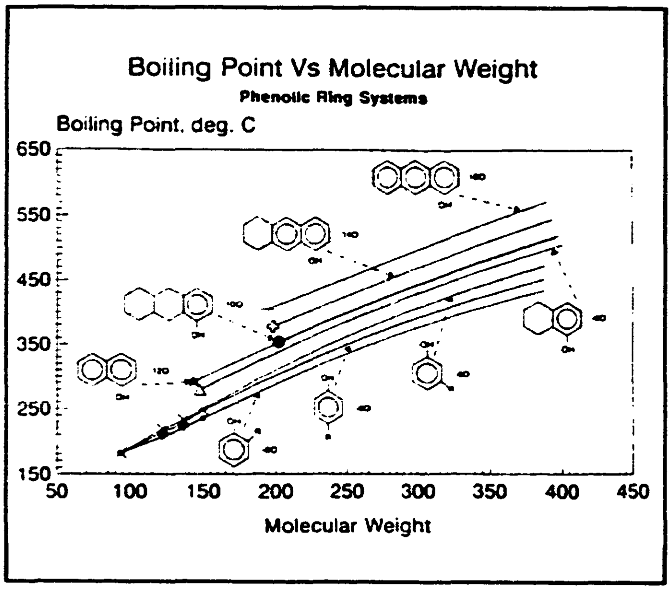

Figure 4.

Table 3
B. P. Correlations Completed

Compound	# of Curves
Nitrogen containing compounds	
1. Pyrroles	14
2. Pyridines	14
3. Anilines, primary amines	9
4. Anilines, secondary amines	9
5. Anilines, tertiary amines	3
Oxygen containing compounds	
1. Furans	12
2. Ethers	6
3. Phenols	14
4. Acids	10
5. Aldehydes	10
Sulfur Containing Compounds	
1. Thiophenes	11
2. Thiols	10
3. Sulfides	6
Nitrogen & Oxygen	
1. -OH on Pyridines	10
2. -OH on Pyrroles	10
3. -C=O on Pyridines	10
4. -C=O on Pyrroles	10
5. Furans & Pyridines	10
Nitrogen & Sulfur	
1. -SH on Pyridines	10
2. -SH on Pyrroles	10
3. Thiophenes & Pyridines	10
Polycyclic Hydrocarbons	8

The basic equations governing the methodology are:

$$tr = to\,\left(1+\frac{k}{v^*} \right)$$

where	tr	retention time
	k	partition coefficient
	to	retention time of non-adsorbing specie
	v^*	ratio of void volume to stationary phase volume in packed column

For a capillary column

$$v^* = \frac{r\,(1-\tau s/r)}{2\tau s\,(1-\tau s/2r)}$$

where	r	radius of the column
	τs	thickness of the stationary phase

This method of solving for thermodynamic properties differs from conventional analysis which is limited to retention times from isothermal operation. Partition coefficient 'k' values are calculated from retention times of temperature programmed runs. The number of runs is proportional to the number of properties to be determined. The solution to the simultaneous equations of properties is obtained by applying a Newton-Raphson technique. A computer program has been developed for the methodology.

Distribution of Partition Functions

The partition coefficient, by definition, is a measure of efficiency of separation for separation processes. It is specific to compound types and solvent systems. For a liquid-liquid extraction system, the distribution of partition coefficient is important for simulation of scaled-up operation from small continuous unit experiments.

To apply this method, mass balance data are required for various solvent loadings. Different data sets for different solvent types are needed to find the best solvent system for any shale oil fraction. GC-MS analysis of these fractions are being used for boiling point and molecular weight distribution.

From experimental data, the following parameters are defined:

$$C_s = \frac{Total\ Moles\ in\ Extract}{Total\ Moles\ in\ Raffinate}$$

$$R_s = \frac{Moles\ of\ Oil\ in\ Raffinate}{Total\ Moles\ of\ Oil}$$

The partition coefficient 'k' is then related to Cs and Rs as shown in the following equation:

$$R_s = \frac{\int_0^\infty \frac{FdK}{1 + C_s K}}{\int_0^\infty FdK}$$

The distribution of partition function is given by the equation:

$$F = K^{d}\ e{-}(ak^{3} + bk^{2} + ck)$$

The solution of this equation requires at least four data points, i. e., four solvent loadings. The distribution of partition coefficient is analogous to the boiling point distribution in a simulated distillation. Even though specific determination of partition coefficient is not measured, the range of partition coefficient values for certain compound types can be experimentally verifiable. This methodology is being used along with the coefficient of separation to evaluate different systems.

Market Research

Certain specific goals for the marketing task have been accomplished including:

(a) Gathering product specifications data and development of a specifications routine;

(b) Conducting company profiles database search by SIC to develop a preliminary list of potential partners in the shale oil project;

(c) Initiation of the Sinor and Zahradnik marketing subcontracts;

(d) Organizing a few companies to test shale oil and its derived fractions for activity testing;

Market Database

The structure of the market database and database files is shown in Figure-5. The areas in white background are completed. Blocks shown by the shaded areas are currently being completed.

Product Type Classifications

Development of a product specifications database is very critical to the marketability of shale oil products. Numerous companies have been contacted to obtain product specifications information. Often, supplier's product specifications are slightly

Table 4

SIC	Product Type Search	# of Potential Companies
2833	Chemical Manufacturing/Medicinal and Botanical	96
2821	Plastic Resins	84
5169	Chemical Products NEC(Misc.)	97
5169	Resins, Chemical products	5
2992	Lubricating Oil	200
2911	Petroleum and Coal products	23
3624	Carbon Products	35
5172	Petroleum Products NEC Oils	21
2899	Chemical Preparations (NEC) Oils	25
2911	Petroleum Refining	235
2834	Pharmaceutical Preparations NEC	66
2843	Surface Active Agents	32
2865	Cyclic crudes and Intermediates	82
2869	Amines, Acids & Esters	6
2879	Agricultural Chemicals	71
2869	Fragrance Chemicals	4
2865	Tar Products	4

different from the standard in order to gain a competitive advantage. Thus, it is required that the database have multiple specifications for the same product depending on the source/supplier.

The product specifications database routine has approximately 50 fields to cover a wide range of specifications from CAS number to composition. At present there are 25 products in the database for which specifications are available from at least one commercial source.

Another part of the database development includes routines for manipulation of historical supply, demand and price data to project growth patterns. Basic data retrieval and recasting is completed. Program features include data retrieval for previous years and annual data for all states. This routine is specially used to integrate subcontractor data input and evaluation.

Company profiles database from DIALOG has been searched by SIC of target chemicals and product types. The main purpose for the compilation of the list is to obtain potential candidate companies for commercialization venture of shale oil project. From this list, it is intended to narrow down the list to a manageable size for first round contact.

The list of SIC numbers with product categories is given in Table 4.

Future Work

In the short term, we are endeavoring to conceptualize a commercial process. To accomplish this, we will extend our search for plausible extraction systems to include all distillation ranges. Secondary extractions/conversion of concentrates will also be explored. For example, we are looking at dealkylation, polymerization and derivatization as selected approaches for conversion of concentrates of compound types to target products.

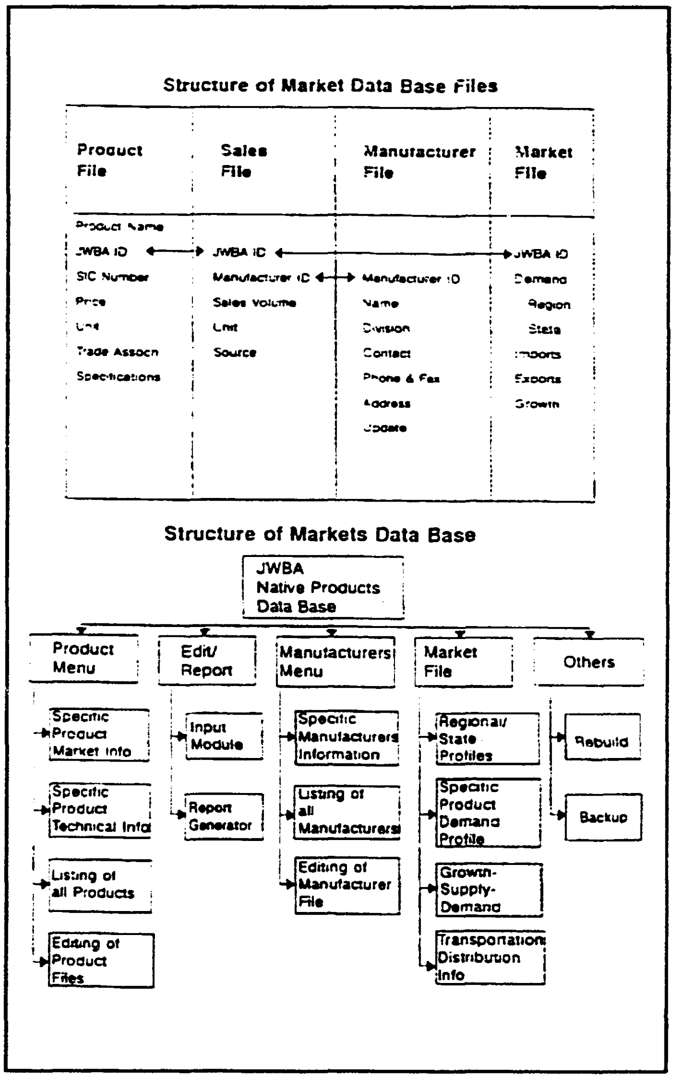

Figure 5

Specifically, we will complete the necessary methodologies for characterization, thermodynamic analysis and process modeling and use these techniques to evaluate separation and conversion performance. Various sequences will be experimentally performed and results analyzed by Z-BASIC techniques. Various integrated sequences will be computerized. From this we can perform initial cost and profitability analysis. Our initial attempts will reveal those areas where additional exploratory research is needed, which will then be performed during the remainder of Phase-I.

At the completion of Phase-I, we expect to have assessed the technical, market and economic feasibility of the Value Enhancement Concept and to have established the basis for engineering development (Phase-II) and market assurances (Phase-III).

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LF-1.4 Oil and Gas Yields from Devonian Oil Shale in the 50-lb/hr KENTORT II Process Demonstration Unit: Initial Results

CONTRACT INFORMATION

Cooperative Agreement	DE-FC21-90MC27286
Contractor	Center for Applied Energy Research University of Kentucky 3572 Iron Works Pike Lexington, KY 40511 (606) 257-0265 (606) 257-0302 (FAX)
Contractor Project Manager	Thomas L. Robl
Principal Investigators	Scott D. Carter Darrell N. Taulbee
METC Project Manager	J. Keith Westhusing
Period of Performance	September 28, 1990 to March 27, 1994
Schedule and Milestones	

FY93-94 Program Schedule

	S	O	N	D	J	F	M	A	M	J	J	A
Retort Shakedown	—	—	—									
Retort Test Matrix			—	—	—	—	—	—				
Product Characterization			—	—	—	—	—	—				
Economic Evaluations						—	—	—				

OBJECTIVES

The broad 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. Many of our objectives have already been realized. The retort has been successfully constructed and the shakedown phase is essentially complete. In addition, much of the coking and cracking kinetics experiments have been completed which will provide important information for the operation of the retort. We are now entering the testing phase for the retort which has the following objectives:

- Determine any relationships between the retorting conditions and the yield and characteristics of the products, and compare the results to those from the bench-scale shale oil cracking and coking experiments.
- Study and develop alternative applications for the products from the KENTORT II process. In particular, asphalt performance tests will be conducted on the heavy fraction of oil produced during the testing phase.

BACKGROUND INFORMATION

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 is not plausible.

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 because of the small size of the unit, 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 study of secondary coking and cracking reactions of model compounds has been initiated to more fully understand these phenomena. By having basic data which is directly applicable for the materials and conditions of the KENTORT II system, we will have a reliable guide for the selection of operating parameters for the 50-lb/hr retort which will either maximize oil yield or improve oil quality.

The scaled-up retort provides the opportunity to conduct tests on larger quantities of oil products. One of the potentially attractive options for the heavy fraction of the shale oil is for use in asphaltic applications. It would be a tremendous economic advantage to recover a high value product from the heavy ends without costly hydrotreating. By producing a high value material, the economy of scale for an oil shale plant would be lowered, and it would be much easier to get an industry off the ground in the near term.

PROJECT DESCRIPTION

The project is divided into three main tasks. The tasks which are yet to be completed are 2.2, 3.2, and 3.3. The task list for the entire project is 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

RESULTS--CONSTRUCTION AND SHAKEDOWN OF 50-LB/HR KENTORT II PDU

Process Overview

Reactor. The KENTORT II process is a fully integrated four-stage fluidized bed oil shale retort. The pyrolysis, gasification and cooling zones are aligned vertically and share a common fluidizing gas. The combustion zone is adjacent to the gasification section and a separate gas stream (air) is used for fluidization (see Figure 1). All beds are designed to operate in the bubbling mode, and cold-flow studies have shown that a gas velocity of about 3 ft/s provides proper fluidization for an 8 x 60 mesh particle size range.[11]

Raw shale at a rate of 50-lb/hr is fed over-bed to the pyrolysis zone which is the uppermost bed of the reactor. The fluidizing medium is a mixture of steam and product gases from the gasification stage below. Heat is provided to the pyrolysis section by a combination of fluidizing gas and recirculating solids from the gasification zone which are injected directly into the bed. The rate of solids which are recycled from the gasifier is controlled by an aerated J-valve. The pyrolysis

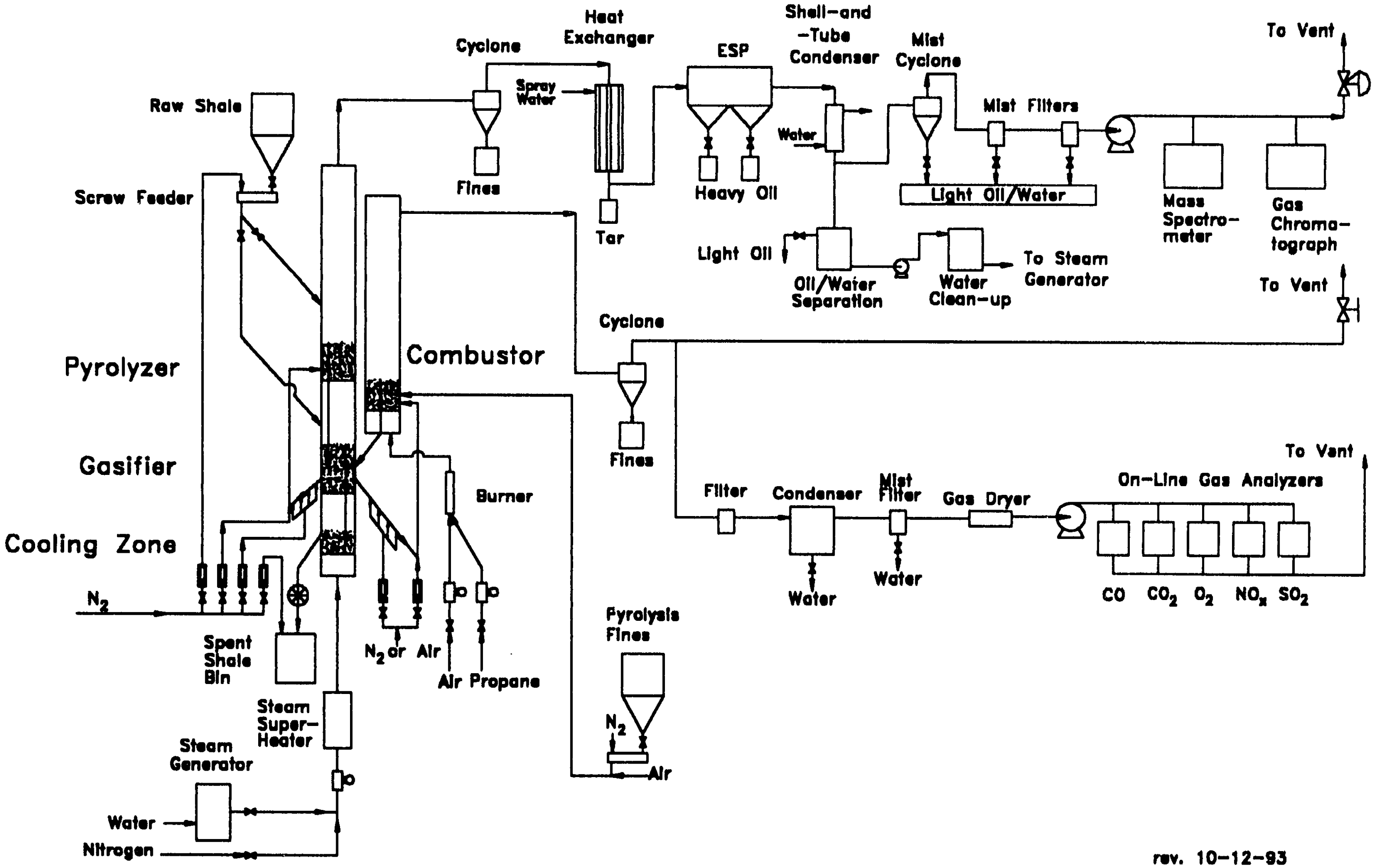

Figure 1. Schematic Diagram of the 50-lb/hr KENTORT II Process

zone is baffled to narrow the particle residence time distribution. The design conditions for the pyrolyzer are: temperature, 500-550°C; raw shale feedrate, 50 lb/hr; mean shale residence time, 3 minutes; bed depth, 12 inches; maximum solid recirculation rate, 200 lb/hr.

Shale from the pyrolysis zone is transferred to the gasifier section via a downcomer. The bed depth in the gasification zone is designed to be adjustable between 15-30 inches so that solid residence time may be varied from 30 to 60 minutes. The design temperature range for the gasification zone is from 750 to 850°C. Hot solids from the combustor enter the lower part of the bed at a rate of up to 500 lb/hr to heat the gasification zone. Steam from the cooling section below is used as the fluidizing medium.

A downcomer transfers shale from the gasification zone to the cooling zone which also serves to preheat the steam that fluidizes the gasification bed. The cooling zone is the primary exit point for solids from the reactor. An overflow outlet in the wall of the vessel creates a 15-inch deep bed.

The combustor provides all the heat required for the pyrolysis and gasification sections of the KENTORT II process. The gasification and the combustion zones are closely aligned to facilitate the transfer of solids. To minimize mixing of the gas streams, however, the pressure between the two vessels is balanced. The bed depth in the combustor is determined by the height of an overflow standpipe. The design bed depth is 12 inches, although this can be adjusted from 6 to 24 inches if necessary. The combustor is fueled primarily by carbon-containing shale which is recycled from the gasification section via a pneumatic lift pipe. Fines recovered by the pyrolysis cyclone are fed into the combustion bed to provide additional fuel. Air is used for fluidization in the combustor.

Oil Collection and Gas Conditioning. Gases and vapors from the pyrolyzer enter a cyclone for fines removal. A combination convection/liquid-injection heat exchanger then cools the vapor stream to 150°C which causes an oil aerosol to develop. This aerosol is trapped by an electrostatic precipitator (ESP) which contains over 100 ft^2 of collection surface area and includes two, two-stage Penney-type collection cells in series to ensure high collection efficiency. Downstream of the ESP, a shell-and-tube condenser is then used to condense steam and light oil that remain. Light oil and water from the condenser are separated, and the water is sufficiently treated to be fed back into the steam generator. Mist collection, further cooling and more mist collection are performed before the gas stream is sampled by an on-line gas chromatograph and mass spectrometer.

Fines are removed from the combustion gas stream by a cyclone before the gas is cooled to approximately 250°C and released to the ventilation system. Fines and water are removed from a small portion of the gas stream for analysis by on-line combustion gas analyzers which provide a continuous measure of all major flue gas components.

Auxiliary Systems. A propane burner is used to heat the fluidizing air for the combustor during start-up. By circulating solids among the zones, most of the heat required for preheating is provided by the burner. A superheater upstream of the cooling zone provides the rest of the energy needed to preheat the system. Nitrogen, rather than steam, is used during most of the preheating period so that the amount of steam condensate is kept as small as possible. Once steady state conditions are approached, the energy provided by the burner and superheater is reduced or eliminated completely.

Raw shale is metered at 50 lb/hr into the pyrolyzer by a screwfeeder which is supplied by a bin with a 300-lb shale capacity. Additional shale can be loaded into the bin during operation, so truly continuous operation may be realized. Processed shale at approximately 400°C exits the cooling zone through a rotary valve and into a sealed bin. Fines recovered from the pyrolysis cyclone during a previous run are loaded into a hopper with a 50-lb capacity and are metered into an air lift into the combustor by a screwfeeder.

Construction Activities

During the last quarter of FY91-92 our machining subcontractor completed fabrication of the main reactor. The retort was set permanently into place early in FY92-93, and then the fabrication and installation of ancillary equipment, utilities, and instrumentation was completed. The most significant pieces of equipment which were custom-fabricated and installed during FY92-93 include:

- aerated J-valves
- electrostatic-precipitator housing
- oil and water collection system
- pyrolysis-gas heat exchanger
- raw shale feed hopper
- retort internals (distributor plates, downcomers, etc.)
- screwfeeder
- spent shale bin
- steam superheater

In addition to these items, the cyclones and the start-up burner were installed. All necessary process fluids (air, nitrogen, steam, and water) were connected to the retort. Installation of the instrumentation, process control, and computerized data acquisition systems were completed.

Retort internals which are exposed to temperatures above 700°C were aluminized, as was the combustor cyclone. The entire reactor was covered with 4 inches of alumina silicate insulation, and heating tapes were installed beneath the insulation around the cooling, gasification, and pyrolysis zones. The heating tapes are designed to compensate for heat losses and facilitate the heat-up process.

By the last quarter of FY92-93, the KENTORT II 50-lb/hr PDU was completely functional and instrumented. All of the equipment shown in Figure 1 is now installed with the exception of the pyrolysis-fines feeding system.

Retort Shakedown and Procedure Development

The objectives of the shakedown procedures were two-fold. The first was to evaluate the operating capabilities and to identify any deficiencies of the system. The second was to develop and refine operating procedures and to modify the PDU so that design conditions could be achieved. The first task was the verification of proper shale movement throughout the system at ambient temperatures. This was done initially at room temperature because the subsequent modification or replacement of retort components would be facilitated without the presence of insulation, heating tapes, etc. Once reactor stability in terms of shale dynamics was verified, the next task was to evaluate the start-up/supplemental heating systems and the resultant temperature distribution throughout the system. Therefore, the two major tasks associated with the start-up of the 50-lb/hr PDU can be roughly termed cold-flow and hot-flow testing, respectively.

Cold-Flow Testing. The major objectives of the cold-flow tests were to determine the capacity of the recirculation loops, assess the operating stability of the retort, and measure the amounts of fines entrained into the combustor and pyrolyzer cyclones. Tests were conducted using room-temperature air which was supplied by a 220-ft^3/min blower. Raw oil shale (20 x 60 mesh) was continuously fed to and withdrawn from the retort at a rate of 50 lb/hr.

The rates of solid recycle from the gasifier to the pyrolyzer and combustor were observed at the design levels of 200 and 500 lb/hr, respectively. These recycle rates were calculated from previously determined empirical relationships for pressure drop and mass-flow rate for this system. The control of the solid-recycle rates by the aerated J-valves was steady, and there were no disruptions of solid recirculation during the tests. Therefore, no modifications to the J-valves or lift pipe designs were deemed necessary.

During 9.5 hours of continuous cold-flow testing, no incidents of unexpected system instability were experienced. The PDU behaved very much like the full-scale cold-flow model except for the cooling zone. The diameter of the cooling zone in the PDU is 2 inches smaller than the cold-flow model because of the temperature difference between the gasifier and the cooling zone in the PDU. Therefore, when operated at room temperature, the superficial gas velocity in the cooling zone is 92% higher than in the gasifier, so the cooling zone is more vigorously fluidized. In spite of this, the stability of the system was not compromised and no elutriation of the bed or bypassing of the fluidizing gas into the gasifier via the downcomer was apparent.

Fines generation during cold-flow testing was not excessive. Approximately 11% of the feed was recovered in the pyrolysis cyclone (10% carryover was the design basis). Most of these collected fines were fed into the retort as undersized material clinging to particles in the 20 x 60 mesh range. Minimal attrition of the particles can be expected at room temperature as demonstrated by the small amounts collected in the combustion cyclone. Since the gasifier and pyrolyzer are the feed points for shale into the retort, any fines which are fed to the system will be entrained before circulation to the combustor. Small quantities of fines were found in the pyrolyzer heat exchanger and in the electrostatic precipitator. It is difficult to determine at this time whether these quantities are excessive. Only under actual pyrolysis conditions will it be apparent whether entrained fines will hamper oil collection, especially in the electrostatic precipitator (ESP).

Hot-Flow Testing. Nitrogen was used for fluidization of the cooling, gasification, and pyrolysis (CGP) zones during the hot-flow tests. This was done for convenience because condensation of steam in undesirable areas of the system would cause unnecessary difficulties during this early phase of testing. The nitrogen was heated by the steam superheater to approximately 500°C which, in turn, heated the CGP zones during the start-up process. The maximum temperature of the nitrogen from the superheater was achieved within three hours when starting from room temperature (see Figure 2). The electrical heating tapes surrounding the cooling and pyrolysis zones also provided some energy during start-up. The heat tapes for the pyrolyzer provide enough energy to make it hotter than the gasifier during this portion of the heat-up process (see Figure 2).

Start-up heat for the combustor was provided by a propane burner which was in line with the fluidizing air. Early in the start-up process, no solids were recycled to the

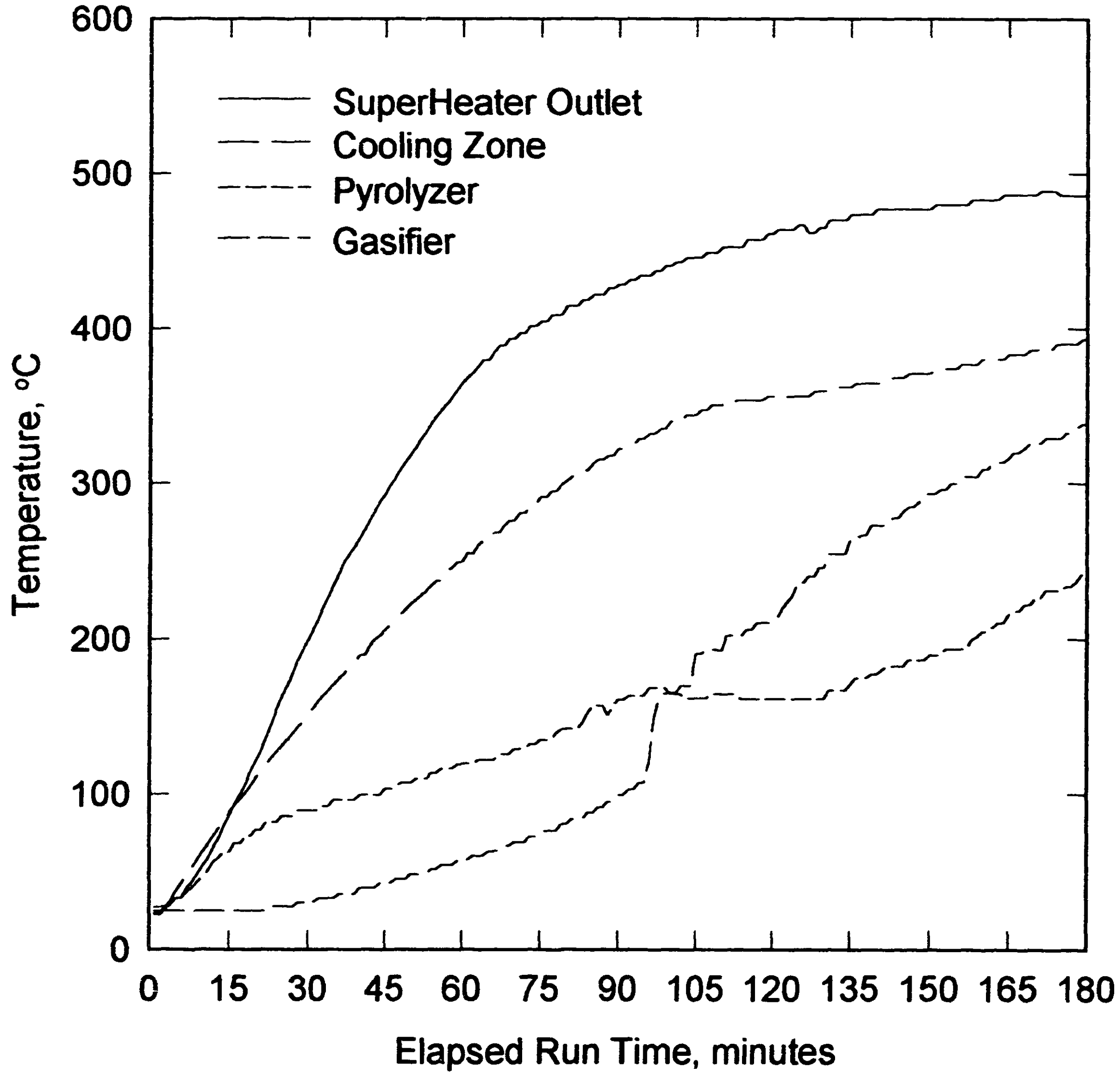

Figure 2. Heat-up profiles of the cooling, gasification, and pyrolysis zones from run KT930902 as a result of heated nitrogen from the steam superheater

combustor so that the temperature would be quickly elevated. Typically, the combustor temperature reached 800°C within one hour (see Figure 3). To avoid over heating the combustor and to heat the remainder of the system, the next step in the start-up procedure was to initiate the recirculation of shale between the combustor and the gasifier. This caused an initial drop in the combustor temperature (Fig. 3), but it caused a corresponding increase in the rate at which the gasification zone was heated. The burner provided approximately 50,000 Btu/hr of gross energy input while the superheater contributed approximately 20,000 Btu/hr of gross heat. The 150% greater energy input by the propane burner is appropriately reflected by the more rapid heat-up rate of the gasifier during the period of solids-recycle between the combustor and gasifier compared to the period when heat was only supplied by the steam superheater.

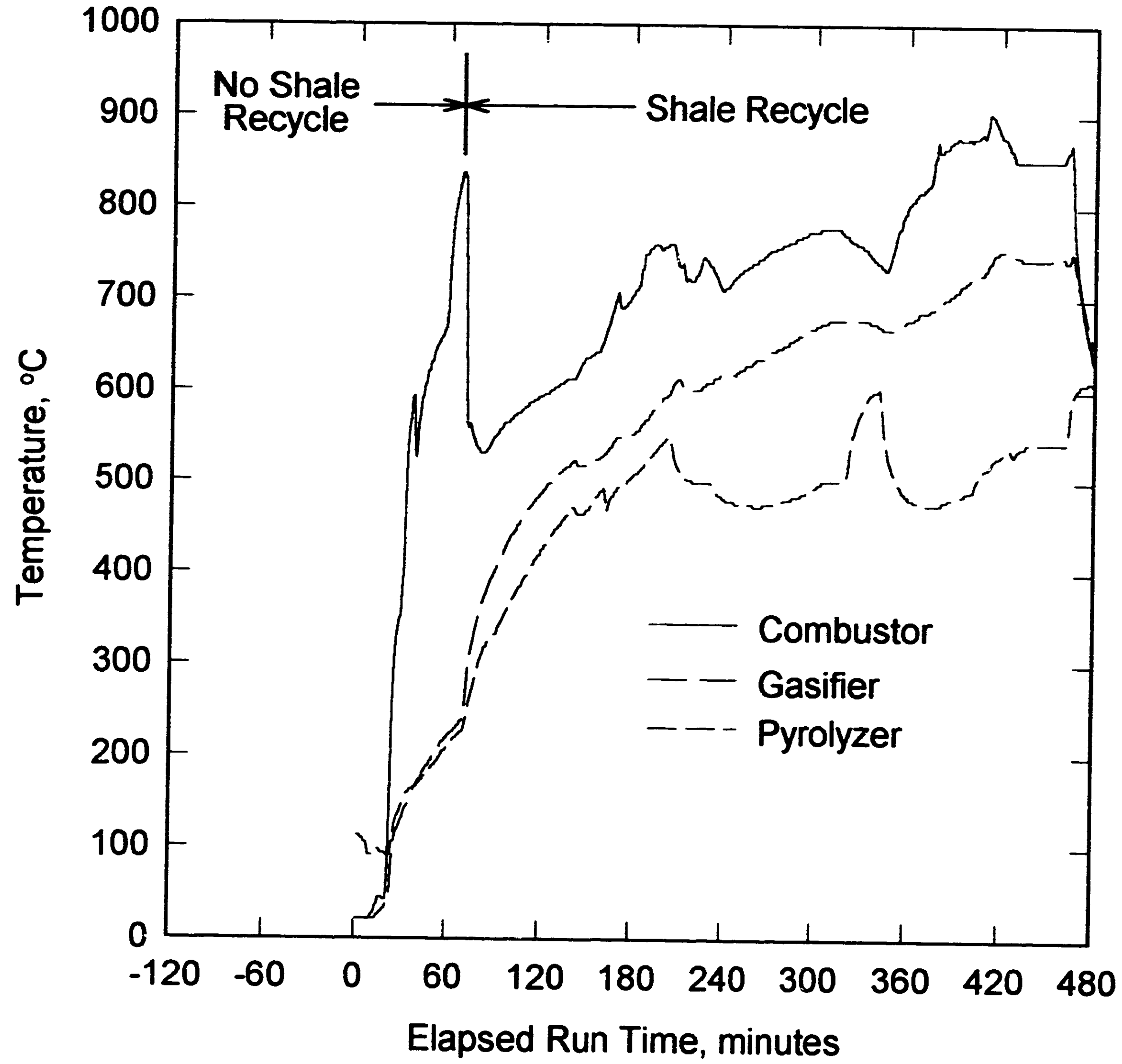

Figure 3. Temperature profiles for the combustor, gasifier, and pyrolyzer from run KT930920 illustrating the effect of shale recycle between the combustor and gasifier on the heat-up rates

Three major shakedown runs were completed during the last month of FY92-93 (see synopses in Table 1), and the successes outweighed the setbacks. The most significant findings were that the system displayed stable operating tendencies and that the design temperatures and shale recycle rates were achieved for each zone. The problems that were encountered had nothing to do with the retort itself as they were all associated with ancillary pieces of equipment. A brief description of each problem and the corrective action taken follows.

- The problem with the burner was solved by using a source of propane which was higher in pressure. In the original configuration, the burner would cease operation whenever the back pressure in the burner increased. This generally

Table 1. Run Synopses

Run	Highlights
KT930902	o From a cold start, the run lasted approximately 8 hours which included about 3 hours where the temperatures of the 4 beds were at near steady state. o The propane burner raised the temperature of the combustor to 650°C before it ceased operation following the initiation of solid recycle between the combustor and gasifier. o The combustor sustained temperatures ranging from 700 to 780°C without the aid of the start-up burner. o Shale was fed to and withdrawn from the retort continuously to provide enough carbon to sustain combustion. o The pressure in the gasifier could not be sufficiently adjusted downward so that it was the same as in the combustor at the balance point. This hindered the operation of the unit, and was at least partly responsible for a process upset that caused termination of the run. o The temperature of the ESP was too low (less than 120°C) to permit operation with steam, so nitrogen fluidization was used for the duration of the test. o Some oil was produced and collected, but because of the relatively short duration of the steady state period and the inability to operate with steam, the amount of oil collected was not meaningful.
KT930920	o Combustion flue gas analyzers were placed on line. o A higher-pressure source of propane was used to fuel the burner, and it operated flawlessly. o Pyrolyzed shale was periodically fed to the system in order to provide carbon for fuel yet not produce oil. o Design temperatures for each of the zones were achieved: Pyrolyzer (500-600°C), Gasifier (750°C), and Combustor (850°C). o Pressure balance between the combustor and gasifier could not be achieved. o The ESP temperature was still too low to permit steam fluidization.
KT930927	o No shale was fed to the system in order to test the capabilities of the start-up heaters without aid from carbon in the shale. o Proper pressure balance between the gasifier and the combustor was maintained. o The temperatures attained for each of the zones were: Pyrolyzer (600°C), Gasifier (725°C) and Combustor (775°C). o Additional insulation was not sufficient to raise the outlet temperature of the ESP above 100°C.

occurred when the proper bed height in the combustor was attained.

o The problem of pressure balancing the combustor and gasifier was solved by installing a gate valve at the outlet for the combustion flue gases. It was found that independent adjustment of back pressure at each of the gas stream outlets was necessary in order to properly pressure balance the retort.

- Excessive heat losses from the pyrolyzer to the inlet of the heat exchanger caused the inlet temperature of the ESP to be much lower than expected. In addition, heat losses from the ESP itself were also quite large. Much additional insulation was installed from the pyrolyzer to the heat exchanger, and electrical heating pads were installed on the ESP to eliminate the large heat losses so that the temperature in the ESP will remain well above 100°C.

SUMMARY AND FUTURE WORK

The 50-lb/hr PDU has been shown to be functional when nitrogen is used to fluidize the CGP zones. To be considered completely operational, however, steam must be used for fluidization. Steam is crucial to the KENTORT II PDU for two reasons. First, steam is a necessary reactant for the gasification zone, and, second, the oil collection system was designed around the use of steam. Shakedown runs using steam for fluidization are planned for the first month of FY93-94. Once the system can successfully operate with steam, an experimental matrix will be initiated. The yield and composition of oil and gas products will be evaluated as a function of the gasification temperature and the rate and temperature of shale being recycled to the pyrolyzer.

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