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**A STUDY CONCERNING THE UTILIZATION OF OCEAN
SPREADING CENTER ENVIRONMENT FOR THE
CONVERSION OF BIOMASS TO A LIQUID FUEL**

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ABSTRACT

The purpose of this study was to determine if a potentially viable process could be found to utilize the energy and local environment of an ocean spreading center. The conversion of municipal solid waste (MSW) biomass to an oil product was selected for study, rough capital and operating costs estimated, and simple economic calculations made based upon estimates for a land-based system. The first order single paybacks of six years showed that such a process may be viable. Consideration of potential new conversion technology using supercritical water which almost completely dissolves organic materials, has the potential of greatly increasing the viability of biomass conversion through simplified processes and increased conversion efficiency. The selection of MSW as a feedstock fits very well with ocean processing because coastal regions are a major source and its use would have a huge positive impact on existing environmental problems related to its disposal.

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1.0 INTRODUCTION

The earth's crust is made up of a number of large plates which are in constant motion relative to each other. Some of the earth's crust is being consumed and deposited back into the earth's mantle as a plate "dives" or subducts under an adjoining plate. The Pacific Plate subducting under the North American Continental Plate is an example of this. At the other end of the colliding plates new earth crust is being formed and added to the plates as the plates move apart or spread. These areas are called spreading centers. An example of this situation is the Mid-Atlantic Rift which extends from Iceland to the Antarctic.

Spreading centers are characterized by active volcanism. Magma raising up from the earth's mantle as the plates part give rise to land surface expressions such as hot pools, geysers, and active volcanos. Iceland, which sits astride such a spreading center, has well known hydrothermal fields which have been extensively developed for commercial uses. Seabed surface expressions of spreading center activity take the form of basalt pillow lava formations that are formed when lava extrudes out of fissures and rapidly solidifies; hot water vents that are heavily mineralized and that support colonies of bacteria, tube worms, clams and other organisms; and lack of sea floor sediment layer. There are approximately 40,000 miles of spreading centers on the earth surface. Ninety-five percent of these lie below the oceans of the world.

Study of the spreading centers has until recently been primarily the province of academia within the United States. Effort has concentrated on obtaining a fundamental understanding of the phenomena which are occurring on the ocean bottoms and the development of theories to explain the observed results. The discovery of large petroleum reservoirs under the ocean floor and massive metallic deposits on the ocean floor has stimulated commercial interest in ocean floor development.

Development of ocean petroleum resources has proceeded rapidly until today we have drilled as deep as 6500 feet in Wilmington Canyon off the East Coast of the United States. Figure 1 illustrates the "learning curve" and expectations of the petroleum industry in drilling in the ocean environment. Development of metal recovery has been slower in development primarily because of uncertainties in economics and ownership of the resources. The United States has recently taken a positive step to help reduce these uncertainties by declaring a 200 mile exclusive economic zone (EEZ) off all United States coastlines. The Department of Interior sponsored a symposium on the assessment and development of mineral resources from the EEZ⁽¹⁾ and the general tone of the conference was that mineral development should be profitable in some areas of the United States exclusive economic zone and that a joint industry government program was required to maintain the United States lead in ocean technology, a lead that is being aggressively challenged and perhaps surpassed by France, England, Germany, Canada, and Japan⁽¹⁾. A second major indication from the conference was that technology to work on the ocean bottom exists, and that development is limited primarily by institutional and economic considerations.

In addition to petroleum and minerals a third deep ocean resource which could have great economic value is the energy associated with the spreading centers. The ocean spreading centers represent a tremendous source of unexplored-untapped energy. A rough estimate of the amount of energy available in the spreading centers is 0.15×10^6 to 7.5×10^6 quads. equivalent to 2,000- to 100,000-year. United States energy supply at the current annual total energy consumption rate of 75 quads⁽¹⁾. It should be noted that this estimate is for energy available IN-SITU in the rift zones. As tectonic plates spread, new magma flowing into these zones replenishes the heat that is lost. As long as tectonic plates continue to move and the earth's core remains hot, this heat source will be available. In other words the spreading centers represent essentially an inexhaustible supply of energy if means can be found to utilize it.

Figure 1. Floating drilling, subsea well and facility capability projection (From Reference 1).

In 1983 the Department of Energy commissioned EG&G Idaho a contractor at the Idaho National Engineering Laboratory to begin studies on how the ocean spreading center energy might be used. Earlier preliminary work concluded that the spreading center energy has great potential and that follow-on studies should be conducted to evaluate some of the more promising concepts identified. Sixty-six processes were visualized which had potential to be feasible in the ocean bottom environments. The feasibility was based on those processes which could take advantage of the unique environmental conditions available at spreading centers, i.e., high temperature high pressure hydrothermal systems, with the possibility of magma, surrounded by a low temperature sea water environment rather than economics. Spreading center hydrothermal conditions which have been measured or are thought to exist are:

1) Temperature

Hydrothermal Water

Measured up to	660°F
Anticipated	750°F(2)
Magma	1800-2200°F

2) Pressure 3500 psi

The high pressure is a part of the environment and thus slow processes which are not feasible on land might show significant advantages in the spreading center environment where time and space could be less critical. Offsetting these potential advantages of the spreading center environment is its remote location, the unknowns associated with the resource and the current high costs which are a part of ocean processing.

The specific tasks that were addressed as part of the FY-84 activities and reported herein are:

1. Examine potential uses of the spreading center energy source.
2. Select a potential application as a reference case and evaluate preliminary economic feasibility.

3. Based upon this reference case, review each of the major steps in the chain to produce the product and roughly status the technology.
4. Identify potential benefits, if any, of the ocean hydrothermal application to the reference process.
5. Identify areas where utilization oriented research is required.
6. Gather information related to possible applications and processes that exist in ocean environment, including petroleum genesis.

In this report, information regarding the conversion process is presented in the main body; background information on natural petroleum genesis is given in the Appendix.

2.0 CASE STUDY OF A SPECIFIC APPLICATION - LIQUID FUELS FROM BIOMASS

The process selected for additional study was the conversion of biomass to petroleum. This appeared to be an ideal application since many synthetic liquid fuel studies show that pressure and temperature conditions required to convert such things as carbonaceous minerals (coal), biomass sources (MSW) and other cellulosic material to fuels are similar to those in existence at the spreading center environment. In addition there is substantial evidence that petroleum is being formed naturally in the area around the vent systems. The deep submersible ALVIN purportedly has a smell similar to diesel fuel when it returns to the surface after studying a vent system. It has also been shown that there is a conversion of kerogen to petroleum in the areas of vent systems in the Guaymas Basin⁽³⁾. The sonar images taken above the Guaymas vents shown in Figure 2 have been interpreted to be plumes containing petroleum like hydrocarbons rising to the surface. Note the magnitude of these images.

In summary, there is considerable evidence that the production of liquid fuels at the conditions of a spreading center vent system is

Figure 2. Concurrent up-look sonar records for the five largest plumes in Guaymas Basin. Note the alignment of features in up-scan records in plume D. (From R. Merewether, M. S. Olsson, and P. F. Lonsdale: Acoustically detected hydrocarbon plumes rising from 2 km depths in Guaymas Basin, Gulf of California.)

fact is occurring. The principal practical concerns are: Can it be accomplished synthetically with current land based technology; is it potentially economical; and, what development would be required for viability.

Three biomass feedstocks were considered for evaluation - kelp, ocean grown algae, and municipal solid waste. Kelp and algae have the advantage that they can be grown above the spreading centers which would minimize transportation problems. Municipal solid waste processing may have significant continental environmental advantages as well as the production of liquid fuels.

2.1 Discussion of Process Selection and Evaluation

The three feedstocks were examined for their potential advantages and disadvantages and then the processing of municipal solid waste was selected for more detailed study including a rough cost economic analysis. The following summarize principal considerations relative to each feedstock.

Kelp

The first feedstock considered was the production of liquid fuel using giant kelp (*Macrocystis pyrifera*). The kelp was to be grown in large ocean-based floating farms (100,000 acres) above spreading centers. The kelp would concentrate the solar energy available into chemical energy with nutrients provided from deep water. The nutrient-rich water would be pumped up from the depths to provide the growth medium. The giant kelp is the largest known marine algae and grows up to 2 feet per day and ocean-based farm productivities of 25 dry ash-free tons (DAFT)/acre-year are believed possible. The concept of the ocean-based floating kelp farm was considered by the Gas Research Institute(4).

For the spreading center application it was conceived that kelp grown above the spreading center site could be harvested and pumped down to the ocean bottom heat source along with any necessary catalysts producing liquid fuel. A conceptual material balance is shown in Figure 3 and an artist's conception of the plant in Figure 4.

If the conversion process has a 50% yield and produces an average quality petroleum crude, it is estimated that as much as 150 million dollars per year worth of fuel could be produced from a 100,000 acre farm. However, this would not be enough income to cover the operating costs of such a plant. It is estimated that the entire system could cost as much as 5 billion dollars to build. A primary problem is the low carbon content per unit volume of space required and very high ash content (~40%) which causes a potential residual solids disposal problem.

Because of the poor economics that result from this feedstock, no additional work was done to consider improvements to the kelp facility. Other problems include the farms vulnerability to storms and currents.

Algae

Ocean grown algae has the theoretical advantages over kelp of a higher productivity, a lower ash content and a higher carbon content. In theory it could be more economical than kelp. However, there currently is no technology for growing and harvesting large algae farms in an ocean environment. Therefore, no detailed studies were done on algae processing.

Municipal Solid Waste (MSW)

The value of land and increased environmental controls have made landfill disposal of urban waste very expensive, especially in the densely populated areas of California. Existing landfills are rapidly filling and the per capita waste load is expected to reach 8 pounds/day by 1990⁽⁵⁾

Figure 3. Kelp to oil conversion process.

(from current levels of about 6 pounds/day), so the problems and costs of conventional disposal encourage municipal governments to look to waste utilization alternatives. New York City has dumped solid wastes into the ocean for some time, however, environmentalists are concerned about the long term effects of the slow decomposition of the organic material. If the wastes could be moved over a high temperature spreading center, theoretically the organic material could be rapidly converted into a high value petroleum product and the remaining benign solid materials could be spread on the ocean floor where the environmental effect could be minimized.

The MSW was selected as the feedstock for the preliminary ocean spreading center liquid fuel feasibility study because the material is 60% cellulosic making it an excellent feed for a conversion facility and a large supply is available. In addition, an urgent need exists to find more environmentally acceptable methods of disposing of the waste from large municipalities than landfills, ocean dumping, or incineration. The following summarizes the basis for costing each system, key assumptions and areas where research is required.

2.2 Conceptual Basis and View of Development Status

A block diagram of the major facilities which must exist is shown on Figure 5. The major elements shown are the feed preparation facility, the transportation system from the feed facilities to the ocean facilities, the ocean surface facilities, the surface to bottom material handling system, and two systems on the ocean bottom: the geothermal system and the conversion plant. This section provides a discussion of each of these steps for the MSW conversion and indicates where development may be required.

Figure 5. Overall MSW conversion process and major facilities location.

MSW Feedstock Facilities

MSW as initially collected is a loosely consolidated mixture of waste materials. This material is presently processed in a variety of manners. It can be transported directly to landfills, to ocean disposal or to mass-burn incinerators. It can also be sent to separation facilities where the combustible material is separated and densified prior to burning. For this study the densified fuel was selected for ocean processing. It was assumed that transportation advantages would justify the separation and densification, however, no tradeoff studies were conducted.

The MSW source was assumed to be a population of 30 million people generating waste at a rate of 8 lbm/day. This number is based on municipal areas of a population of 100,000 or more in California, Oregon, and Washington. This source was supplemented by crop residue and other agriculture wastes which are estimated at 482 million tons per year on a national level⁽⁶⁾. It was assumed that 5% of this resource could be tapped and shipped out. Other possible supplements are in the form of sewage sludge and industrial waste but were not considered in this evaluation. These supplemental sources would undergo any preliminary processing on land in a similar manner to the MSW.

The technology to separate waste is well established and plants have been designed and built to produce densified refuse derived fuel (DRDF) from the combustible part of MSW. The principal problem preventing large-scale development is the fear of potential customers that the densified fuel will cause environmental problems due to the stack emissions.

Research is being conducted MSW processing to form DRDF type materials by the Department of Energy and the Environmental Protection Agency and no additional research would be necessary as part of an ocean technology program.

Feedstock Transportation

It was assumed the feedstock would be handled as bulk cargo on ocean going barges or equivalent. The DRDF is roughly equivalent to coal in its transportation characteristics if kept dry. No research is required in this area to support an ocean hydrothermal energy technology program.

Ocean Surface Facilities

Great strides have been made in ocean surface facilities by the petroleum industry. Figure 6 shows progress which has been made in the past and also shows projections through the year 2000⁽¹⁾. These projections indicate there would be no problem establishing a processing platform over a spreading center site. The required surface facilities would be the DRDF unloading and storage facility, mixing tanks to slurry the DRDF prior to pumping it to the reactor, gas-oil separation tanks and petroleum storage and loading facility. Power generation facilities would also be required for transferring materials pumping, etc. Since current platform facilities are designed primarily to handle crude oils some changes would be required to handle the solid bulk of the DRDF and the slurry. Design of the surface facility is considered to be a normal engineering task and no research is required.

Surface to Subsurface Transportation

The petroleum industry has considerable experience in laying pipelines to deep water locations but there is no experience with the movement of the solid material to the ocean bottom. In the plant considered here, the feed will be slurried with 70% recycled oil and it should not give great handling problems. However, research is required to assure there would be no surprises in attempting to install the pipelines and pump the slurry to the ocean bottom.

Figure 6. Industry platform capability projection.(1)

Conversion Facility

Several conversion schemes were found in the literature for the production of liquid fuel from cellulosic material (biomass). These processes typically involve high pressure (2000-3000 psi) and temperature (300-400°F) conditions and the use of reducing agents and/or catalysts. One of the better conversion processes found was the conversion of biomass to liquid fuel by reductive formylation. In this process biomass is reacted at high temperatures in the presence of formate or carbon monoxide gas to form a liquid fuel. The process has been demonstrated on a laboratory scale by the United States Bureau of Mines and other researchers^(7,8,9). A design and cost estimate for the conversion of MSW to a liquid fuel by this basic process has been produced⁽¹⁰⁾ and was selected as a basis for scaling the process to the size required for this study. The assumptions upon which the conversion process is based are presented in Table 1.

TABLE 1. MSW CONVERSION PROCESS ASSUMPTIONS

Feed Slurry Concentration	30% by weight solids
Operating Temperature	660°F
Operating Pressure	3000 psi
Normal Residence Time	40 minutes
Feed Slurry Vehicle	Recycle Oil
Heat of Reaction	Negligible
Oil Yield	58 lbm/100 lbm organics

An overall process flow diagram from feedstock source to the final product is shown on Figure 7. Based upon the assumptions of feedstock availability previously given and the conversion plant parameters listed above, the facility would be capable of producing about 85 million barrels of

Figure 7. Process diagram for conversion of MSW to petroleum.

crude per year (233,000 b/d). It is recognized that this would be a very large single facility and thus is not representative of a first generation plant. Moreover, the process described here is based largely on the conceptual design presented in Reference 10 for a much smaller plant. To our knowledge there are no land-based conversion plants operating, however, research has confirmed the basic process involved. An extension of this utilization process to the scale indicated here, with consideration of its location on the ocean bottom would require a significant engineering effort to arrive at a somewhat optimized process and mechanical design. In view of this, and the potential improvements such as supercritical processing discussed later, a significant amount of research and engineering work is required on the utilization process. In addition, since both the process and the geothermal production equipment will be subjected to a high pressure, high temperature and highly saline environment, difficult materials problems may exist.

Synthesis Gas Facility

A reducing agent such as carbon monoxide, hydrogen or a formate is required to remove the oxygen from the DRDF to produce the petroleum. While hydrogen could be generated by the electrolysis of sea water the power requirements would be excessive. In this study it has been assumed that the reducing agent will be carbon monoxide which will be produced from a synthesis gas facility in essentially the same manner as is used in surface facility designs.

No development is necessary for the relatively conventional synthesis gas facility, however, other options may be possible utilizing the spreading center environment which would require development.

Geothermal Wells and Submerged Production Systems

The petroleum industry is continually improving in their capability to drill and produce from ocean sites. Figure 1 showed the current experience and expectations. Drilling in depths typical of those found at the spreading

centers will be possible in the near future. The oil wells typically penetrate the earth to substantial depth. Drilling in a vent area is, however, an entirely different technology. Existing drilling is conducted in sediments and the wells are drilled 6-8,000 feet below the sea floor. The drilling is conducted with muds which are returned to the sea surface greatly adding to the cost. The spreading center energy fields are in freshly formed basalts and are apparently quite shallow. Current thinking by personnel studying the hot black smokers is that the magma heat source is probably quite close to the surface and that a minimum of drilling would be required.

Some information on drilling in the spreading center region will be obtained from the off-shore drilling being financed by the National Science Foundation, however, as valuable as this information will be, more geological and technological development will be required for drilling of production wells. Productivity, one of the key measures of a successful well, is completely unknown although much higher production rates than obtainable on land have been speculated because of the porous basalts from which the geothermal fluid will be produced.

The petroleum industry has demonstrated the capability to fabricate fairly sophisticated subsurface petroleum collection and manifold systems. Figure 8 illustrates the complexity of systems which are operating or under design at the present time.

In summary, the off-shore petroleum development provides a high technology base from which to build the geothermal technology. However, drilling and field development will be a major area where research and development is required.

2.3 Economics of the Proposed System

This section presents the capital and operating costs and the results of a simple payback calculation based upon these cost estimates to see if the proposed system is remotely feasible and thus provide a first order indication of the merits of ocean floor processing of MSW.

Figure 8. Exxon submerged production system. (1)

To arrive at a cost estimate for the overall process, a number of assumptions and extrapolations were made so that information existing in the literature could be used. In the case of the DRDF, commercial facilities exist with established costs for the product. Similarly, ocean transportation costs for coal are well known and it is assumed that the cost of shipping DRDF would be similar. However, costs for ocean bottom processing and the harnessing of the hydrothermal energy do not exist. The oil companies provide order of magnitude estimates for portions of these costs since they have drilled in depths similar to those where the vent areas are located and have installed ocean floor handling systems. However, the extension of this data to a chemical processing plant is significant and as with other assumptions to be made is acceptable only as a first order estimate.

The basis for handling capital cost, estimating operating costs and the revenue stream is given in Table 2.

TABLE 2. GENERAL ASSUMPTIONS USED IN ECONOMIC ANALYSES

Plant Scale-Up Exponent	0.7
On-Stream	330 day/year
Labor Cost	\$26,500/man year, average
Supervision	15% of labor
Maintenance and Supplies	5% of installed plant cost
General and Administrative	1.5% of installed plant cost
Insurance	1.0% of installed plant cost
DRDF Feedstock (delivered)	\$22/ton
Other Feedstock (delivered)	\$5/ton
Operating Cost Scale-Up Factor (Labor and Utilities Only)	0.5

2.3.1 Capital Cost Basis

The capital costs, with some discussion of their basis, is given in this section for the major cost areas of conversion plant, platform, well development and ancillaries. The estimated cost of these items is given in Table 3 which totals \$7.4 billion including a 50% contingency. Comments on this estimate and the equipment contained in each category are provided below.

Conversion Plant

The capital cost estimates for reaction, gas production, and auxiliary equipment are based on estimates of the capital cost of similar land-based plant. The land-based plant is sized to convert 705,000 tons per year of DRDF while the ocean-plant would be a 55,000,000 tons per year plant. The estimates for the land-based plant were given in 1975 dollars⁽¹⁰⁾ which were scaled up using a 0.7 exponent as the scale-up factor and brought to current (1984) dollars using the CE plant Cost Annual Indices for 1975 and June, 1984.

It should be remembered that the land-based cost estimates include capital for the pumps and heating equipment necessary to create the high temperature and pressure reaction conditions and the vessels and pipe for containing these conditions. This high pressure equipment would not be necessary in the ocean-based plant, but its economic advantage is not included in the estimate, because it is probably off-set by other problems. Other economic advantages may be realized in the ocean environment which were not determined in this analysis.

The ocean bottom conversion facility is a quantum jump more complicated than the manifold and pumping systems currently being placed on the ocean floor. The ultimate cost of the conversion facility will depend on how much advantage the high pressure, high temperature ocean environment actually has when more detailed concepts are developed. Development of detailed designs was beyond the scope of this study and it was assumed the savings in vessel costs would be counteracted by the higher costs of deep ocean assembly.

A brief description of the major equipment considered as part of the conversion plant is given below. No consideration was given to the practicality of specific processes for the ocean application but were used to obtain representative costs.

Reaction Equipment. Reaction system consists of a slurry tank, slurry pump, slurry preheater, reactor vessel, gas preheater, off-gas cooler, reactor bottoms flash tank, piping, and oil recovery system. The oil recovery system takes the reactor bottoms product and separates this stream into three streams (oil, solid ash, and water) using a solids ejecting-type centrifuge. The aqueous stream is passed through a catalyst recovery system and the solid ash stream passes through a solvent extraction system to recover oil.

Synthesis Gas Facility. A Linde Oxygen Refuse Converter ("Purox Process") is used for process gas production in the base plant. This plant uses part of the shredded waste as the carbon source. The waste is fed to a shaft furnace with oxygen introduced to the bottom and process gas drawn from the top. This is one of several ways synthesis gas could be produced. Hydrogen could also be produced as the reducing gas at an unknown cost. Gas purification is accomplished with a modified Stretford unit, the cost of which is included here.

Ancillary Equipment

This category includes equipment for DRDF load-out, on-shore, and unloading at the ocean site. This category also includes utilities, equipment for waste water treatment and for solvent recovery from the solid ash. Equipment for the storage and disposal of the ash is also included.

Well Field Systems

This category includes all the costs associated with providing geothermal fluid to the conversion facility and thus includes the cost of the wells. The cost of drilling an oil well at ocean depths of 3,000 to 6,000 feet is on the order of \$25 to \$50 million each. However, these wells

typically penetrate the earth to substantial depths and drilling such an oil well in 10,000 feet of water might cost on the order of \$75 million. As noted earlier, the geothermal resources is expected to be much nearer the sea bottom than are oil resources and thus the costs may be much lower. In addition, drilling with water rather than mud would lower the cost. For this cost estimate the low end of the oil well range of \$25 million per well was used and was assumed to include the complete well system.

The number of wells required to support the conversion facility will depend upon the average well productivity. An average flow rate of 5000 gpm was assumed for this estimate resulting in a requirement for eight wells. This high productivity was used because the basalts may be very porous. Although the \$200 million cost estimate is very uncertain, inspection of the relative costs of the major facilities given in Table 3 indicates that even if this value was cut in half (cost doubled) it would only have a minor effect on the total cost.

Platform

This study has assumed that all the necessary facilities to support the plant can be housed on a single large platform. At this time we do not know if this is feasible or even desirable - perhaps satellite systems or smaller mooring stations could be utilized. The use of the single platform cost provides a rough estimate of the cost expected.

TABLE 3. PLANT CAPITAL COSTS

Conversion Plant		\$2,600
Reaction Equipment	\$1,900	
Gas Plant and Purification	700	
Ancillaries		1,100
Platform		1,000
Well Development		200
Contingency (50%)		<u>2,500</u>
TOTAL		\$7,400

The platform capital cost presented is the published cost of a tension-leg platform. It is a 57,000 ton, 90,000 sq. feet platform set on eight 212 foot hollow columns, connected at the bottom by horizontal pontoons. Each corner column is moored by three nine inch diameter tubular steel tethers to an anchor, which is fixed to pilings driven 375 feet into the seabed.

2.3.2 Operating Costs

The operating costs for the land-based plant have been scaled to the reference system. The basis for developing the operating costs is given below in Table 4.

TABLE 4. BASIS FOR OPERATING COST ESTIMATE

<u>Operating Costs</u>	
On-Stream Factor	330 days
Labor	\$26,500/man-year
Supervision	15% of labor
Maintenance & Supplies	5% of installed equipment cost*
General and Administration	1.5% of installed equipment cost*
Insurance	1.0% of installed plant cost
Office Services	20% of labor
Depreciation	20 years
Fringe Benefits	30% of labor & supervision

*Well development and platform costs not included.

Labor force requirements for the ocean-based plant were scaled up from the 53 required in the land-based plant using a 0.5 scale-up factor. Utility costs were scaled up in the same manner. No state and local taxes were

included since the plant is ocean based. The annual operating costs are given in Table 5 and total \$1.27 billion. Approximately 63% of this cost is related to the feedstock (DRDF).

For the ocean study it was assumed the DRDF could be purchased at a bulk loading facility with ocean access for \$17/ton. This is about 14% below the equivalent energy cost of coal. Considering that municipalities are having trouble finding customers for DRDF at any price, this may be a conservative cost estimate. Transportation would cost \$5/ton, based on current costs, for transporting bulk cargos. This is a realistic cost estimate and no problems would be anticipated in transporting the DRDF. Thus, a major portion of the operating costs are derived from a fairly firm basis and has less uncertainty than the capital cost estimates. The other costs are based upon representative percentages of the plant costs.

2.3.3 Payback

The conversion facility was estimated to produce 83.4 million barrels of oil per year. At this production rate, the break even selling price to pay operating expense is \$15.2 per barrel. Thus, unlike the kelp to oil conversion system that could not recover the operating expenses, the MSW system shows considerable potential.

At a selling price of oil of \$29 per barrel, the 83.4 million barrel per year plant will produced a gross revenue of \$2419 million/year. The simple payback period would then be about 6.4 years.

If one required a return on investment on the order of 30% for such a venture, an oil selling price of about \$42 per barrel would be required (using a capital recovery factor based upon 30% over 20 years). This value would represent an average annual differential escalation rate for oil of less than four percentage points over a 10 year period which may not be unreasonable when one considers the long range time frame of the ocean development discussed here.

We feel that this study has demonstrated that an ocean site is feasible for at least one application.

TABLE 5. ESTIMATE OF ANNUAL OPERATING COSTS

	(\$Millions)
Labor	12
Supervision	2
Fringe Benefits	4
Maintenance and Supplies	278
General and Administrative	83
Insurance	74
Office Services	2
Utilities	10
Feedstock Costs (DRDF)	<u>802</u>
Yearly Operating Costs	<u>\$1,267</u>

3.0 POTENTIAL ADVANTAGES OF SPREADING CENTER LOCATION

Potential advantages exist if a portion of the conversion process is located on the ocean floor in the vicinity of a high temperature hydrothermal resource. These advantages will be discussed and compared where possible with land-based capability. For the most part attempting to quantify the economic potential of any proposed concept is beyond the scope of this paper except where existing information as presented in Section 2 may be used. While the following concept descriptions are simplistic, they suggest possibilities that may exist.

3.1 Reaction Pressure Vessels

To convert the DRDF into petroleum the DRDF and other organic waste material is mixed with some of the recycled oil product at high pressure to form a slurry which is heated to about 660°F and held at this temperature and a pressure of about 3000 psi for about 40 minutes (see Section 2). The large plant, such as the one considered would require a reaction vessel throughput on the order of 1,000,000 cu. ft./hr of the slurry. The consequences of this in terms of the reaction vessel size and design is shown in Figure 9. Pressure vessel sizes are limited in part by fabrication limits on diameter and wall thickness, the ability to maintain material properties through heavy sections and limitations on shipping. Using about a 15 inch wall thickness as a practical limit for the pressure vessel one can see that the maximum diameter would be limited to about 15 feet. Thus, a minimum of 110 pressure vessels 50 feet long and of this diameter and wall thickness would be required for the 1,000,000 cu. ft./hr throughput. Of course large diameter vessels can be field erected but they are for lower pressure applications and have thinner walls that can be heat treated at the location.

Consider now, the placement of the reaction vessel at the spreading center location. The ambient pressure is about 3000 psi (if it were higher the yield would be increased), just what is needed for the conversion process. The only vessel requirements are to separate the reactants from the

Figure 9. Reaction vessel number and size limitation for DRDF conversion system.

sea and be adequately corrosion resistant. The pressure requirement has essentially disappeared since it has been reduced to accommodating the small pressure drops in the components and the pressure differential due to relative hydrostatic heads between the inside and outside of the vessel. High pressure piping, valves and pumps are not needed on the sea floor. Pressure regulation would be required and would be provided by pumps at the platform. If the depth of the spreading center exceeds the reference process requirement, the yield of the system is increased with a corresponding increase in the output and relative profits. Thus, the reaction vessel can be very large by normal standards, limited only by transport or local capability (platform fabrication and handling ability), and the ability to distribute and mix the heat and material as necessary. Two large thin walled bins on the order of 80 feet in diameter and 100 feet in length (or if rectangular—70x70x100 feet) would be sufficient. This concept would result in significant system simplification since the complexity of distribution headers would be greatly lessened—from at least 1100 to 2.

3.2 Supercritical Reactions

If pure water is heated above the critical point of 3206 psia and 705°F, it has the ability to dissolve organic materials almost completely. Moreover, it has been shown that such an organic will drop out as oil (or a petroleum-like substance) when the fluid is cooled below the critical point. If such a process could be utilized, the yield of the process would be increased by almost two-fold, the synthesis gas generator and equipment to get the gas to the reaction vessel would not be required, thereby reducing the payback period almost in half or about 3 years using values given in Section 2. The cost savings that would result from using a few thin walled vessels would result in some reduction in the capital cost. However, it is not known if supercritical fluids (or near supercritical fluids) exist or could be utilized as described. This is an area for future research. It has been postulated that this could be one of the mechanisms at work producing petroleum-like products naturally in the vent areas. Natural petroleum genesis in the sea is just starting to be studied and may lead to the discovery of previously unknown means of making petroleum synthetically (see Appendix A).

Unit Carriers

An alternative to pumping a slurry containing the organic material is place it in a box and lower the box to a geothermally heated oven located on the sea floor. The internal pressure would always be equal with that of the sea surrounding it. When placed in the oven, geofluid would be introduced to heat the contents of the box to supercritical conditions and hold it at those conditions for the time required for the waste to dissolve. The box would then be removed and allowed to cool. Upon cooling, oil will drop out of the condensed water and the box will be brought to the surface where the product would be recovered.

Although the process just described was for a single box one can envision a system with a whole train of containers being used in this manner to form a virtually continuous process. Such a system would result in more efficient use of the geofluid since a countercurrent arrangement could be achieved. Such an arrangement is shown in Figure 10. The containers have large tubes through which the hot fluid passes (as well as around the outside to achieve even heating. Position and check dampers are used for the flow control.

Direct Contact Heating

When the conversion process is on the bottom of the ocean, the reaction vessel is at the local ambient pressure as described above, and this is the same pressure as the hydrothermal resource. Thus, direct contact heating of the slurry mixture may be practical and large surface type heat exchangers eliminated, along with the concerns of maintaining such units at an undersea facility.

A direct contact supercritical conversion process is probably the simplest conversion process possible. A conceptual arrangement, assuming supercritical conditions can be achieved, is shown in Figure 12 where a thin sea water - MSW slurry is pumped into a container. The MSW being lighter than the sea water will stack against the top of the container until it is

Figure 10. Unit carrier system for MSW conversion.

Figure 11. Supercritical direct contact concept.

it is full of MSW. Geothermal water (assumed to be supercritical) is then introduced at the outside and flows radially inward, sweeping out the sea water and heating the biomass. Temperature is maintained until the conversion process is complete (the organics go into solution into the supercritical water). Upon cooling, the petroleum-like substance drops out, is separated and transferred to the surface. The process is then repeated. The container vessels can be very large since only small pressure differences will exist across the vessel walls. While a batch process has been described, arrangements can be envisioned in which a continuous conversion process may be possible.

4.0 CONCLUSIONS

1. The depth capability of off-shore oil well drilling into the earth's crust exceeds that necessary to tap ocean bottom hydrothermal systems. However, drilling into the basalt associated with the geothermal resource is a new venture which will be initially evaluated as part of the deep ocean drilling program sponsored by the National Science Foundation. Significant development for production well drilling will be required.
2. In general, the basic technology necessary to work off-shore at the depths of many of the spreading center systems exists or will exist in the near future. Developments for specialized applications will be necessary.
3. The potential costs of large scale ocean bottom processing systems are highly uncertain. The assumption made in this study that the advantages of the high pressure environment would offset the higher construction costs and the use of a 50% contingency on capital cost is at best a guess. However, it is clear that any ocean bottom processing system must be able to take advantage of some aspect of the ocean bottom environment in order for it to be an economically viable project.

4. MSW appears to be very well suited as a feedstock for conversion to a petroleum product in an ocean bottom processing facility. The supply is vast and is currently being wasted. Its utilization would represent a major conservation of our resources. The significant environmental problems associated with current methods of disposing of MSW in large urban areas would be greatly reduced. A strong synergism exists in this application: The largest urban areas are located along coastal regions, a waste collection and handling system exists in these areas and techniques exist for separating and classifying the collected waste materials. Conversion processes have been studied and have been demonstrated on a laboratory scale. The need for alternative methods of waste disposal are becoming increasingly critical.
5. Ocean floor processing is within the realm of feasibility using existing technology provided large plants can be economically fabricated and operated on the ocean floor.

5.0 RECOMMENDATIONS

1. The current scientific research on ocean floor hydrothermal systems should be increased to obtain engineering information. This should include information on flow rates, resource size, resource longevity, chemical content and temperatures at subsurface depths. Information is needed to develop theoretical models which permit life cycle calculations.
2. Basic research on petroleum formation around vent systems should be increased. A fundamental knowledge of processes involved could assist studies searching for commercial applications. Basic research should also be started in other areas which have the potential to lead to uses for the ocean bottom hydrothermal energy.

3. Conversion of MSW to liquid fuels at an ocean spreading center appears to be an interesting potential application of the hydrothermal energy. Engineering studies should be initiated at a low level to continue the identification of problems associated with ocean bottom processing. The studies should concentrate on novel engineering approaches which have the potential to take advantage of the unique ocean bottom environment.
4. A low level effort should be continued to identify alternate processes which might benefit from the ocean bottom environment.

APPENDIX A

HYDROTHERMAL PETROLEUM GENESIS

Gregory J. Stormberg

July 16, 1984

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EXECUTIVE SUMMARY

Petroleum-like products are being generated at active ocean spreading centers as a result of naturally occurring thermal processes. The predominant control in hydrothermal petroleum genesis is temperature (150°C - 350°C^{+}), whereas time is the major control in geothermal petroleum genesis.

Hydrothermal petroleum production can in essence be called an "instantaneous" process. This is because generation times are tied closely to the magmatic processes (magma bodies, sill intrusions, and thermal water convection) operating at spreading centers. The temperatures generated have the effect of thermally cracking sedimentary organic matter into petroliferous products. Although the physical setting (spreading center with sediments) is fairly unique, it demonstrates that the thermogenic characteristics of active spreading centers provides a mechanism for the conversion of immature organic matter to petroleum-like products. Once generated, the petroleum is then removed by hydrothermal convection and diffusion through permeable sediments and along fault zones, followed by condensation at the seabed.

The type of organic matter incorporated into sediments is an important consideration in petroleum formation. The quality (hydrogen and lipid content) and quantity, as well as the diagenetic history of the organic matter, all play a role in the chemical composition of the final product. Marine source material is more desirable than terrestrial (higher plant) sources. Marine organic detritus has a higher hydrogen content (desirable) and is more easily converted to petroleum than terrestrial organic detritus. Recently deposited sedimentary organic matter undergoes diagenesis (microbial transformation, chemical rearrangements etc.). The end result is that the organic matter is in a chemical state that can then be converted to petroleum with increasing temperature.

The Guaymas Basin, Gulf of California is an excellent example of an ocean hydrothermal system that is generating petroleum-like products. Organic geochemical analysis of samples from the Guaymas Basin yields

information concerning the composition, the thermal origin, as well as the similarities and differences of hydrothermal petroleum to geothermal petroleum.

The products in the Guaymas Basin are generated from the thermal alteration of immature organic matter. The evidence of a thermogenic origin includes: (1) composition and stable carbon isotope data of interstitial gas; (2) the presence of gasoline-range hydrocarbons (and odorous compounds); (3) the relative amounts of aromatic (unsaturated hydrocarbons with at least one benzene ring)/naphthenic (saturated hydrocarbon rings) and asphaltic material versus straight chain hydrocarbons; and (4) the broad distribution of complex hydrocarbons.

The hydrothermal petroleum in the Guaymas Basin is derived from a high temperature pyrolysis process (150-350°C). The evidence for this process and not one of normal petroleum genesis (150° max) includes: (1) the presence of olefins (unsaturated hydrocarbons with double bonds), (2) large amounts of asphaltic material, and (3) the presence of polynuclear aromatic hydrocarbons.

Hydrothermal petroleum has both similarities and differences with reservoir petroleum. The similarities include: (1) gasoline-range hydrocarbons, (2) a full range of n-alkanes (saturated, straight chain hydrocarbons), (3) naphthenic hump (complex, unresolvable, polycyclic hydrocarbons), (4) pristane and phytane significant (biological fingerprints), and (5) stabilized molecular markers (chemically mature molecular fingerprints). The differences with reservoir petroleum include: (1) alkene content (olefins--double bond, unsaturated) (2) polynuclear aromatic hydrocarbons, and (3) immature molecular markers present.

The hydrothermal systems of ocean spreading centers are areas where significant energy resources are being discovered. Polymetallic sulfide ores, thermal waters with temperatures up to 350°C, diverse and abundant biota, and hydrothermal petroleum generation have all been documented. Serious consideration should be given to any or all aspects of ocean hydrothermal energy technology.

I. INTRODUCTION

This report presents a general overview into the genesis of petroleum-like products resulting from naturally occurring thermal processes at active oceanic spreading centers. The predominant control in hydrothermal petroleum genesis is temperature (e.g., 150°C- 350°C+). This is in contrast to geothermal petroleum processes where formation temperatures are 50-150°C (peak generation) and where "time" is an all-important parameter.

Hydrothermal petroleum can in essence be called an "instantaneous" process, with generation times tied closely to the magmatic processes occurring at the oceanic spreading centers. The temperatures generated in these areas have the effect of pyrolyzing (thermally cracking) sedimentary organic matter into smaller molecular weight compounds, which are then transported to the seabed by hydrothermal fluids and advection/diffusion. It should be noted that the formation of commercial amounts of petroleum at active oceanic spreading centers requires the deposition of sediments which contain organic matter of sufficient quantity and quality. Although this physical setting is fairly unique (e.g., Guaymas Basin, Gulf of California), it demonstrates that the thermogenic characteristics of active spreading centers provide a mechanism for the conversion of immature organic matter to petroleum-like products.

II. PHYSICAL ENVIRONMENT AND THERMAL PROCESSES

Hydrothermal petroleum genesis from an active oceanic spreading center can be illustrated by using the extensively studied Guaymas Basin, Gulf of California as an example. Guaymas Basin is a ridge-crest hydrothermal system with a sediment cover and a maximum water temperature measured at 315°C at 200 atmospheres (Simoneit, 1983). The process of ocean plate accretion results in high conductive heat flow (average 1.2 Wm^{-2}) and dike and sill intrusions into unconsolidated sediments. Sediment accumulation is approximately 1-4 m/1000 years and sediment thickness is $\leq 500 \text{ m}$. (Curry et al., 1979, 1982). The most recent tectonic activity, inferred from seismic evidence and heat flow data, ranges in age from approximately

10 years to 18,000 years (Williams et al., 1979). Leg 64 of the Deep Sea Drilling Project, dredging, piston coring and diving with the DSRV Alvin provided conclusive evidence of active hydrothermal vents, polymetallic sulfide ores, diverse and abundant biota and petroleum-like products in the Guaymas Basin (Curry et al., 1982; Simoneit, 1984).

Petroleum genesis occurs as a result of the thermal alteration of sedimentary organic matter. The temperatures of the intruding dikes and sills, the thermal waters, and also the deeper regional heat sources (magma bodies)--all result in the pyrolyzation of the sedimentary organic matter into smaller molecular weight compounds. Figure 1 shows that with increasing proximity to the sills and with increasing depth (e.g., toward

Figure 1. Effects of sill intrusion and deeper heat source on sedimentary organic matter. A, D--Immature, unaltered B, E--Moderate alteration C, F--Severely altered (Simoneit et al., 1984).

regional heat source), the resulting products give pyrogram traces that appear thermally altered, even though the sedimentary organic matter in the region as a whole is immature.

It appears that the sill intrusions have only a local and lateral thermogenic effect on the organic matter. They probably play a greater role in pore water expulsion and as a source of heat for thermal water generation and convection. The thermal alteration of the organic matter is primarily attributed to the convecting hydrothermal system and deep regional heat sources (oral communication, B. Simoneit, 1984). Thermal vent water has been measured as high as 315°C and there is evidence to suggest that temperatures at the sill-sediment contact may rise as high as 400°C. This is based on:

1. Hydrothermal minerals present--epidote, chlorite, albite, etc. In ridge-crest geothermal systems, estimated temperatures at which seawater-rock interactions occur are at least 300°C (Einsele et al., 1980).
2. Increase in dissolved chloride, lithium and manganese.
3. C/N ratios approach infinity below 150 m and increase at sill contacts. The removal of organic N is an indicator of thermal stress (see Figure 2).

It has been suggested that the emplacement of sills in the Guaymas Basin leads to the heating and expulsion of pore waters. The heated pore water then reacts with the basalts and surrounding sediments, becoming laden with dissolved minerals and hydrocarbons. Migration occurs vertically and laterally through permeable sediments, eventually traveling along fault and fracture zones to the surface where the dissolved substances are precipitated. This mechanism does not require the recharge by seawater that has been suggested for sediment deficient spreading

Figure 2. Atomic ratios of organic carbon to nitrogen versus depth (DSDP Site 477).

centers (Einsele et al., 1980). Figure 3 gives a general overview of a hydrothermal system operating in the Guaymas Basin that incorporates a seawater recharge system. This model (less sediments and hydrocarbon products) is thought to operate at most spreading centers with hydrothermal systems. Note: It includes both a seawater recharge and a stockwork zone (e.g., mechanism of pore water expulsion). The figure also shows the process involved in polymetallic sulfide ore enrichment and the characteristics of the physical environment.

Summary

A mechanism for the generation of petroleum does exist at active ocean spreading centers. Deep-seated regional magma chambers, sill intrusions, and convecting thermal water all play a role in the conversion of sedimentary organic matter to petroleum. The temperatures generated at these spreading centers (350°C max.) are high enough to thermally crack the indigenous organic matter into smaller molecular weight hydrocarbon compounds. The petroleum is then removed by hydrothermal convection and diffusion, followed by condensation at the seabed.

Figure 3. Overview of a Hydrothermal System
(Adapted from Scott, 1983)

III. ORGANIC SOURCE MATERIAL CONSIDERATIONS

The quality of the source material used in the formation of petroleum has an important impact on the chemical composition of the final product. Although all organisms are basically composed of the same chemical constituents (lipids, proteins, carbohydrates and lignin in higher plants), there are characteristic differences with respect to relative abundances and detailed chemical structures. For example, terrestrial higher plants are mainly composed of cellulose and lignin which have supportive functions not needed in aquatic planktonic organisms. Higher plants have detrital organic matter with H/C values around 1.0 and it is more aromatic in nature (due to lignin). On the other hand, marine plankton is mainly composed of proteins, carbohydrates and lipids, which have detrital organic matter with H/C values around 1.5 to 1.9 (desirable) and which is more aliphatic or alicyclic in nature. Although aromatic compounds yield the highest octane ratings in petroleum, they also tend to be concentrated in the heavier fractions. Aliphatic compounds dominate in the gasoline range. Figure 4 presents examples of source material chemical constituents and their relative abundances.

The most desirable starting material is one that is both hydrogen and lipid rich (Demailson and Moore, 1979). Lipid concentrations and chemical structures are variable, being primarily dependent on the type of organic matter incorporated into the sediments. Lipids encompass fat substances, waxes and lipid-like components, such as oil-soluble pigments, terpenoids, steroids and many complex fats. Hydrogen concentrations are controlled to a large extent by the oxicity/anoxicity of the depositional environment and the diagenetic history of the organic detritus.

Although the hydrogen and lipid content of the initially deposited organic detritus is important, the direct precursor of most petroleum is kerogen. Kerogen is the result of diagenetic processes acting on the organic matter (see Figure 6). It is the composition of the kerogen that determines whether petroleum or gas is the predominant final product. The diagenesis of marine organic matter results in kerogen that is more

COMPOSITION OF BIOMASS AND PRODUCTIVITY OF VARIOUS TYPES
OF ORGANISMS IN THE BLACK SEA

Organisms	Biomass, 10 ⁶ t	Production per year 10 ⁶ t	%
Plankton	15.0	2,745	13.22
Phytoplankton (without bacteria)	13.5	2,700	13.0
Zooplankton	1.5	45	0.22
Benthos	40.0	80	0.38
Makrophytes	30.0	40	0.19
Zoo-benthos	20.0	40	0.19
Bacteria in water	30.0	12,000 - 18,000	57.60
Bacteria in sediment	10.0	6,000 - 8,000	28.80
Fish	1.0	0.17	—
Total	96.0	> 23,000	100

THE MAIN CHEMICAL CONSTITUENTS OF MARINE PLANKTON

	Protein	Lipids	Carbo- hydrates	Ash
Diatoms	24-44%	2-10%	0-31%	30-50%
Dinoflagellates	41-48%	2-6%	6-36%	12-77%
Copepods	71-75%	5-19%	0-3%	4-6%

(% dry weight)

MEMBRANE CONSTITUENTS OF BACTERIA

Type of organic compound	Percent of membranes of	
	<i>Micromonas lyubskii</i>	purple bacteria
Lipid (neutral)	28-37 (9)	40-50 (10-20)
(phospholipids)	(28)	(30)
Protein	50	50
Polysaccharide	15-20	5-30

(% dry weight)

COMPOSITION OF LIPID FRACTION (WT. %) OF CALANOID COPEPODS

Fraction	<i>Calanus helgolandicus</i> wild type	<i>Gammarus princeps</i> wild type
Hydrocarbons	3	Trace
Wax esters	30	73
Triglycerides	4	9
Polar lipids	17	
Phospholipids	45	17
Total lipid (gross dry wt.)	15	28.9

Figure 4. Examples of source material chemical constituents and relative abundances. (Simoneit, 1984.)

aliphatic in nature, whereas the diagenesis of terrestrial organic matter results in kerogen that is more aromatic in nature.

Figure 5 represents various H/C^a and O/C^b ratios for source organic matter and their approximate maturation paths through oil and gas production. Type I Kerogen, which represents an algal or bacterial source material, has higher H/C and lower O/C values than Type III Kerogen (terrestrial source). Algae and bacteria also have lipid contents with dominant n -alkane^c carbon chain lengths from C_{16} to C_{22} . Terrestrial higher plants, on the other hand, have lipids with dominant C -chain lengths around C_{29} to C_{31} . Therefore, algal and bacterial organic matter are more suitable for conversion to petroleum than terrestrial plants with longer C -chain lengths.

a. H/C = Hydrogen/Carbon.

b. O/C = Oxygen/Carbon.

c. n -alkane = normal (straight chain) alkanes.

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- I. High H/C, low O/C (possible algal origin)
- II. Intermediate (possible mixed marine and terrestrial source).
- III. Low H/C, high O/C (possible terrestrial source)

- The organic matter of the Guaymas Basin is predominantly marine in origin with some terrestrial input and is composed of the various operational fractions as shown in Table 1. All these carbonaceous fractions are very sensitive to thermal stress and are thus easily pyrolyzed.

The interstitial gas in recent sedimentary environments consists primarily of methane, carbon dioxide, and sometimes hydrogen sulfide. Biogenic hydrocarbon gases usually have $C_1/C_2 + C_3^a$ ratios greater than 1000, while those of a thermogenic origin have ratios less than 50.

a. $\text{CH}_4/\text{CH}_2\text{H}_6 + \text{C}_3\text{H}_8$.

TABLE 1. ORGANIC MATTER OF SEDIMENTS: CONTEMPORARY AND RECENT (Generally Biogenic Components) Simoneit, 1983

<u>Gas</u>	<u>Lipids</u>	<u>Humic and Fulvic Substances</u>	<u>Carbonaceous Detritus (humin, pseudokerogen)</u>
(CH ₄ , CO ₂ , H ₂ S) minor amount of total C _{org}	(C ₈ - C ₄₀ ⁺) minor amount (max. ~10%)	(macromolecular M.W. ~10 ³ to >10 ⁶) variable amount	(macromolecular, >humates) major amount

The compound classes commonly found as lipid components in immature sediments are: hydrocarbons (normal, iso-, anteiso-, alkene, aromatic and isoprenoid), fatty acids (also normal, iso-, anteiso-, unsaturated and isoprenoid), fatty alcohols, ketones, wax esters, steroids, terpenoids (sesqui-, di-, sester-, tri- and tetra-) and tetrapyrrole pigments (Simoneit, 1978a; 1982a; Cranwell, 1982; Mackenzie et al., 1982a). Other compound classes include: amino acids and peptides, pyrimidines and pyrimidines, and carbohydrates (Simoneit, 1978a; Simoneit, 1983).

Humic and fulvic substances (solubles in aqueous base) are mixtures of complex macromolecules, the latter are of lower molecular weights and thus soluble in dilute HCL. Little else is known about the detailed structures of the compounds. However, it has been shown that humic and fulvic substances decrease in concentration with depth of burial or geologic age (e.g., Nissenbaum and Kaplan, 1972; Huc and Durand, 1977; Stuermer and Simoneit, 1978).

Recent sediments yield a "pseudokerogen," which is a lipid macromolecular material, constitutionally less complex than ancient kerogen, but related to it. Figure 6 shows the fate of organic matter during sedimentation and diagenesis. Included is the approximate location of organic matter at the pseudokerogen state (represented by the horizontal dashed line).

Figure 6. Fate of organic matter during sedimentation and diagenesis.

Summary

It is evident that the type of organic matter incorporated into sediments is an important consideration in petroleum formation. The quality (hydrogen and/or lipid content) and quantity, as well as the diagenetic history of the organic matter, all play a role in the chemical composition of the final product. Marine source material (e.g. algae and

bacteria) is generally considered more desirable than terrestrial (higher plant) sources. Organic matter of marine origin has H/C values around 1.5⁺ and dominant n-alkane carbon chain lengths around C₁₆₋₂₂, and is therefore more easily converted to petroleum than terrestrial organic matter (H/C ~ 1.0 to 1.2, C₂₉₋₃₁ dominant).

IV. HYDROTHERMAL PETROLEUM PRODUCTS AND GEOCHEMISTRY

Organic geochemical analysis can yield extensive information concerning the formation, maturation and chemical make-up of petroleum (crude oil). Questions about such things as thermal history, source material, depositional environment and degradation can be answered, thus providing a better understanding of the mechanisms and processes involved in petroleum genesis. Analysis of the various hydrocarbon fractions (e.g. aliphatic, aromatic/naphthenic and asphaltic) and biological markers (geochemical and molecular finger prints) allows for the interpretation of the maturity, thermal history and source material of a given petroleum. The following discussion of the hydrothermal petroleum from Guaymas Basin will characterize its composition, give evidence of a thermogenic origin, as well as show some of the similarities and differences to geothermal petroleum.

Petroleum Products and Geochemistry (Guaymas Basin)

The collection and subsequent analysis of samples from the Guaymas Basin, Gulf of California has confirmed that petroleum is being generated at an active oceanic spreading center. The sediments recovered from coring and dredging operations were stained with a petroleum-like oil and also had a strong odor similar to diesel fuel (Simoneit and Lonsdale, 1982).

Thermogenic gas, as well as H_2S and CO_2 were identified from all sites based on composition and stable carbon isotope data.^a At shallow

$$a. \delta^{13}C = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000$$

where

$$R = {}^{13}C/{}^{12}C \text{ ratio, expressed per million, } 0/00.$$

depths (see Figure 7) the data shows a biogenic pattern. However, with increasing depth $\delta^{13}\text{C}$ values become heavier, indicating the removal of the lighter $^{12}\text{CH}_4$ due to thermal stress (Simoneit, 1984).

Figure 7. Trends of carbon-12 depletion versus depth in interstitial methane at DSDP sites 477 (---o---), 478 (---Δ---) and 481 (---□---), ■ = canned or frozen samples ($\delta^{13}\text{C}$ data reported versus PDB standard, the intrusions are indicated at the appropriate depth for each site). (Simoneit, 1984.)

Table 2 (A and B) gives concentrations and ratio values for the C_1 - C_5 gaseous hydrocarbons as observed in the Guaymas Basin. It is evident from Figure 7 and Table 2 that the thermal alteration of organic matter has produced gaseous hydrocarbons (principally methane but also C_2 - C_5 gases).

TABLE 2. CONCENTRATIONS AND VARIOUS RATIOS OF C₁-C₅ HYDROCARBONS
OBSERVED ON LEG 64 OF THE DEEP SEA DRILLING PROJECT

A

Maximum Concentrations of C ₁ -C ₅ Hydrocarbons Observed on Leg 64					
Site	CH ₄ (%)	C ₂ H ₆ (%) ^a	C ₃ H ₈ (%) ^a	C ₄ H ₁₀ (%) ^a	C ₅ H ₁₂ (%) ^a
474	98.8	0.08	0.017	0.007	--
475	No gas observed	--	--	--	--
476	No gas observed	--	--	--	--
s-rift 477	93.2	0.50	0.040	0.003	--
478	97.2	0.10	0.007	0.001	--
479	92.2	0.122	0.010	0.016	0.0015
480	91.8	0.035	0.003	0.0003	--
N-rift 481	98.7	0.634	0.024	0.015	0.022

a. Based on 100% methane, includes all isomers.

TABLE 2. (continued)

B

Various Ratios of C ₁ -C ₅ Hydrocarbons Observed on Leg 64			
Site/Core	$C_2/C_1 \times 10^{-4}$	$C_1/(C_2 + C_3)$	$C_1/(C_2 \text{ to } C_5)$
474-8.3 ^a	0.56	16050	16050
474A-11-3 ^b	5.65	1470	1380
477-5-1 ^a	0.30	22500	20810
Gasoline HC 17-3 ^b	59.6	157	156
479-3-2 ^a	0.50	17430	17430
44-2 ^b	18.8	1020	878
Gasoline HC 481A-4-1 ^a	7.0	15070	12330
12-5 ^b	64.4	316	302

a. Biogenic gas.

b. Biogenic gas with admixed thermogenic gas.

Gasoline-range hydrocarbons were analyzed in two dredge samples and the results are listed in Table 3. In both cases the concentrations of branched and cyclic compounds (possibly also olefins) far exceed the abundance of normal hydrocarbons (Simoneit and Lonsdale, 1982). Although there are differences between the samples (e.g. total C₂-C₁₀ concentrations are ~ 10 times greater in sample 7D-5A than in 7D-3B, etc.), the relative distributions of all hydrocarbons are very similar for both samples. It is the relatively large amounts of C₂-C₁₀ hydrocarbons and their structural diversity that confirm an origin by thermal generation (Whelan and Hunt, 1982).

TABLE 3. VOLATILE HYDROCARBONS IN DREDGE SAMPLES FROM GUAYMAS BASIN
(Simoneit and Lonsdale 1982)

Compound ^a	Retention time (min)	Approximate Concentration (ng cm of headspace headspace--150 cm total)	
		7D-3B	7D-5A
2- Methylbuntane	5.1	2.6	14
n-pentane	5.4	1.4	39
Cyclohexane	7.3	0.5	6
4-Methyl-2-pentene	8.0	0.8	6.3
3-Methylpentane	8.3	1.4	11
2-Methylpentane + benzene	8.6	0.9	44
n-Hexane	9.7	9.2	260
C ₂ -Cyclopentane	10.3	3.3	46
Methylcyclohexane	10.7	14	1.050
3-Methylhexane	12.1	3.3	--
2-Methylhexane	12.4	5.8	210
n-Heptane + toluene	13.5	>130	950
n-Octane	16.4	24	29
n-Nonane	19.2	48	26
n-Decane	22.2	17	40
Total C ₂ -C ₁₀ hydrocarbons (mg)		80	875

a. Identifications based on GC retention time only.

To compare the effects of thermal stress, the total hydrocarbon fractions of the lipids were evaluated for two samples; one of unaltered biogenic lipids and one of thermogenic petroliferous bitumen. The examples are shown in Figure 8. The unaltered sample (8A) exhibits n-alkanes ranging from C_{14} to C_{35} with a strong odd carbon number predominance, especially $>C_{23}$ (terrestrial plant wax). There are also subordinate amounts of C_{20} and C_{25} natural cyclic olefins, triterpanes and elemental sulfur, S_8 . The thermally altered sample (8B) is characterized by n-alkanes with a range from C_{15} - C_{31} and essentially no carbon number predominance. Primary olefins and elemental sulfur are also dominant components. The thermal alteration of lipids is indicated by the loss of the carbon number predominance of the n-alkanes, the appearance of a broad hump of unresolvable complex material, and the presence of large amounts of primary olefins and elemental sulfur, etc. (Simoneit, 1983).

Figure 9 represents gas chromatograph (G.C.) traces of the aliphatic hydrocarbon fraction for two samples dredged from a hydrothermal mound in Guaymas Basin. Trace 9a exhibits a pattern typical of petroleum, where the dominant n-alkanes range from C_{12} - C_{33} with no carbon number predominance ($CPI_{12-33} = 1.03$)^a and a maximum at C_{21} . Also typical of petroleum is the complex, unresolved mixture of branched and cyclic hydrocarbons (hump) ranging from C_{11} - C_{31} (Simoneit and Lonsdale, 1982). Pristane and Phytane (Pr and Ph) are biological markers and their ratio is often used as an indicator of environmental conditions of sedimentation (oxidizing or reducing). The Pr/Ph value for 9a is 1.06. On the other hand, trace 9b exhibits a narrower G. C. profile skewed to lower carbon numbers. The major peaks represent mono- and di-olefins (alkenes) ranging from C_{12} - C_{19} and the unresolved hump ranges from C_9 - C_{21} . This is very unlike typical petroleum as olefins are not found in mature crude oils. The n-alkanes are present only as minor components

a. CPI - Carbon Preference Index: for hydrocarbons it is expressed as a summation of the odd carbon number homologs over a range divided by a summation of the even carbon number homologs over the same range; for fatty acids and alcohols it is the same ratio only inverted to have even-to-odd homologs (Simoneit, 1978a).

Figure 8. GC-MS total ion current traces for total hydrocarbon fractions from (a) an unaltered, immature sample and (b) a thermally altered sample (a: DSDP 64-481A-8-7; b: 64-477-17-3; numbers indicate n-alkanes) (Simoneit, 1983).

Figure 9. Gas chromatograms of the aliphatic hydrocarbon fractions for: (a) sample 7D-2B; and (b) sample 7D-4A,B. The carbon chain length of the n-alkanes is indicated by the arabic numerals, olefins are indicated by chain length: double bond equivalent, Pr = pristane, Ph = phytane (Simoneit, 1983).

(C₁₀-C₂₃), with a slight odd carbon number predominance (CPI₁₀₋₂₃ = 1.2) and a maximum at C₁₅. Pristane is greater than Phytane (Pr/Ph = 1.6) (Simoneit and Lonsdale, 1982).

The G.C. trace of the aromatic/naphthenic fraction (Figure 10) indicates that the major resolved peaks are polynuclear aromatic hydrocarbons (PAH). This group of compounds, like olefins, are rare in petroleum but common in higher temperature pyrolysis residues. A further indication of a pyrolytic origin of the samples is the presence of five-membered alicyclic rings. A list of the compounds found in this fraction is given in Table 4. The fact that the dominant analogs for both samples (10a,b) are the pericondensed aromatic series (reactive form), indicates rapid quenching by hydrothermal removal and subsequent condensation at the seabed.

Figure 10. Gas chromatograms of the aromatic/naphthenic hydrocarbon fractions for: (a) sample 7D-2B; and (b) sample 7D-4A,B. Numbers and corresponding compounds are listed in Table 4 (Simoneit and Lonsdale, 1982).

Molecular markers are organic compounds whose carbon structure or skeleton is sufficiently stable to be recognized in crude oil. These markers are good indicators of thermal stress since they tend to go to their more stable (mature) form with increasing thermal stress. The major

TABLE 4. POLYNUCLEAR AROMATIC HYDROCARBONS IN DREDGE SAMPLES FROM GUAYMAS

Compound	No. ^a	Formula	MW	7D-2B (ng per g bitumen)	7D-4A.B (ng per g bitumen)
Indane	1	C ₉ H ₁₀	118	0.5	0.4
Tetramethylbenzene		C ₁₀ H ₁₄	134	0.6	4.5
Naphthalene		C ₁₀ H ₈	128	4	12
2-Methylnaphthalene		C ₁₁ H ₁₀	142	8	6
1-Methylnaphthalene		C ₁₁ H ₁₀	142	6	4
Biphenyl		C ₁₂ H ₁₀	154	3	1.2
Dimethylnaphthalene		C ₁₂ H ₁₂	156	50	8
Acenaphthene		C ₁₂ H ₁₀	154	0.8	2.8
Trimethylnaphthalene		C ₁₃ H ₁₄	170	16	40
^a Fluorene		C ₁₃ H ₁₀	166	5	0.8
Dibenzothiophene	2	C ₁₂ H ₈ S	184	12	8
Phenanthrene		C ₁₄ H ₁₀	178	27	8
Anthracene		C ₁₄ H ₁₀	178	5	10
^a Fluoranthene	3	C ₁₆ H ₁₀	202	40	34
Pyrene		C ₁₆ H ₁₀	202	200	178
2,3-Dibenzofluorene	4	C ₁₇ H ₁₂	216	40	40
Benz(a)anthracene		C ₁₈ H ₁₂	228	15	16
Chrysene (triphenylene)	5	C ₁₈ H ₁₂	228	42	38
Benzo(b)fluoranthene		C ₂₀ H ₁₂	252	40	28
Benzo(k)fluoranthene		C ₂₀ H ₁₂	252	10	6
+Benzo(e)pyrene	7	C ₂₀ H ₁₂	252	62	45
+Benzo(a)pyrene	8	C ₂₀ H ₁₂	252	25	16
Perylene	9	C ₂₀ H ₁₂	252	45	40
1,2,5,6-Dibenzanthracene	10	C ₂₂ H ₁₄	278	3	2.4
Benzo(g,h,l)perylene		C ₂₂ H ₁₂	276	100	24
Coronene	11	C ₂₄ H ₁₂	300	64	5

a. See Fig. 10

diagnostic molecular markers consist of triterpenoids, extended diterpanes, and steranes with their rearranged analogs (diasteranes) (Simoneit and Lonsdale, 1982). Figure 11 gives the relative distributions of the major molecular markers for sample 7D-2B (thermally altered) and for sample 30G (unaltered). Sample 7D-2B (11a,c) shows the following marker distribution.

- o Extended diterpanes: Distribution pattern similar to other mature petroleum samples, range C_{20} to C_{29} .
- o Triterpenoids: In thermodynamically more stable form. Characterized by 17α , $21\beta(H)$ --hopane series from C_{27} to C_{35} (no C_{28}). Also present are the homologies from C_{31} to C_{35} as 22-S and R diastereomeric pairs in a ratio of about unity. This series constitutes the stable mature form of these compounds, and seems to have been generated by hydrothermal activity.
- o Steranes: The large $5\alpha(H)$, $14\alpha(H)$, $17\alpha(H)$ -sterane concentration is a result of elevated thermal stress, which probably converted other steroidal compounds to these hydrocarbons. The steranes range from C_{26} to C_{30} with cholestane the major homolog.

In contrast to the thermally altered sample, 30 G (11b) shows a very different molecular marker distribution pattern.

- o Extended diterpanes: There are no extended diterpanes found in sample 30G.
- o Triterpenoids: Biogenic markers of the $17\beta(H)$, $21\beta(H)$ -hopane series and other triterpenes predominate. This represents the immature form of the triterpenoids.

Figure 11. Relative distribution diagrams for triterpenoids in: (a) sample 7D-2B; and (b) an unaltered sample, station 30G, and steranes in C, sample 7D-2B (Simoneit and Lonsdale, 1982).

Table 5 shows the composition and yields of hydrothermal petroleum from the Guaymas Basin (does not include volatile compounds $< C_{15}$). The data for the various samples shows a wide variability. These differences can be attributed to varying degrees of thermal stress, the nature of the source material (marine or terrestrial predominance), the diagenetic history of the source material, etc. There are also differences between the compositions of average petroleum (geothermal) and hydrothermal petroleum. Guaymas Basin petroleum has large amounts of NSOs,^a non-hydrocarbons and asphaltenes. These compounds are indicative of petroleum generated from immature organic matter by pyrolysis.

Summary

The petroleum products in the Guaymas Basin are generated from the thermal alteration of immature organic matter. The evidence for a thermogenic origin includes: (1) composition and stable carbon isotope data of interstitial gas; (2) the presence of gasoline range hydrocarbons (and odorous compounds); (3) the relative amounts of aromatic/naphthenic

a. NSO compounds = Nitrogen, sulfur, oxygen compounds.

TABLE 5. COMPOSITION AND YIELDS OF HYDROTHERMAL PETROLEUM--GUAYMAS BASIN (Simoneit, 1984)

Sample	Total Extract Yield (mg/g sed)	C + Hexane Solubles			Non-Hydrocarbons (%)	Asphaltenes (%)
		Saturates (%)	Aromatics (%)F	NSOs (%)F		
1168-1-2	81	7	16	25	78	52
-3B	19	2	7	21	91	70
1172-3	12	53	18	16	30	13
-4	350	72	12	11	16	5
1173-3	--	23	10	22	66	45
-8	97	45	23	23	32	9
1177-2E	63	41	25	18	35	16
-2D	71	48	25	15	27	12
-4B	10	51	15	20	34	14
Average		38	16.8	19	45.4	26.2
Average Petroleum	N/A	57.2	28.6	--	14.2	--
Average Source Rock Bitumen		29.2	19.7	--	51.1	--

and asphaltic material versus aliphatic hydrocarbons; and (4) the broad distribution of hydrocarbons (hump), C_{13} - C_{33} , and the presence of pristane and phytane.

These oils are derived from higher temperature pyrolysis processes (150-350°C). The evidence for this process and not one of normal petroleum genesis (150° max) includes: (1) the presence of branched and in-chain olefins, (2) large amounts of asphaltic material, and (3) the presence of peri-condensed PAH.

The presence of minor biogenic marker residues (17 β (H), 21 β (H)-hopanes and triterpenes) is another indication that these oils are derived from the thermal alteration of immature organic matter. These compounds are not found in mature petroleums (e.g. they have the more mature stable 17 α (H), 21 β (H)-series, etc.).

It has been shown that the sediments at depth contain interstitial gas (admixed thermogenic and biogenic), as well as thermally derived bitumen. Also, there are petroleum-like products being precipitated at the seabed. These facts indicate that the vent water must be carrying the petroleum products to the surface where they condensate.

V. CONCLUSION

Hydrothermal petroleum genesis from an active oceanic spreading center has been illustrated by using the Guaymas Basin as an example. This ridge-crest hydrothermal system generates water temperatures up to 315°C at 200 atmospheres. It is different from most other active spreading centers in that there is a sediment cover ranging up to 500 m in thickness. The magmatic processes occurring at this spreading center generate temperatures which can thermally crack the sedimentary organic matter into smaller molecular weight compounds (e.g. petroleum-like products). Although most active spreading centers do not have a sediment cover, they do have the same thermal processes operating (e.g. deep regional magma bodies, hydrothermal systems, and dike and sill intrusions). Thus, if organic matter is present, there exists (at active spreading centers) a mechanism for its conversion to petroliferous products.

The type of organic matter present has an impact on the chemical composition of the final product. Terrestrial higher plants are predominantly composed of cellulose and lignin, whereas algae and bacteria (marine organisms) are mainly composed of proteins, lipids and carbohydrates. Marine detrital organic matter has higher H/C values, higher lipid contents, and smaller dominant C-chain length n-alkanes than terrestrial organic matter. Therefore, marine organic matter is more easily converted to petroleum.

Closely associated with organic matter quality (e.g. hydrogen and lipid concentrations) is the diagenetic history of the organic matter. The conditions of the diagenetic environment (reducing or oxidizing) either promotes or inhibits the preservation of the organic matter in a form that is favorable to its subsequent conversion to petroleum.

There are both similarities and differences between hydrothermal petroleum and geothermal petroleum. Like geothermal petroleum, hydrothermal petroleum has a dominant n-alkane range from ~ C₁₂ to C₃₁, no carbon number predominance (CPI ≈ 1.00), a pristane and phytane ratio of about unity and a complex, unresolved mixture of branched and cyclic hydrocarbons ranging from C₁₁ to C₃₁. Hydrothermal petroleum

differs from geothermal petroleum by the presence of branched and in-chain olefins, peri-condensed polynuclear aromatic compounds and minor biogenic marker residues.

The petroleum products of the Guaymas Basin have resulted from the high temperature pyrolysis (150°-350°C) of immature organic matter. This is different from geothermal petroleum genesis where formation temperatures are $\leq 150^{\circ}\text{C}$. This origin is indicated by the presence of the olefins, the peri-condensed PAH and the large amounts of asphaltic material.

One of the most important advantages of hydrothermally produced petroleum is time. This is an "instantaneous" process, where as geothermal petroleum genesis requires millions of years.

Whether or not areas like Guaymas Basin are commercially viable will be answered by further exploration. There is abundant energy available for use at active oceanic spreading centers and methods for its utilization should seriously be considered.

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