**A PRELIMINARY STUDY OF IN SITU COMBUSTION IN
DIATOMITES**

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ABSTRACT

Diatomaceous sediments of California host large reserves of oil and gas but are incompletely exploited. The matrix of these sediments is comprised largely of the frustules of diatoms (microscopic marine plants). Punctae in the frustules are responsible for the high porosities characteristic of diatomites (up to 70 vol. %), but because of the very small size of the pores, permeabilities are low (commonly around 1 md). Furthermore, the oil contained in the reservoirs is often either immature or heavily biodegraded, hence viscous.

In order to test the feasibility of applying in-situ combustion techniques to diatomaceous reservoirs, a laboratory test was conducted for a section of core taken in the south plunge of the anticline in the Lost Hills field of the San Joaquin Valley in California.

During the experiment, a fast steam plateau, good oxygen utilization, and an unusual front were observed. Fingering caused formation of a second front downstream. This finger stabilized and later became very hot (1600°F). Velocity of front movement through the core almost doubled after the two fronts joined. API gravity of the oil extracted from the core ranged between 28 and 45, compared to the original value of 28° API.

Tests were conducted to compare the cores before and after combustion, using scanning microscopy, power x-ray diffraction, and extraction techniques. After burning, the sediments changed from dark brown to red in color as a result of oxidation of organic and iron phases. Small numbers of diatom frustules were transformed from amorphous opal to quartz, with accompanying occlusion of pore spaces. With the exception of the color change, however, the sediments remained largely unaltered.

It is especially interesting to note that the kerogen within the sediments appears to supply a portion of the fuel required for combustion. Kerogen is detrital organic matter that can be burned but cannot be extracted easily from a core in the laboratory. Kerogen's presence could make in-situ combustion more economical and efficient than other EOR methods in diatomites.

INTRODUCTION

Diatomaceous sediments are composed mainly of diatom frustules of microscopic algae which comprise a large part of the marine planktonic flora. Diatom accumulations in a reducing environment are potential oil-source rocks. Because diatomites have high porosities, they may also be reservoir rocks. Indeed, large diatomite oil reservoirs occur in California in the oil-producing San Joaquin Valley and the coastal borderland.

Diatoms are very fine-grained sediments ranging in diameter from tens to hundred of microns, with a high porosity largely formed by microscopic punctae of individual frustules. The geometry of this microporosity results in excellent bulk porosities (as high as 70%) and poor permeabilities (as low as 1 md or less).

In the Cenozoic, diatoms were an important component of earth's biota. During the Tertiary, active wrench tectonism altered the major organic-siliceous deposits in California. In the San Joaquin Valley, diatomite ultimately is preserved on the crests of structural features. Oil found in these shallow sediments is either immature or highly biodegraded and, hence, very viscous.

It was not until the recent oil price increase that producing oil from diatomites become profitable. As a result, increased recovery efforts were undertaken in areas of California where oil-saturated diatomites and cherts (the diagenetic end product of these microfloral accumulations) occur.

Diatomite reservoirs are often highly fractured, significantly increasing permeabilities and improving recovery rates. Still, primary production from these reservoirs amounts to only about 5% of original oil in place.¹ Consequently, enhanced recovery methods must be used to make the venture economical. The most commonly used methods--hydrofracturing and steam injection--are costly or limited in effectiveness. Soft formations and high clay content restricts the applicability of these techniques in diatomite reservoirs.²⁻⁴ Currently, extensive oil mining operations are underway at McKittrick shallow diatomite formations.⁴ However, no reported in-situ combustion recovery has been attempted in these fields.

The core used in this study was taken from a well on the South plunge of the Lost Hills field anticline in the San Joaquin Valley (Fig. 1). This core is a sample of the Mio-Pliocene Etchegoin Formation between the 'D' and 'W2' e-log correlation points.⁵

The Lost Hills field is developed on an antithetic fold of the San Andreas wrench fault system and has apparently been an active structure principally since the Pliocene, just after diatomaceous sedimentation ceased in this area. The trap is anticlinal, enhanced by lithofacies variations. Lost Hills is typical of oil fields in the San Joaquin Valley. Because such folds have been growing through most of the mid-to-late Cenozoic period in a basin which has been passively filling in with diatomaceous sediments and clastics, the reservoir rocks on the anticlines have been at insufficient burial depths to crack the in-situ organics. However, sufficient burial depths have been achieved in the associated synclines. Mature hydrocarbons have then migrated into the anticlinal reservoirs. Because the reservoir rocks are also immature source rocks, they contain significant amounts of detrital organic matter in addition to the mature oil which has migrated into the available pore space.

APPARATUS

The combustion tube apparatus used in this experiment has been discussed in the literature.⁶ Figure 2 shows a schematic diagram of the apparatus. Minor changes were introduced to accommodate the problems that might be encountered during this run. These changes were: 1) use of a new tube without the gas sampling ports along its length; and 2) use of continuous gas analyzers for analysis of the effluent gas. Because of these changes, no use was made of the Fischer Gas Partitioner.

PREPARATION OF PACK

The cores used in the experiment were shaped in half-cylinders of approximately 10" in length and 5" in diameter, and were coated with wax and covered in plastic-and-aluminum wraps. Too wide to place directly in the tube, the cores were first pulverized in a mill. After sieving, the finer grains (smaller than mesh 8) were used to pack the tube. Care was taken to tamp the pack uniformly and continuously. After packing, the flanges were bolted to the tube and a leak test was done. The tube was then positioned inside the pressure shell. The annulus between the tube and the pressure shell was filled with sodium silicate (Dacotherm^{*}). It was found that this material was very effective in reducing heat loss. Prior to air injection, the tube was pressurized with nitrogen and was subjected overnight to an ambient temperature of about 165°F. Table I shows the initial pack conditions for this run.

OPERATION

The ignitor was turned on when air began flowing. Spontaneous ignition occurred, because the oil was very reactive. Initial pressure drop along

^{*} Provided by Diamond Shamrock Corporation in Texas.

the tube was 3 psi. After the establishment of the combustion front, the ignitor was turned off. In general, the combustion run was very smooth with no blocking in the flowline. The front temperature sometimes exceeded 1550°F, but these temperatures created no special problems.

RESULTS

Figure 3 shows the temperature profiles taken along the combustion tube at different times. As is shown, the steam plateau developed immediately upon application of the ignitor (time = 0 hours). The steam front moved quickly toward the bottom of the combustion tube. The locations of both steam plateau and burning front are shown on Fig. 4. Taking the 225°F isotherm as the leading edge of the steam plateau, it was found that velocity of the steam plateau was about 50 cm/hr. This rapid advancement may be due to the high porosity of the system.

The burning front temperature varied between 1250°F and 1570°F. After approximately ten hours, a second burning front was formed which moved very slowly. It is speculated that the secondary front was formed due to finger-ing into a higher porosity section. This hypothesis is supported by the fact that the burning front velocity almost doubled after the formation of the secondary front. Because this front consumed some fuel, there was less fuel available for the first front, and consequently, it moved faster.

Oxygen utilization was nearly 100% (Fig. 5), and most of the oxygen was consumed in the first front. Consequently, the second front did not move as fast. This interplay between fuel and oxygen is the main reason for movement of the burning front in the field. Table II summarizes the results obtained in this run.

ANALYSIS OF PRODUCED FLUIDS

The cumulative oil and water produced in both separator and condenser are plotted as a function of the total volume burned (Fig. 6). However, both axes have been normalized to present a clearer picture of the production. Oil produced early in the run was rather light and yellowish in color (around 45° API). As time progressed, darker and heavier oil was produced (around 28° API). Figure 7 presents the density of produced oil as a function of time. The pH of the produced water is plotted on the same graph. As is shown, mainly fresh water (pH = 7) was produced during the steam plateau breakthrough, but following this stage, the effects of produced-acidic-solutions were observed in a lower pH. Finally, pH increased as a result of alkaline solutions.

The oil kick occurred after about 50% of the bulk volume was burned. The viscosities of two samples of produced oil are graphed in Fig. 8. The viscosity of the native oil was not plotted for comparison because data were not available.

MATERIAL BALANCE

To estimate the initial oil and water contents of the core, three samples of the pulverized core were used in an ASTM extraction test. These results are summarized in Table III. After extraction, the samples were put in an oven and heated for three hours at 1112° F to determine whether there was kerogen in the core. Care was taken in excluding the effect of air moisture on sample weights by keeping them in a vacuum. The results of this test show a 5% reduction in weight of samples before and after burning (Table III). There may have been some bond water evaporation during heating, but this weight reduction coupled with microscopic observations suggest that loss of bond water during crystallization was of minor importance compared

to the loss of kerogen (refer to the following section). The color of the matrix changed from greenish-grey to a reddish-pink during heating. This color change was similar to the one observed in the combustion test.

After the run, the pack was analyzed for the oil and water saturations left ahead of the combustion front. Figure 9 shows the results. The results of material balance calculations are shown on Table IV. It is interesting to observe an increase of about 5% in the weight of produced oil and water. This, in conjunction with the results of the extraction and burning test (Table III), demonstrate the existence of kerogen in the core. It appears that kerogen supplies part of the fuel necessary for in-situ combustion. This information may be an important factor in choosing this process over other thermal methods for oil recovery from diatomaceous zones.

ANALYSIS OF THE MATRIX

The cored interval consisted of dark brown, poorly indurated diatomaceous sediment that was laminated through most of the interval. Pre- and post-burn samples of the core material were examined using scanning electron microscopy, power x-ray diffraction, and grain mounts to determine the effects of combustion on the core matrix.

Figure 10a shows that the major mineral assemblage of the sediment is a simple one, consisting dominantly of quartz and amorphous opal with accessory albite. SEM and grain mount observations confirm this. Diatoms in the core are pristine and the opal-A of frustules has undergone little or no diagenetic transformation. The quartz is detrital rather than biogenic in origin. The feldspars may be authigenic, clastic, or both. Solid organic material is the other major component, often in the form of brown amorphous peloid-like aggregates of uncertain origin. Detrital clays are also visible, although occurring in quantities too low to be reflected in x-ray traces (i.e., < 5 vol. % of the bulk rock). No evidence of clay diagenesis was noted.

Diatoms are for the most part broken (Fig. 11). The frustule walls and covering pore plates sometimes remain in contact, but more commonly the pore plates have separated completely from the frustules and only the more robust frustule wall is visible. Since wall layers and pore plates, as well as frustules of different species, are characterized by punctae of different dimensions, the effect is one of a multi-layered molecular sieve. As shown in Fig. 12, almost all of these punctae, regardless of diameter, are open. This accounts for the high porosities indicated on density logs within the interval (Fig. 13).

Surprisingly little happens to the sediment in the combustion process. The most obvious alteration is a color change (from dark brown to red) caused by oxidation of ferrous iron in the sediments. The brown organic aggregates are not prominent in grain mounts of the postburn sample; much of the solid organic material appears to have been oxidized (which adds support to the material balance calculations in this report). Figure 10 documents that there is no change at all in major mineralogy before (Fig. 10a) or after (Fig. 10b) the experiment.

It is well documented⁷⁻⁹ that the opal-A of diatom frustules undergoes transformation to a poorly crystalline phase termed opal-CT at approximately 122°F, and recrystallizes to quartz at approximately 212°F. Since combustion temperatures reached a maximum of 1600°F, one would expect to see extensive recrystallization within the core sample. This was not the case. SEM photos reveal some alteration of the diatom frustules. Some of the pore plate fragments, with punctae less than one micron in diameter, have been recrystallized, and those pores have been totally occluded. As shown in Fig. 14, the surface takes on a glazed appearance. Frustule walls, with punctae diameters greater than or equal to one micron appear unaffected by heating.

Grain mounts reveal that the affected fragments have indeed recrystallized to microcrystalline quartz. The fragments observed to be thus altered are relatively few (less than 5% of the diatom debris in the sample). Rare evidences of clay authigenesis were observed with the scanning electron microscope.

OTHER STUDIES

Two experiments were conducted to measure the combustion reaction rates of oil in the diatomite matrix using a previously built set-up for this purpose.⁶ Unfortunately, because of the occurrence of spontaneous ignition, the data were not useful. It appears that the crude oil in this formation was very reactive with oxygen.

Although sufficient air permeability was obtained by crushing the core in the laboratory, the poor permeability in a diatomaceous formation may restrict the applicability of in-situ combustion. For comparison, studies in which an uncrushed core is used in the combustion tube are now underway.

CONCLUSIONS

In-situ combustion was tested on a core taken from a diatomaceous reservoir. The following conclusions were drawn:

1. A fast steam plateau, a slow burning front, and good oxygen utilization were characteristics of the in-situ process in this experiment.
2. Kerogen appears to supply part of the fuel for combustion.
3. A small number of diatoms were transformed from amorphous opal to quartz.
4. Poor permeability in a field may restrict the applicability of these results.
5. Similar studies should be carried out using an uncrushed core in the combustion tube to determine the effect of low permeability in diatomites on combustion behavior.

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Table I
INITIAL PACK CONDITIONS

Porosity, [*] % bulk volume	65
Initial Oil Saturation, ^{**} % pore volume	27.8
Initial Water Saturation, ^{**} % pore volume	19.4
Initial Gas Saturation, % pore volume	52.8
Average Ambient Temperature, °F	165
Length of Pack, cm	85

* Assuming $\rho_{\text{formation}} = .1.7 \text{ g/cc.}$

** This estimate is based on the extraction test data, assuming 28° API as the oil density.

Table II

SUMMARY OF COMBUSTION TUBE RUN RESULTS

Average Inlet Pressure	100 Psig (791.4 kPa)
Average Exit Flow Rate	5.93 scfh (46.7 cc/s)
Air Flux	123 scfh/ft ² (1.046 cm/s)
Front Temperature	1200 - 1570° F
Front Velocity	3.46 - 60.4 cm/hr
Steam Plateau Velocity	50 cm/hr
Produced Gas Analysis, Vol. %	
CO ₂	15
O ₂	0
CO	2.5
N ₂	81.5
Atomic H/C Ratio	1.35
Fuel Burned Per Hour	0.0345 lb/hr
Water Formed/Fuel Burned Ratio	0.84 lb/lb
Fuel Burned/Rock Volume Ratio	6.2 - 4.1 lb/ft ³
Air/Fuel Ratio	170 scf/lb

Table III

EXTRACTION RESULTS

Weight of Extracted Oil/Weight of Original Core (from ASTM extraction test)	0.182
Weight of Extracted Water/Weight of Original Core (from ASTM extraction test)	0.155
(Weight of kerogen + bond water)/Weight of Original Core (from post-ASTM test heating procedure)	0.0529
(Weight of extractable oil and water + kerogen + bond water)/Weight of Original Core	0.243

Table IV
MATERIAL BALANCE

Original Weight of Diatomite Core	3370 g
Weight of Core after Combustion Run	2424 g
Weight of Produced Liquids	
Oil	213 g
Water	760 g
Average Extractable Oil Originally in Core (estimated)	614 g
Average Extractable Water Originally in Core (estimated)	524 g
Average Fuel Burned (calculated)	250 g
Average Water Formed (calculated)	210 g
Water Left in the Core (estimated)	25 g
Oil Let in the Core	250 g
(Water produced - Water formed + Water left in core)	575 g
Weight of Bond Water (by difference)	51 g
(Oil Produced + Fuel Burned = Fuel Left in Core)	713 g
Weight of Kerogen (by difference)	99 g
(Kerogen + Bond Water)/Original Core	0.045

Figure 1. Locality map of the well site in the Lost Hills Field, southwest side of the San Joaquin Valley. Taken from California Oil and Gas Fields, Vol. 1 (1973) of the California Division of Oil and Gas.

Figure 2. Schematic diagram of the combustion tube apparatus

EQUIPMENT USED IN THE CIRCUIT (Fig. 2)

1. Pressure Gauge	15. Back-Pressure Regulator
2. Drierite Holder	16. Needle Valve
5. Mass Flow Controller	17. Fischer Gas Partitioner
7. Temperature Controller	19. 2- μ Filter
8. Digital Temperature Reader	20. Carbon Dioxide Analyzer
9. Temperature Recorder	21. Carbon Monoxide Analyzer
10. Separator	22. Oxygen Analyzer
11. Ice Bath	23. Rotameter
12. Pressure Transducer	25. Wet Test Meter
13. Pressure Indicator	29. Variac
14. Recorder	30. Condenser
	31. Flow Meter

Figure 3. Ten temperature profiles along the combustion tube, as measured at discrete intervals throughout the 16 hours of the run.

Figure 4. Locations of combustion front (open circles) and steam plateaus (triangles) as a function of time throughout the experiment.

Figure 5. Gases extracted from the core, as measured at discrete time intervals throughout the experiment.

Figure 6. Liquids extracted from the core, reported as a percentage of the total liquid which could potentially be produced vs the percentage of total volume which had burned at the time each measurement was taken. (Amounts extracted in the separator and in the condenser have been combined.)

Figure 7. Density of produced oil and pH of produced water as a function of time. Note increase in density of oil produced after approximately 7 hours of run time had elapsed.

Figure 8. Kinematic viscosities of two samples of produced oil.

Figure 9. Degree of oil and water saturation ahead of the combustion front as measured after the run.

Figure 10. Powder x-ray diffractograms of core sample prior to the combustion run (Fig. 10a) and after the combustion run (Fig. 10b). The traces are virtually identical. (Horizontal scale of 1" = $1^{\circ} 2\theta$.)

Figure 11. Scanning electron micrograph of the sediment matrix, which consists largely of broken diatom frustules intermingled with detrital quartz and feldspar silt and clays. Note that the punctae of the frustules are for the most part open.

Figure 12. Scanning electron micrographs of pre-burn sample.

Figure 12a. Close-up of a frustule with pore plate. The portion of the pore plate which remains contains punctae of less than 1 micron diameter, while the coarser-punctae wall contains punctae of 1 micron diameter.

Figure 12b. Close-up of pore plate, showing that the tiny micropores are unoccluded.

Figure 12c. Sieve-type punctae of a different diatom species. These punctae are also open.

Figure 13. Density and neutron for a portion portion of the well. The cored interval used in this study is indicated on the log.

Figure 14. Scanning micrographs of post-burn sample.

Figure 14a. Frustule with pore plate as in Fig. 12a. Note that 1 micron diameter punctae of wall are open.

Figure 14b. Close-up of a portion of the pore plate. Less than 1 micron diameter punctae of this plate are totally occluded.

Figure 14c. A similar diatom frustule. Frustule wall pore spaces remain open. Pore plate pores are occluded.

Figure 14d. Close-up of Fig. 14c. Note "glazed" appearance of recrystallized frustule wall. The material of this wall has undergone recrystallization from opal-A to microcrystalline quartz.

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