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E. T. Premuzic, M. S. Lin, and B. Manowitz*

**Department of Applied Science
Biosystems and Process Sciences Division
*Physical Sciences Division
Brookhaven National Laboratory
Upton, NY 11973**

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COMPARISON OF BIOCHEMICAL MICROBIAL EFFECTS IN

ENHANCED OIL RECOVERY (MEOR)

Eugene T. Premuzic, Mow S. Lin, and *Bernard Manowitz

Department of Applied Science
Biosystems and Process Sciences Division
*Applied Physical Sciences Division
Brookhaven National Laboratory
Upton, NY 11973

Extended Abstract

Experimental data dealing with the interactions between certain microbial species and crude oils indicates that these interactions are selective and occur via biochemical pathways which can be characterized by the chemical composition of the initial crude oil and that of the end products. In the studies to be discussed in this paper, the microbial species used were thermophilic and/or thermoadapted microorganisms which thrive in harsh environments (e.g., pH, temperature, pressure, salinity). Crude oils chosen for biotreatment represented a wide range of oils, which varied from relatively light oils to heavy, high sulfur content oils. The crude oils used have also been distinguished in terms of their geological history, i.e., heavy, because they are immature or heavy, because they have been biodegraded. The significance of "biodegraded" vs. "biotreated" crude oil in MEOR will also be discussed.

1. Microbial Enhanced Oil Recovery (MEOR) is an emerging biotechnology which now claims several successes in this country and abroad. These have been reviewed and discussed by (Moses 1991; Bryant 1991) and most recently at the International Conference on MEOR (Premuzic and Woodward 1992). Successful microbial candidates are capable of growth under reservoir condition which include high salinities, some up to 75,000 ppm, temperatures (~80°C) and pressures ~1500 psi). As a consequence of their metabolic activity they produce gases, acids, surface active polymers and reduce viscosity of crude oils.

2. Studies in this laboratory have shown (Premuzic and Lin 1990, 1991, 1992) that the interactions between microorganisms and crude oils are selective and occur via biochemical pathways which can be characterized by the chemical composition of the crude oil and that of the end products. "Biomarkers", i.e., chemical signals which describe chemical changes in the crude oil due to maturation, biodegradation, migration, and others have been used extensively in oil exploration and characterization (Peters and Moldovan 1992). The data discussed in this paper differentiate between the terms "biodegradation" and "biotreatment." The latter means biochemical conversion of crude oils due to introduced microorganisms and the former means changes which have occurred in the reservoir over geological periods of time. Introduction of nutrients in to a reservoir may also be considered as

biotreatment, because it does stimulate the growth of indigenous microorganisms, however, over a much shorter period of time (relative to geological scale, i.e., months vs. millions of years). Under the experimental conditions used, biotreatment of crude oils with thermophilic and thermoadapted microorganisms affects a number of parameters which are listed in Table 1. A brief discussion in terms of some typical examples follows.

Table 1. Biochemical Effects on Crude Oils Due to Microbial Treatment

-
- Variation in the extent of emulsion.
 - Presence or absence of an added surface active agent.
 - Duration of treatment.
 - Changes in chemical markers: hydrocarbons.
 - Changes in chemical markers: organic sulfur compounds.
 - Changes in chemical markers: organometallic compounds.
 - Action on different types of heavy crude oils, i.e., heavy, because they are immature or heavy because they are biodegraded.
 - Introduced microorganisms appear to become dominant.
 - The effects due to biotreatment are not random, but follow distinct trends which are both microbial species and chemical compositions of crude oils dependent.
-

Biotreatment with several microorganisms of heavy fraction of different crude oils, leads to emulsification of the crudes. The results shown in Table 2, indicate that the extent of emulsification varies with microbial species used and the type of oil treated. In all the cases, the oil was the sole source of carbon.

Table 2. Extent of Emulsification Due to the Action of Various Microorganisms on Heavy Fraction of Crude Oils. The Results are Expressed in Klett Units (Roseberg 1979).

	Asphalt	Wilmington (California)	Goch Saran (Iran)	Recluse (Wyoming)	Prudhoe (Alaska)
BNL-4-24	35	115	168	250	215
BNL-4-23	250	290	238	225	195
BNL-4-22	275	252	320	175	285
BNL-4-21	475	515	142	600	615

Similar effects are observed in an identical treatment of Venezuelan Boscan crude, a heavy immature crude, and Cerro Negro a heavy biodegraded crude oil. The results of biotreatment of these oils with several microorganisms are represented graphically in Figure 1a,b for two Media (Premuzic and Lin 1991, Premuzic et al. 1992). Media 1 contains inorganic salts only with oil as the sole carbon source, while Media 2 contains inorganic salts, a small amount of added organic nutrient (< 0.008%) and crude oil. In some cases, a

BIOTREATMENT OF BOSCAN CRUDE

40 DAYS MEDIA 1 vs MEDIA 2

BIOTREATMENT OF CERRO NEGRO CRUDE

40 DAYS MEDIA 1 vs MEDIA 2

Figure 1

considerable enhancement as well as shortening in the duration of biotreatment can be achieved by adding a surface active agent to the reaction mixture as shown in Figure 2. Concurrent effects on other biomarkers, specifically distribution of hydrocarbons, conversion of organic sulfur compounds and organometallic compounds have been reported and discussed in detail (Premuzic and Lin 1990, 1991a,b,c). The results are summarized as follows:

1. There is a decrease in C_{30} fraction of crudes with an increase in the concentration of the lighter ($< C_{20}$) fractions.
2. There is a conversion of complex asphaltene fraction rich in organic sulfur compounds to lighter components with a net result of a decrease in the total organic sulfur content.
3. Analyses indicate that the conversion of organic sulfur compounds decreases the sulfide and thiophene contents and increases the sulfoxide contents.
4. During the biotreatment there is an overall removal of trace metals from the organic phase, i.e., the crude oil phase. At present it is thought that this is due to solubilization of metallic species in the aqueous phase.

Further refinement and optimization of bioprocessing has led to shortening in the time of biotreatment and choice of oil-microorganism combinations. The latter, support the view that the study of trends in the biochemical interactions between crude oils and microorganism selected for MEOR may lead to the development of a data base identifying chemical markers as diagnostic tools in determining MEOR process strategies. Examples of this type of information are given in Figure 3, in which biotreatment of two crudes is compared: Monterey A837 an immature heavy off-shore crude, and Monterey A851 a heavy on-shore biodegraded California crude oil. Gas Chromatography-Mass Spectroscopy (GC-MS) fragmentograms are given for the hydrocarbon distribution before and after the biotreatment. In all cases, the crude oils were the sole source of carbon biotreated over a period of seven days and the absence of an added detergent. These results clearly indicate that BNL-4-23, a thermoadapted microorganism and BNL-NZ-3 a thermophilic, act effectively on A837, however, only BNL-NZ-3 is highly efficient in the bioconversion of the A851 crude. A plausible mechanism by which the biochemical conversion of crudes may occur, would involve initial reactions at the functional sites of the complex polar fractions of the crudes, such as, those present in the asphaltenes. Monterey A851 is rich in the content of the polar N, S, O compounds, therefore, the effect, for example, on the organic sulfur compounds should be significant as shown in Figures 4 and 5. In routine analyses of organic sulfur components by Gas Chromatography equipped with sulfur specific Flame Photoemission Detector (FPD), the crude oil sample is injected at a relatively low fixed temperature (typically $\sim 350^{\circ}\text{C}$). Under these experimental conditions it is the volatilized fraction of the sample that is chromatographed. Thus, if the proposed mechanism involving functional sites is correct, then the untreated control and the sample biotreated with BNL-4-23, should have little or no effect on the Monterey A851 crude, a very heavy, non-volatile oil. The resulting FPD chromatogram should show a low response even at high sensitivity settings of the instrument. The results shown in Figure 4 are consistent with this. Chromatograms of both treated and untreated oil were recorded at the same sensitivity (attenuation 32). In both cases identical sample injections were used. Identical experimental conditions were used for the biotreated sample. Control sample at a higher sensitivity (attenuation 16) relative to that in Figure 4 did not even come close to the BNL-NZ-3 biotreated A851. In fact, the sensitivity

BIOTREATMENT OF BOSCAN CRUDE IN THE PRESENCE OF A DETERGENT

PLUS DETERGENT 20 vs 40 DAYS

Figure 2

Figure 3a - GC-MS Fragmentograms, M/Z 57, Monterey, CA, Crude A837
Treated with BNL-4-23 and BNL-NZ-3.

Figure 3b - GC-MS Fragmentograms, m/z 57, Monterey, CA, crude A851 treated with BNL-4-23 and BNL-NZ-3.

Figure 4 - Monterey, CA, A851 crude, A: Control, media 3, seven days;
B: Biotreated with BNL-4-23.

DETECTOR 1 — ATTN 16

CONTROL A

B

DETECTOR 1 — ATTN 64

Figure 5 - Monterey, CA, A851 crude, A: Control, media 3, seven days;
B: Biotreated with BNL-NZ-3.

(attenuation 64) had to be lowered to get the corresponding signal, indicating that the bioconversion of A851 resulted in generation of a more volatile product. The results of these studies also stress the significance of the terms of "biodegraded" and "biotreated". Both Cerro Negro and Monterey A851 are heavy oils because they were biodegraded in reservoirs over geological periods of time. Therefore, biotreatment as referred to here converts crude oils, including those that were biodegraded into forms more amenable to enhanced recovery. Concurrent desulfurization and demetallization contribute additional downstream quality enhancement of the crude oil.

Since all of the experiments were carried out under identical experimental conditions the differences in the attenuation may be used as an approximation of the bioconversion. Experimental approaches such as described above have been extended to other oils and used as "diagnostic" guide in the choice of the core-flooding experiments to be discussed in concluding remarks of the presentation.

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