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EFFECTS OF SELECTED THERMOPHILIC MICROORGANISMS ON
CRUDE OILS AT ELEVATED TEMPERATURES AND PRESSURES

QUARTERLY REPORT (04/01/93 - 06/30/93)

E. T. Premuzic and M. S. Lin

September 1993

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U.S. DEPARTMENT OF ENERGY
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ENHANCED OIL RECOVERY
BARTLESVILLE PROJECT OFFICE
BARTLESVILLE, OKLAHOMA

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Prepared by

E. T. Premuzic and M. S. Lin

Department of Applied Science
Brookhaven National Laboratory
Upton, New York 11973

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QUARTERLY REPORT

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TITLE: Effects of Selected Thermophilic Microorganisms
on Crude Oils at Elevated Temperatures and
Pressures

CONTRACT NO.: AS-219-ECD

CONTRACTOR: Associated Universities, Inc., Brookhaven
National Laboratory

PRINCIPAL INVESTIGATORS: E. T. Premuzic and M. S. Lin

OBJECTIVES OF RESEARCH PROJECT

The objective of this program is to determine the chemical and physical effects of thermophilic and thermoadapted organisms on crude oils and cores at elevated temperatures and pressures. Ultimately a data base will be generated which will be used in technical and economic feasibility studies leading to field applications.

SUMMARY OF PROGRESS

1. Core-Flooding Experiments

Core-flooding experiments were continued and the yields of additional oil recovered were calculated as usual according to the following equation.

$$\% \text{ Oil recovery by Brine} = \frac{\text{oil recovered by brine (g)}}{\text{oil sample wt. (g)}} \times 100$$

* Additional oil recovered by growing microorganisms -

oil recovered by microorganisms (g)

oil sample wt. (g) — oil recovered by brine (g)

x 100

The results for the Wilmington, CA, crude oil treated with several different microorganisms at two different temperatures are shown in Table 1. These results show two important aspects of the thermophilic process(es): (1) there is a significant additional recovery of crude oil with thermophilic microorganisms and (2) variations due to different species also occur under the experimental conditions used in core flooding experiments. Further, as shown in Figure 1, relative to recovery of crude by saline drive (Fig. 1(b)), additional lighter crude is being recovered by treatment of Wilmington with BNL-NZ-3. The results of the above experiments further support the diagnostic significance of chemical markers in predicting efficiency of biochemical treatment (see also previous reports and publications and the most recent reprint by Premuzic et al., Biohydrometallurgical Technologies, 1983, pp. 401-413).

2. Duration of Biotreatment and Media Effects

A detailed study of the emulsification effect of BNL-4-23 on the Monterey A837 California crude has been completed. The results shown in Figure 2 are consistent and clearly indicate that in addition to microbial species specificity vs. chemical composition of the crude, there also exists a need to predetermine medium, pretreatment, and duration of parameters. Medium 1 and 3 are inorganic media, where in Medium 3, the sulfate has been replaced by a chloride salt. Medium 2 contains 0.08% of added carbon. The experimental scenarios described in Figure 2 suggest that in terms of emulsification for Monterey A837, the best experimental conditions are in the order of E > D > F. We reported earlier (Premuzic and Lin, Resources, Conservation and Recycling 5 (1991), pp. 277-284) that the composition of the emulsified aqueous fraction of the BNL-4-22 treated PR3 crude is a complex multicomponent mixture. Only several of these components have so far been identified by high pressure liquid chromatography. These include lactic, propionic and isobutyric acids as well as n-butane. Further sophistication of the chemical analysis using a different crude oil-microorganism system has revealed the presence of other components in the emulsified phase. Details of these experiments will be described elsewhere, however, for the purposes of this discussion, several typical examples will be described. Thus, the treatment of Wilmington crude with BNL-TAQ-1 yielded an aqueous phase which was chemically processed for derivatization of surfactants and metabolites leading to trimethyl-silyl (TMS) derivatives. The silyl derivatives were then analyzed by gas-chromatography/mass spectrometry and marker compounds identified by matching with library data. In addition to already mentioned derivatives (e.g. propionic acid) several aromatic compounds have been identified. It is worth noting that this is the first time that such compounds have been identified in the aqueous phase under the experimental conditions used. Typical examples are given in Figures 3 and 4. Further work will identify the chemical nature, as well as the efficiency of other components and surface active agents present in the aqueous phase. At this stage, it is not unreasonable to expect variations in

chemical structures and diversity of products comparable to that of diagnostic chemical markers whose usefulness even in the early stages of this R&D, has already been established.

3. Recent Presentations and Publications

Premuzic, E. T., Lin, M. S., and Manowitz, B. Comparison of biochemical microbial effects in enhanced oil recovery (MEOR). Presented at the American Chemical Society Spring 1993 Conference, Denver, March 28-April 2, 1993.

Premuzic, E. T., Lin, M. W., and Manowitz, B. Parallel trends in the biotreatment of fossil fuels. Presented at the American Chemical Society Conference, Denver, March 28-April 2, 1993.

Premuzic, E. T., Lin, M. W., and Manowitz, B. Diagnostic significance of chemical markers in bioprocessing of crude oils. Presented at the American Chemical Society Conference, Denver, March 28-April 2, 1993.

Premuzic, E. T., Lin, M. W., and Manowitz, B. Biochemical alteration of crude oils in microbial enhanced oil recovery (abstract). Presented at the International Biohydrometallurgy Symposium, Jackson Hole, WY, Aug. 1993. Published, Biohydrometallurgical Technologies. Eds., A. E. Torma, M. I. Apel, and C. I. Brierly, The Minerals, Metals and Materials Society, p. 401-413, 1993.

Premuzic, E. T., Lin, M. W., and Manowitz, B. The significance of chemical markers in bioprocessing of fossil fuels. Presented at the "Fourth International Symposium on Bioprocessing of Fossil Fuels," Alghero, Italy, Sept. 21-23, 1993. To be published in a book form of Proceedings, by Elsevier.

Table 1

Oil Recovery as % of Residue Oil in Core at 65 °C (Wilmington, CA. Crude)

	Recovered by brine only	Recovered by biotreatment (additional oil)
<i>Clostridium acetobutylicum</i> *	34	<1
<i>Clostridium collagenovorans</i> *	33	<1
<i>Clostridium acetobutylicum</i>	26	25
<i>Clostridium collagenovorans</i>	33	24
Thermophilic BNL-TAQ1	36	34
Thermophilic BNL-TAQ2	34	29
Thermophilic BNL-NZ-3	28	46
Thermoadapted BNL-4-23	38	28
Thermoadapted BNL-4-22	41	31

* fully grown outside the core at 28 °C,
then applied to the core at 28 °C.

(a) Untreated Wilmington crude oil.

(b) Wilmington crude recovered by saline drive

(c) Wilmington crude recovered by BNL NZ-3

Figure 1

Monterey A837

Figure 2. Emulsification effects of BNL-4-23 on Monterey A837 crude.

Library Search

Comment: WILMINGTON/TAQ-1

100% Sample

Base Peak 295

Intensity 453

Scan number 690

Figure 3. Mass fragmentogram of Wilmington crude BNL-TAQ-1 system TMS derivatized sample (a) and the corresponding library match compound, 1,2-benzenedicarboxylic acid, bis-trimethyl-silyl ester.

Library Search

Comment: WILMINGTON/TAQ-1

100% Sample

Base Peak 295

Intensity 453

Scan number 690

Figure 4. Mass fragmentogram of Wilmington crude BNL-TAQ-1 system TMS derivatized sample (a) and the corresponding library match compound benzenepropionic acid, trimethyl-silyl ester.

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