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CONVERSION OF LOW GRADE OILS**

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

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Environmental Significance of Biocatalytic

Conversion of Low Grade Oils

M.S. Lin, E.T. Premuzic, H. Lian, W.M. Zhou, and J. Yablon
Biosystems and Process Sciences Division
Department of Applied Sciences
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ABSTRACT

Studies dealing with the interactions between extremophilic microorganisms and crude oils have led to the identification of biocatalysts which through multiple biochemical reactions catalyze desulfurization, denitrogenation, and demetalation reactions in oils. Concurrently, the oils are also converted to lighter oils. These complex biochemical reactions have served as models in the development of the crude oil bioconversion technology to be applied prior to the treatment of oils by conventional chemical processes. In practical terms, this means that the efficiency of the existing technology is being enhanced. For example, the recently introduced additional regulation for the emission of nitrogen oxides in some states restricts further the kinds of oils that may be used in burners. The biocatalysts being developed in this laboratory selectively interact with nitrogen compounds, i.e. basic and neutral types present in the oil and, hence, affect the "fuel NO_x" production. This, in turn, has a cost-efficient influence on the processed oils and their consumption. In this paper, these cost-efficient and beneficial effects will be discussed in terms of produced oils, the lowering of sulfur and nitrogen contents, and the effect on products, as well as the longevity of catalysts due to the removal of heteroatoms and metal containing compounds found in crudes.

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INTRODUCTION

In the industrialized and newly industrialized countries, petroleum continues to be a major energy resource. The projected petroleum consumption is steadily on the increase worldwide (1). The environmental impact associated with increasing petroleum utilization is going to increase significantly. Concurrently, federal and state agencies are already imposing tighter regulations on the production and utilization of petroleum to assure a cleaner environment (2).

Chemically, the oil fractions containing organic nitrogen, sulfur, and oxygen compounds (NSO) contribute to environmental pollution because their combustion products, e.g. nitrogen oxides NO_x and sulfur oxides SO_x, are the major air contaminants. Fractions of crude oil rich in NSO compounds are associated with heavy crude oils (3). Refining of such heavy crude oils by thermocracking processes, for example, yield products of high sulfur contents as shown in Table 1.

Petroleum feedstock utilized in the U.S. is becoming increasingly heavier and higher in sulfur content as shown in Table 2. Consequently, refineries have to adapt to the use of heavier feedstocks (2). It is, therefore, imperative to establish future energy sources to meet our needs and to maintain and improve the U.S. economic competitiveness without compromising a cleaner environment.

Hydrotreating and hydrocracking processes are two conventional methods used to remove oil contaminants which consist mainly of compounds containing NSO heteroatoms and trace metals. Both processes use pressurized hydrogen gas with catalysts which convert the species of sulfur and nitrogen to H₂S and NH₃ respectively. These gaseous products are treated separately in subsequent processes. The catalysts used in both processes become gradually deactivated as the contaminants and trace metals start to deposit on their surface (4). Then fresh catalyst has to be brought in to make up for the loss of activity. Also, the deactivated catalysts have to be disposed as spent catalyst wastes. Both hydro-processes are expensive in terms of construction and operation costs (4). Moreover, these hydroprocesses together with other refining processes, e.g. distillation, thermal and catalytic cracking generate in an average plant tons of SO_x, NO_x, CO, hydrocarbons, waste waters, and solids emitted daily to the environment (5).

There are two approaches for processing the increasing heavier petroleum feedstocks into cleaner products. They are to either design a new refinery or to revamp the existing plants. Both options have considerable costs attached. In addition, new innovative methods will have to be explored and developed into cost-efficient and environmentally acceptable processes.

Contrary to conventional refining process conditions, biochemical treatment takes place at much lower temperatures and pressures. Significant R&D effort at Brookhaven National Laboratory (BNL) and elsewhere has shown that there are advantages in the application of several biochemical reactions in the treatment of fossil fuels (6,7,8,19). A demonstration plant for biological coal desulfurization is currently in operation (9). Biochemical petroleum desulfurization, denitrification and demetalization has been shown to be scientifically and technically feasible. Economic analysis indicates that the biochemical processing of petroleum is also cost-efficient (6,15).

MATERIALS AND EXPERIMENTAL

Details describing the preparation of biocatalysts, experimental procedures, chemical analyses, and instrumental protocols have been reported elsewhere (6,7,16,19). Any variation or modification in procedures that differ from the references cited is specified in the text.

RESULTS AND DISCUSSION

Organosulfur compounds found in petroleum oils can be classified as cyclic sulfides, thiophenes, disulfides, mercaptans, large polycyclics and polyaromatic sulfur compounds. (10,11). Most sulfur compounds are concentrated in heavy fractions of crudes with the highest concentration in fractions containing resins and asphalt (3).

Organonitrogen compounds in petroleum can be classified as basic and non-basic. The basic nitrogen compounds consist of pyridine types and are distributed in all boiling ranges. The non-basic nitrogen compounds include the pyrrole, indole, and carbazole types and are distributed mainly in higher boiling and residue fractions (3,13). Heteroatoms with an unshared pair of electrons are capable of chelation formation of clathrates, charge transfer complexes, and coordination compounds. Such chemical structures contribute to the formation of three dimensional matrices, micelles, colloidal fluids, and molecular solutions which are characteristic of crude oils (14,16,6). Current evidence supports the view that the biocatalysts act at the heteroatom sites which leads to a breakdown of the three-dimensional structures and, in a manner of speaking, "depolymerize" the heavy crude (16).

In the development of biochemical processes for the upgrading of fossil fuels, it is important to retain most of the heating value of the fuels after treatment. This can be accomplished if the chosen biocatalysts are selective so that the processed fuels contain less heteroatoms and the biochemical treatment causes a minimum loss of

hydrocarbons. Thus the removal of sulfur, nitrogen, and trace metals and the conversion of heavy crudes to lighter oils is the main objective in the development of biochemical upgrading of heavy crude oils. Some of the recent results will be discussed in the following paragraphs.

Results shown in Figure 1, indicate that the biochemical desulfurization reactions take place in the lighter diesel as well as in the heavier fuel oil fractions of bunker oil. Comparison of this result with the corresponding gas chromatographic mass spectrometric (GC-MS) analysis in selective ion mode ($m/e=57$ for $C_4H_9^+$) of untreated and treated samples (Fig. 2) indicated that the main hydrocarbons content of the treated sample was not significantly affected by the biotreatment.

Additional systematic chemical analysis of untreated and treated oils have shown that the oil/biocatalyst reactions depend on the chemistry of oils and a particular biocatalyst used (5,6,16,19). Some typical examples are given in Table 3. Several different types of heavy crudes and processed oils have been treated with different biochemical catalysts which yielded a range of products.

The GC-MS results of biochemical treatment of a steam recovered heavy crude, Midway Sunset (MWS) are shown in Figure 3. The chromatographic analysis indicates that a substantial amount of sulfur content has been reduced. In addition to sulfur, the organonitrogen content was reduced as well as shown in Table 3. Comparable analysis using three other oils, (MWS, Offshore California OSC, and bunker oil) are given in Figure 3. The results are different because the chemistries of the oils, MWS and OSC, are different from the refined petroleum products of Bunker oil. OSC is a heavy immature crude. MWS has been steam treated and the bunker oil is a distilled fraction, therefore, the chemical composition and history differs. In terms of heteroatoms such as nitrogen, for example, the lighter molecular weight heterocyclics would have been removed and larger molecules redistributed in favor of heavy fractions. In the case of OSC, the biocatalyst(s) are introduced in a sense into a "chemically" unaltered oil and, therefore, the biochemical effect is more apparent.

The chemistry of a feedstocks affects strongly the yield and the quality of the refined products. For example (Table 1), thermal cracking processes of vacuum residue feedstocks from four typical crude's yield products with sulfur contents which are directly related to the sulfur content of the feedstock used. Therefore, fuels derived from low grade high sulfur crudes are undesirable both in terms of process technology and environmental consequences. Further, the results from a typical hydrotreating process of feedstocks with increasing sulfur contents, e.g. naphtha, distillate and vacuum gas oil showed that the feedstocks with higher sulfur content require a six fold increase in the consumption of reagent hydrogen and the catalyst for the process (4). This results in an increase in the processing costs for hydrogen and to a lesser extent in the cost of consumed catalyst.

However in the case of the latter, the cost of spent catalyst disposal and its impact on the environment is significant (5).

The removal of vanadium and nickel by biochemical treatment, shown in Table 4, is of particular significance to refineries. These trace metals are known to affect the cracking and hydrotreating processes and also poison the catalysts used (4,14). The removal of these metals reduces operational costs and subsequent emissions to the environment.

A conceptual block diagram of a biochemical process is shown in Figure 4. The produced biocatalyst is mixed with a heavy crude feed in a biochemical reactor with a reaction time of 36 hours. The reaction mixture is separated in an oil water settler where the separated aqueous phase containing active biocatalyst(s) is recycled back to the bioreactor or sent to waste water treatment unit for recycling of water. The upgraded oil is separated and fed to an existing refinery stream.

An economic analysis based on the addition of a bioprocessing system to an existing refinery has shown that such a process is economically feasible (6,15). Assume that the plant is constructed with a loan at 10% annual interest rate and operated for a life span of ten years. During operation the plant desulfurizes a 3% weight sulfur heavy crude to a 2% weight sulfur lighter crude in 36 hours. For such an operation, the profit gain from the upgraded oil over the low price of heavy crude feedstock is sufficient to pay back the investment in eight years. Extended cost analysis has also shown that a higher desulfurization rate, lower loan interest rate and shorter reaction time make the process more profitable and reduce the pay-back time to less than two years (6).

The above economic analysis was based on price evaluation of the upgraded crude oil in terms of sulfur reduction only. In general, the market price of crude oils is related to the sulfur content. The lower sulfur oils have higher market value, therefore the value of desulfurization process can be evaluated. The whole biochemical process, however, also reduces nitrogen, metals, and improves lighter fraction yields. At present, these additional credits are hard to estimate, because refineries have their own formulas to determine the characteristics and values of their feedstock which are proprietary. Therefore, no market prices are available which explicitly relate to the nitrogen and metal contents in a manner comparable to that of sulfur. The additional credits may be calculated in an indirect manner such as tradable credits under the Clean Air Act (17).

CONCLUSIONS

Biochemical processes have been shown to be cost efficient and technically feasible in desulfurization, denitrification, demetalization and depolymerization of low grade heavy crude oils. When fully developed, they will be complimentary to the existing oil process technologies and simultaneously contribute in a cost-efficient manner to a better environment.

ACKNOWLEDGMENT

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Table 1.
Feedstock and Product Characteristics of Refining Processes

Process	Visbreaking		Delayed Coking	
	Louisiana Residue	African Residue	Middle East Residue	Mexican Residue
Feedstock				
TBP cut point, °C	480+	482+	538+	538+
Gravity, °API	11.8	12.8	8.2	4.0
Sulfur, wt %	0.61	0.6	3.4	5.3
Products				
Dry Gas and wt %	0.6	6.2	9.2	10.5
Naphtha, wt %	6.2	18.5	17.4	21.4
Gravity, °API	51.6	56.1	58.3	54.9
Sulfur, wt %	0.26	0.1	0.5	0.9
Gas Oil, wt %	6.3	65.3	48.5	33.0
Gravity, °API	46.5	22.4	25.3	20.5
Sulfur, wt %	0.33	0.59	2.28	4.26
Coke or Tar, wt %	87	10.0	24.9	35.1
Sulfur, wt % ref. 13, 18	0.58	1.1	5.1	6.4

Table 2.
U.S. Utilization of Heavier, High Sulfur Crude Oil, 1981-1992

Year	Sulfur Percent by Weight	API Gravity (degrees)
1981	0.89	33.74
1982	0.91	33.11
1983	0.90	33.19
1984	0.94	32.96
1985	0.91	32.46
1986	0.96	32.33
1987	0.99	32.22
1988	1.04	31.93
1989	1.06	32.14
1990	1.10	31.86
1991	1.13	31.64
1992	1.16	31.32

Sources: Energy Information Administration, Petroleum Supply Annual, Vol. 1, 1991, Tables FE9 and 16, and 1992, Table 16.

Table 3.
Biochemical Treatment of MWS, OSC and Bunker Oil at 55°C

Biotreatment	% Oil Recovered	Elemental Analysis %				% Heteroelement Removal	
		C	H	N	S	N	S
Control MWS Oil untreated		86.45	10.99	0.79	1.00		
MWS treated with BNL 4-23	101	86.02	11.67	0.64	0.50	20	50
MWS treated with BNL 4-22	94	86.00	11.21	0.59	0.80	25	20
Control untreated OSC		82.31	11.17	0.66	4.40		
OSC treated with BNL 4-22	100	83.87	11.75	0.53	4.20	20	5
OSC treated with BNL 4-23	99	84.45	12.39	0.36	2.40	45	45
Control Bunker untreated		85.71	9.99	0.42	2.86		
Bunker treated with BNL 4-23	96	84.38	10.11	0.43	2.58	0	10
Bunker treated with BNL 4-22	95	84.00	10.06	0.40	2.33	5	20

Table 4.
Oil Metal Removal by Biotreatment

Element	Bunker oil untreated	Bunker oil treated		Bunker oil treated		MWS untreated	MWS treated		MWS treated	
	$\mu\text{g/g}^a$	BNL 4-23	BNL 4-23	BNL 4-22	BNL 4-22	$\mu\text{g/g}^a$	BNL 4-23	BNL 4-23	BNL 4-22	BNL 4-22
		$\mu\text{g/g}, \%^b$	$\mu\text{g/g}, \%^b$	$\mu\text{g/g}, \%^b$	$\mu\text{g/g}, \%^b$		$\mu\text{g/g}, \%^b$	$\mu\text{g/g}, \%^b$	$\mu\text{g/g}, \%$	$\mu\text{g/g}, \%$
Vanadium	5077	3076	40	4397	24	24	15	37	18.8	20
Nickel	627	344	45	513	19	63	47	25	52	18
Lead	22	22	0	21	2	2.9	2	30	0.14	95
Mercury	152	32	79	43	72	0.6	0	100	0.02	96
Zirconium	11	19	0	13	0	1.1	0.6	50	1.2	0
Silver	30	0	100	4	8	0.7	0.0	100	0.0	100
Molybdenum	13	0	100	7	46	0.7	0.1	85	0.2	72
Strontium	13	2	85	0	100	0.3	0.09	72	0.38	0
Selenium	0	0	NA	0	NA	0.04	0.0	100	0.0	100
Arsenic	0	0	NA	0	NA	0.51	0.01	98	0.06	88

^a Metal content in oil samples as μg of metal/g of oil.

^b Percentage metal removal by biotreatment in comparison to corresponding untreated samples.

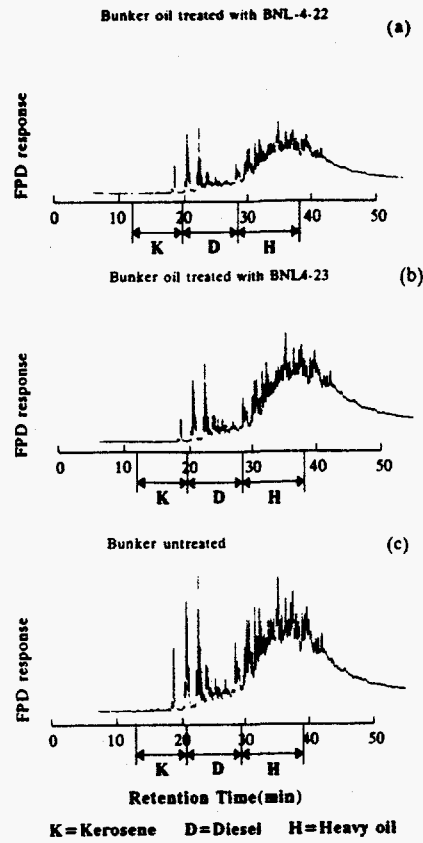


Figure 1. Sulfur specific trace (FPD) chromatogram of biochemical treated Bunker oil. (a) Bunker treated with BNL 4-22, (b) Bunker treated with BNL 4-23, (c) Bunker untreated

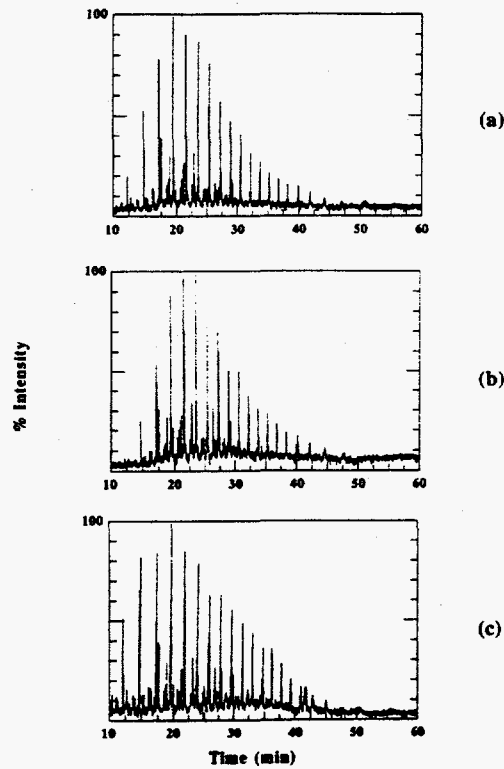


Figure 2. Gas chromatogram of Bunker oil M/e57 trace for hydrocarbons trace of (a) treated with BNL 4-22, (b) treated with BNL 4-23, (c) untreated

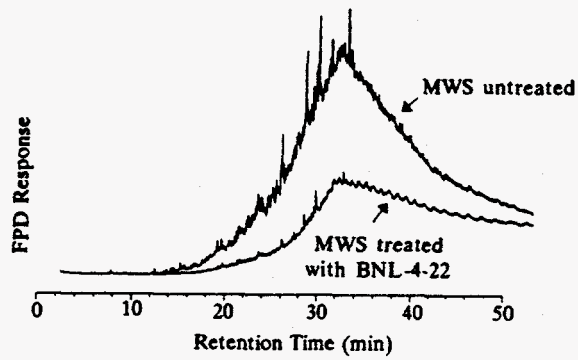
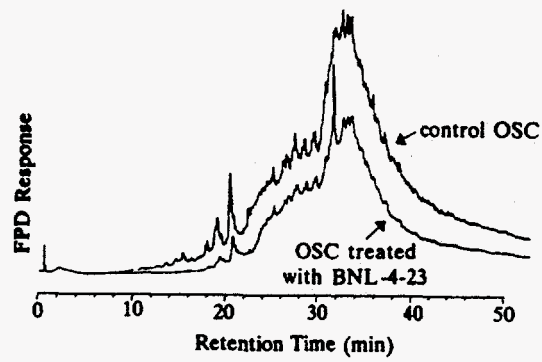


Figure 3. Gas chromatogram selective (FPD) analysis of OCS and MWS oil.

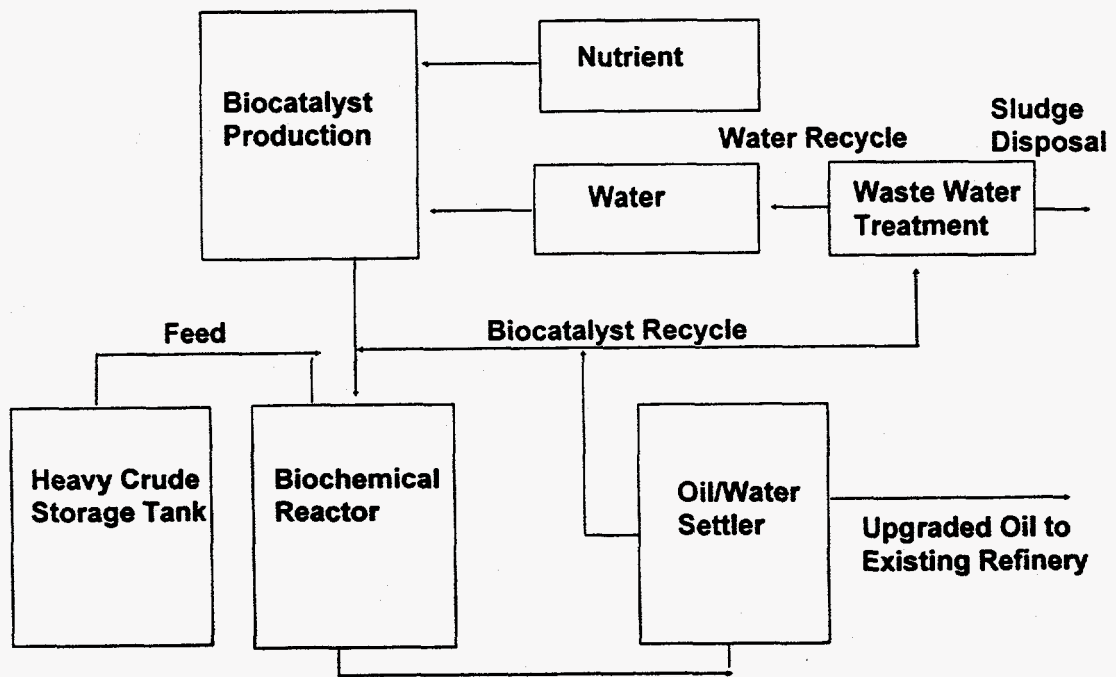


Figure 4. Block Diagram of Biochemical Process