BIOPROCESSING OF CRUDE OILS

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INTRODUCTION

Research on using microorganisms to upgrade or improve crude oil properties is a high risk venture but the potential rewards of achieving such a process are significant both environmentally and economically. The main drivers for this work are: 1. tightening of environmental restrictions on total sulfur in refined oil products and lower refinery CO_2 emissions; 2. the diminishing availability of high gravity sweet crudes; 3. the rising cost of coking and hydrotreating operations; and 4. the increasing cost of meeting CO_2 and sulfur restrictions as future emission allowances are reduced.

Coking and hydrotreating operations are refinery processes to upgrade and remove sulfur from heavy crudes. Cokers use heat to remove hydrogen deficient portions of the feed as coke. The process produces a significant amount of carbon waste that must be disposed. Hydrotreating removes feed sulfur and olefins, but requires high pressure equipment, heat, hydrogen, and expensive chemical catalysts. Repeated hydrotreating to achieve very low sulfur levels becomes uneconomic. The main incentives for crude oil upgrading and desulfurization prior to refining are the economics of higher oil value, lower processing costs, and reduced air pollution that causes smog, acid rain and global warming. Refinery processing costs are projected to steadily increase as reserves of high gravity and low sulfur crude feedstocks are depleted because these feedstocks are currently used to dilute heavy oil feeds.

The use of microorganisms or their enzymes provides potential processing advantages of low pressure, low temperature, no hydrogen required, low chemical costs, and minimal equipment investment when compared to refinery operations.

RESULTS AND DISCUSSION

Potentially High Payback

Texaco has significant holdings in heavy and high sulfur crude oil reserves. The value of those reserves can be significantly increased with gravity improvement or viscosity reduction and sulfur removal. An oil field bioprocess that would reduce sulfur would significantly improve the quality and value of oil piped to a refinery. Refining a low sulfur crude would reduce refining costs and achieve lower sulfur product streams. The value of biodesulfurized oil will steadily increase as reserves of low sulfur crude oil are depleted. An estimated \$295 million (Table 1) could be realized annually from four selected Texaco's fields if the sulfur content of each oil was lowered to a total sulfur percentage of 0.5% or less. These estimates do not include any savings in refining cost or environmental emission improvements.

Envisioned Advantages of Bioprocessing Crude Oil

Bioprocessing crude oil has several application advantages that make it attractive for use in the oil field prior to shipment or pipelined to a refinery. The first advantage is the potential simplicity of the process. Bioprocessing oil basically involves mixing the water soluble biocatalyst (either the microorganism or the enzyme) with air and the oil. After reaction, the formed water-oil emulsion is separated to recover the upgraded oil. The biocatalyst remains with the water potentially available for reuse. In an oil field, both water and oil are routinely coproduced at the well head as emulsions so separations of oil-water mixtures are standard procedures. The only added feature for bioprocessing is the addition of a mixing reactor prior to separation. Fit of such a bioreactor in an oil field operation are illustrated and described below.

A second advantage of bioprocessing is the selectivity of biocatalysts. Desulfurizing biocatalysts contain enzymes generated by microorganisms that need sulfur for energy and growth. Specifically, these generated enzymes catalyze oxidative cleaving of sulfur atoms from organic sulfides forming sulfate salts. The sulfate salts then migrate from the organic oil phase to the water phase. These microorganisms can be modified to remove specific sulfur structures or broader classes of sulfur compounds. Biocatalysts that can upgrade oils modify specific organic structures like cleaving or opening aromatic rings. The motivation for the organism again is to obtain chemical components for energy and growth. The advantage of this selectivity is that a process user knows what chemical changes or potential losses will occur. Unfortunately, crude oil is a complex mixture of organic compounds and all crude oils do not have the same chemical makeup. Therefore, for crude oil applications the biocatalysts will have to be customized for each crude. The total process may involve multiple biocatalysts. Again, the oil field application is felt to be more suited to bioprocessing than at a refinery where multiple crude feeds are handled.

A third advantage is that the bioprocessed oil can be processed at a refinery using current technology at a lower cost. For sulfur, hydrotreating is very effective for removing mercaptans and straight chain sulfides, whereas biodesulfurization is more effective with organic ring sulfides like dibenzothiophene (DBT). The hydrotreating conditions are less severe (lower cost) for straight chain sulfur compounds so an economic advantage is achieved when both hydrotreating and biodesulfurization processes are used.

A fourth advantage of a bioprocessing is improvement in oil properties that affect handling the bulk oil. These property improvements could include viscosity reduction, shifts to lower molecular weight distributions, or lower asphaltene content all of, which reduce fluid piping and transportation problems and costs. Basically, a higher grade and cleaner oil (low sulfur content and high gravity) is transported and refined cheaper and lowers sulfur and CO_2 emissions.

Process Location: Refinery *vs.* Field

The bioprocess can be applied either on a crude oil in the field or later at the refinery. Five factors will be considered in comparing the advantages and disadvantages of applying biodesulfurization near the well head location or at a refinery location. The five comparison factors are greatest product value, biocatalyst solubility, reaction time, process integration, and waste stream disposal. These five points are basic, but they illustrate the envisioned application of bioprocessing a crude oil.

Processing costs will have the greatest effect on product values where the pricing margins are the smallest. In other words, one is more inclined to pay the cost of processing where the greatest product value increase can be obtained. For example, the value of a desulfurized crude oil could increase from $1 - $3/barrel assuming sulfur is reduced to less than 0.5%. In a refinery, product profit margins are squeezed by competition and environmental regulation costs. In general, refined product margins are usually much lower than $1.00/barrel. The maximum benefit of desulfurizing occurs closest to the well head based on improvement in product value.

The current envisioned biocatalysts for crude oil upgrading and desulfurization are water soluble. In an oil field operation, water is coproduced with the oil so the process of water/oil separation is a routine field process. The agitation of the oil and water mixture with biocatalyst would be the only added process step. However, prior to oil transportation to a refinery most of the water has been removed to minimize corrosion and viscosity problems. Water/oil mixing at a refinery is minimized to prevent water and emulsion carry over into the oil processing. Water/oil mixing followed by separation would be added process steps which means added capitalization and operating costs. Again, oil bioupgrading in the oil field has advantages over refinery processing.

Longer reaction times or longer biocatalyst contact with the oil results in greater oil property improvement and sulfur removal. In an oil field setting, the reaction time can range from hours to days depending on oil production rate, storage capacity, and shipment timing. Bioprocessing reaction times allowable in a refinery operation are limited to hours or less. Material holding times at a refinery are limited and most refineries maintain continuous operation and high throughput unlike a field operation where in some cases oil can be held in a tank for several days awaiting transportation.

Another major difference in chemical processing between a refinery and a field situation is the quantities of material handled. A refinery deals in volumes greater than 50,000 gallons whereas a producing field generally works with volumes less than 50,000 gallons. The size aspect with addition of process steps affects the ease of integration of bioprocessing to a refinery or a field facility. For the field case, the process integration is relatively simple. The field already has holding tank capacity and necessary oil/water separators. Added equipment is a mixing reactor. Process integration for a refinery is similar but on a much larger scale with accompanying higher cost.

A bioprocessing operation will generate a waste water stream. All sulfur removed is converted from an organic form to a sulfate salt which is soluble in the reaction water. The biocatalyst will be removed from the water and recycled but the remaining process water will contain metal, sulfur, and organic salts. The new water waste stream must be handled whether it is generated in the oil field or at the refinery. In a refinery, this new waste stream becomes an added problem.

However, in the field the water containing the formed salts can be diluted and reinjected as part of the field water flood program so waste stream has minimal effect on oil field operation. The water soluble salts may also have minimal surfactant properties which could improve the water flood sweep efficiency.

Generic Oil Field Production Facilities

A basic field production facility is illustrated in Figure 1. As the oil and water are produced accompanying gas is separated and collected for sale. The water oil mixture or emulsion is then sent to a heater treater also called a gun barrel to separate the oil and water. Any residual gas released during separation is used to blanket the rest of the separation system. The separated water and oil are transferred to separate tanks. The oil is collected for sale and transportation and the water is filtered and reinjected as part of the field water flood. A bioprocessing step can be inserted after the initial gas separation. The biocatalyst can be added to the produced water/oil emulsion and mixed. After a sufficient reaction time the oil/water emulsion would be handled as before in the field separating facility as illustrated.

Bioprocessing Results

Biodesulfurization results on a crude oil are illustrated in Figure 2. The curves are GC detector signals from a sulfur specific detector (Sievers Model 355) where the Y-axis is the detector signal and the X-axis is time in minutes. The lower curve with the single peak labeled DBT is a dibenzothiophene standard. The next two curves are the biodesulfurized oil and original oil respectively. The reaction period was 24 hours at room temperature. A reduction in sulfur content is indicated.

CONCLUSION

The potential benefits and payback justify further research on using microorganisms to upgrade crude oil. There are distinct advantages in applying a crude oil bioupgrading process in the oil producing fields rather than a refinery. Lower process temperatures, lower reaction pressures, and more environmentally friendly waste streams are a significant paradigm shift from current petroleum technology.

TABLE 1 - Estimates of the Increased $/Yr. by Reducing Sulfur in Crude Oil

A	$900,000
B	$29,200,000
C	$120,450,000
D	$146,000,000
Total	$296,550,000

Estimates based on $1 - $3 per bbl increase in price for low sulfur crude

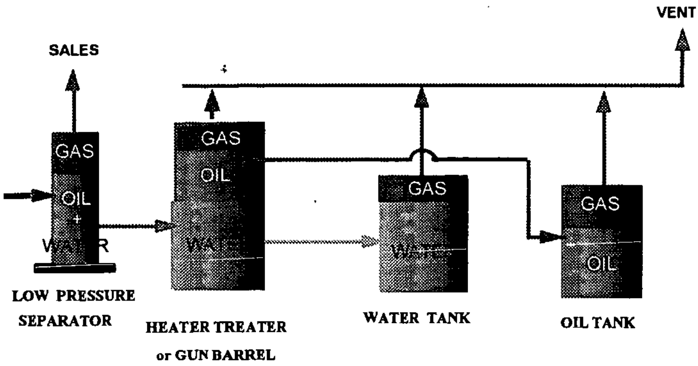

FIGURE 1 - Oil Production Facility

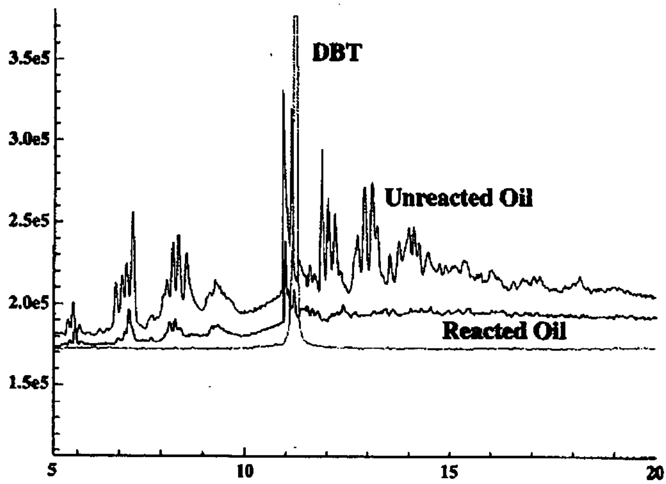

FIGURE 2 - Biodesulfurized Crude Oil Result