EXAMINING THE FATE OF EMULSION BREAKERS USED FOR DECANTING[1]

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ABSTRACT

Skimmers operating in waves often recover a large amount of water, both in the form of water-in-oil emulsions and free water. Recovered water dramatically reduces the temporary storage capacity available for oily fluids offshore. The addition of chemical emulsion breakers to the recovery system has been shown to increase the amount of water that can be quickly decanted when recovering emulsions. A significant potential impediment to the application of emulsion breakers to extend temporary storage capacity is the ultimate fate of the emulsion breaking chemical(s). If they end up in the separated water, they will be discharged into the marine environment when the water is decanted.

The objective of this study was to research the partitioning of emulsion breakers injected into an oil spill recovery system at both lab-scale and mid-scale, at Ohmsett. The experiments were designed to simulate the conditions in an offshore oil spill recovery operation. The ability of emulsion breaker addition to reduce water contents of the recovered fluid and the effects of demulsifier addition of the oil content of decanted water were also assessed.

The formation of micelles by the surfactants in the water at high concentrations and the resulting limitations of the analytical technique used to measure high concentrations of the demulsifiers in the decanted water make definitive, quantitative conclusions about the partitioning of the demulsifier between oily and water phases impossible. The following general conclusions could be made:

- *A large fraction of the demulsifier injected into the recovered fluid stream appears to end up in the decanted water.*
- *The concentrations of demulsifier in the decanted water are well in excess of 100 ppm and could be as high as 1000's of ppm.*

The use of a demulsifier injected into a recovery system, combined with decanting, substantially reduced the volume of water in temporary storage tanks and the water content of emulsions for disposal/recycling. The efficacy of the demulsifier was a strong function of free water content: if the free water content exceeded approximately 55%, the effect of the surfactant was substantially reduced. The degree of emulsion breaking increased with increasing mixing energy applied to the fluid. Increasing the flow rate (and hence turbulence level) and increasing the length of the flow path both resulted in increased emulsion breaking. Primary break occurred in only a few minutes: the application of demulsifier

did not appear to affect the time required compared to previous tests without demulsifiers. The results indicated that the use of a demulsifier increased oil droplet concentrations in the decanted water by approximately a factor of two compared to similar tests without demulsifier.

INTRODUCTION

The most common type of high-capacity skimmer in use today is the weir skimmer. These skimmers often recover a large amount of water, both in the form of emulsified water and free water, when operating in waves. In some cases, the transfer pump built into the skimming system can impart enough energy to cause additional emulsification of the recovered fluids. The problem is that the recovered water (both emulsified and free) dramatically reduces the temporary storage space available at the site of skimming operations; this can result in having to stop skimming prematurely when the storage capacity is reached and having to wait until empty, temporary storage containers arrive at the response site.

Over the last six years a series of lab-scale and mid-scale tests with and without the use of emulsion breakers were completed that give some quantitative insight into the oil/water separation processes occurring in temporary storage devices (SL Ross 1998, 1999 and 2002 as summarized in Buist et al. 2003). The objective of these earlier tests was to determine the optimum time to decant the water and maximize the available on-site storage space during a skimming operation as well as the efficacy of adding emulsion breakers into the recovery stream to allow decanting of emulsified water. The results indicated that "primary break" (the initial separation of the recovered fluid into a layer containing most of the oil and a layer containing most of the free water) occurred within a few minutes to one hour, depending on the physical characteristics of the oil. Rapidly decanting this free water layer, in appropriate situations, produced immediate increases of 200 to 300% in available temporary storage space. The addition of emulsion breakers increased the amount of water that could be decanted, in the same time frame. Addition of the emulsion breaker increased the oil content of the separated water significantly. During the last decanting experiments at Ohmsett using emulsion breakers (SL Ross 2002), the separated water foamed easily when agitated, providing strong qualitative evidence that it contained significant amounts of surfactant.

A significant potential impediment to the application of emulsion breakers to extend temporary storage capacity is the ultimate fate of the emulsion breaking chemical(s). Being surfactants, the active ingredients of demulsifiers are not truly soluble in either water or oil; the minimum surface free energy is achieved when the surfactant molecules are orientated at an oil/water interface. This property results in their surface-active nature. The molecules of surfactants can orientate into "micelles" or "reverse micelles" to accommodate their dissolution in either water or oil. These are less preferred arrangements than orientation at an interface, but it is critical to the behaviour of these chemicals. It is therefore possible for surfactants to be present in bulk in either the water or oil phases, as well as at the oil/water interface. This tendency is known as 'partitioning'. Of course, if a demulsifier is effective, it greatly reduces the amount of oil/water interface originally in a water-in-oil emulsion, and much of the surfactant would move back into the bulk liquid phases. The proportion of surfactant that will be present in the oil or water phases depends on the relative proportion of oil and water phases that are available for them to be dissolved in as well as the surface-active properties of the demulsifier itself.

If the bulk of the surfactants in the demulsifier remain with the oil, there should be no problem with their use; the recovered oil will be collected and disposed of. However, if the majority of the surfactants partition into the separated water (either initially free or emulsified water), they will be discharged into the environment if the separated water is decanted overboard. Some partitioning is an inevitable consequence of surfactant behaviour. The relative tendency to partition, either as individual molecules or as micelles and reverse micelles between oil and water is very dependent on molecular structure.

The environmental consequences of demulsifier use will depend on:

- Their effectiveness in breaking emulsions
- Their partitioning behaviour into the different water and oil phases
- Their toxicity to marine organisms
- The potential for dilution of the decanted water in the receiving water body

The objective of the present study was to research the partitioning of different emulsion breakers injected into a recovery system at both lab-scale (at SL Ross) and mid-scale (at Ohmsett). A series of small-scale tests with a scale-model piping system simulating a weir skimmer recovery system was completed in the summer of 2003 to determine the effects of several variables on the concentration of demulsifier in decanted water. In addition, a technique for determining the concentration of demulsifier in the decanted water was developed. In the fall of 2003 a series of mid-scale experiments was conducted at Ohmsett.

ANALYTICAL TEST FOR DEMULSIFIER IN WATER

Prior to carrying out the study, it was necessary to develop a simple, inexpensive test to measure the concentration of demulsifier in decanted water. The approach taken was to adapt a technique developed to measure the concentration of dispersants in Ohmsett tank water (SL Ross 2003). This method involves measuring the interfacial tension between a highly refined mineral oil (USP, or pharmaceutical grade) and the water containing the surfactant using a DuNouy ring apparatus (ASTM-D971). The interfacial tension value obtained is compared to a plot of interfacial tension vs. concentration of prepared aqueous solutions of the demulsifier in question to obtain an estimate of the concentration of the demulsifier.

Figure 1 shows the calibration curves prepared for the four demulsifiers considered for use in the lab-scale tests. Although
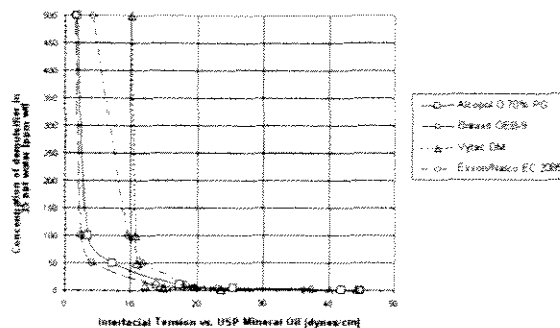

FIGURE 1. CALIBRATION CURVE OF INTERFACIAL TENSION VS. DEMULSIFIER CONCENTRATION.

the interfacial measurement technique gives a reasonable fit of the data for most of the demulsifiers to a power law relationship of the form:

$$\text{Concentration} = C_1 \, (\text{IFT})^{-C_2} \qquad (1)$$

Where: C_1 and C_2 are demulsifier-specific constants

It is clear that the relationships will not give very accurate results at concentrations of demulsifier above about 100 ppm. This is because there is very little change in interfacial tension with a large change in demulsifier concentration above this point, most likely due to the fact that the demulsifier has exceeded its Critical Micelle Concentration (CMC) and the oil/water interface is saturated with surfactant molecules. A difference of only 0.3 dynes/cm in interfacial tension in the 1.5-dyne/cm range results in a 300+ ppm difference in calculated demulsifier concentration.

Despite its shortcomings, the interfacial tension technique was used as the method for estimating the concentrations of demulsifier in the decanted water for this study. This was primarily because the other available techniques (High Pressure Liquid Chromatography [HPLC], complex titrations, etc.) are very expensive and time consuming.

PARENT OIL BLEND FOR EMULSIONS AND DEMULSIFIERS USED

In the previous series of tests using demulsifiers (SL Ross 2002, Buist et al. 2003) it was observed that the demulsifiers could not completely resolve the emulsions created using a blend of 95% Hydrocal and 5% No.6 fuel oil (used to add asphaltenes). This was presumed to be because this parent oil contained no aromatic compounds (Hydrocal is a de-aromatized lube stock) to act as a sink for the asphaltenes displaced from the water/oil interface by the demulsifier. As such, a series of emulsion stability tests with various mixtures of Hydrocal, No. 6 Fuel Oil (2.5 or 5 % by volume) and automotive diesel (5, 10 or 15% by volume) were conducted to select a mixture that would form a stable, 50 % salt-water emulsion that could be completely resolved by the demulsifiers to be used. Based on the stability results and the demulsifier effectiveness tests, the parent oil blend was selected to be 80% Hydrocal, 5% No. 6 Fuel Oil (aka Bunker C) and 15 % automotive diesel. For some tests, emulsion created using fresh Endicott crude (which met the stability criteria), from Alaska, was also used. The three demulsifiers selected for testing in the lab-scale tests were: Alcopol O 70% PG (aka Drimax), Breaxit OEB-9 and Exxon Nalco EC2085, an older product specifically blended as a generic production emulsion breaker for Alaska North Slope crudes.

LABORATORY TESTS

The apparatus and the procedures used in the laboratory tests are described in detail in the report (SL Ross 2004). To summarize, samples of stable 50% water emulsion prepared using a small gear pump from the parent oils described above were pumped with nominally 50% free water, at measured, pre-determined rates, to the suction of a small progressing cavity pump, representing the pump type used in most weir skimmers. The fluid was then directed through a 1/2" diameter scale-model piping network consisting of a static in-line mixer, copper pipe and valves, either a 6-foot or 36-foot length of 1/2" ID plastic tubing and then to six cylindrical receiving tanks where samples were taken at different intervals to characterize the separation of the aqueous phase and the dehydration of the emulsion. Demulsifier was injected, at different dosages, into the system before the progressing cavity pump using a chemical metering pump.

At pre-determined intervals over one hour, the cylinders were decanted and the volume of water removed was measured. A sample of the water was obtained for determination of the concentration of demulsifier, as described above, and a sample of the oily phase remaining in the cylinder was taken to determine its water content.

A total of 25 test runs were completed using the laboratory scale model piping setup. The complete results may be found in the final report (SL Ross 2004). The following summarizes the findings.

Primary Break

In almost all of the tests, primary break occurred in two to five minutes.

Partitioning of the Demulsifiers

The formation of micelles by the surfactants in the water at high concentrations and the resulting limitations of the analytical technique used to measure the concentration of the demulsifiers in the decanted water make definitive conclusions impossible. The following general observations can be made:

- A large fraction of the demulsifier injected into the recovered fluid stream appears to end up in the decanted water.
- The concentrations of demulsifier in the decanted water are well in excess of 100 ppm and could be as high as 1000's of ppm.

Effectiveness of the Three Demulsifiers in Breaking Emulsions of the Two Oils

Overall, it was apparent that the Alcopol demulsifier was the best of the three demulsifiers tested on 50% salt water emulsions made from both parent oils (the Hydrocal blend and the fresh Endicott crude). The next most effective demulsifier on the Hydrocal blend emulsions was Breaxit. The Alcopol was better than the Exxon Nalco demulsifier on the fresh Endicott emulsions, and seemed to work as well with the Endicott as it did with the Hydrocal blend. The effect of the Exxon Nalco product seemed to be to create a very fine dispersion of oil droplets in the water, which made subsequent separation of the oil and water very slow.

Effect of Demulsifier Dose Rate

It was observed that a higher Alcopol dose rate (ca. 2600 ppm) provided better resolution of the emulsion than did a lower rate (ca. 900 ppm). The same was true for the Breaxit demulsifier. In one case with the Exxon Nalco product, the lower dose rate resulted in better breaking of the Endicott crude emulsion than the higher dose did.

Effect of Free Water

As was the case with the previous series of tests (SL Ross 2002, Buist et al. 2003), when the free water content in the treated fluid exceeded 55%, the efficiency of the demulsifier was reduced. When the demulsifier was injected into a fluid stream that contained only emulsion, the separation initially was much poorer than in tests where the free water was less than 50%, but after 60 minutes, the demulsifier effectiveness was about the same for both cases.

Effect of Tubing Length

Pumping the treated fluid down either a 6-foot or 36-foot long length of 1/2"-tubing was the only variation in mixing level used in the lab-scale test series. As was observed in the earlier demulsifier lab-scale tests (SL Ross 2002), better resolution of the emulsion was obtained when the treated fluid was pumped through the 36-foot length than the 6-foot length. This was likely related to greater mixing of the demulsifier and the emulsion in the longer length of tubing.

OHMSETT TESTS

The apparatus and the procedures used in the Ohmsett tests are described in detail in the report (SL Ross 2004) and generally followed those used in previously reported tests (Buist et al. 2003). Only a summary of the equipment and procedures is given here. All tests were conducted in a stationary position (i.e., no towing down the tank).

The test area consisted of 11.5 m (37.5 feet) of 24-inch Globe boom deployed in a triangle (12.5' per side) between the Auxiliary Bridge and the Main Bridge (Figure 2). The boomed area was approximately 6.2 m² (67 ft²). A Desmi Terminator skimmer was placed in the test area and operated from the deck. The skimmer discharge was directed to four of the oil recovery tanks on the Auxiliary Bridge (Figure 3) via 3-inch flexible hose. For all tests, the skimmer discharge was directed through a Lightnin Series 45 Model 4 Type 12H in-line mixer. The separated water from the oil recovery tanks was directed to a temporary holding tank (Figure 4) for water sampling, and then sent to a holding tank for eventual treatment and return to the tank.

Demulsifiers (Alcopol O 70% PG, aka Drimax 1235B, and Unichem RNB-60425, an emulsion breaker specifically designed for Endicott crude) were injected using a fixed-rate (0.25 gpm) peristaltic pump directly into the skimmer weir. Two different wave conditions were generated during this test series.
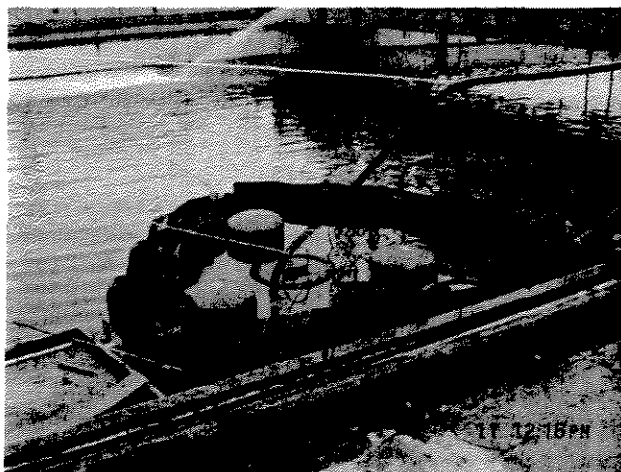

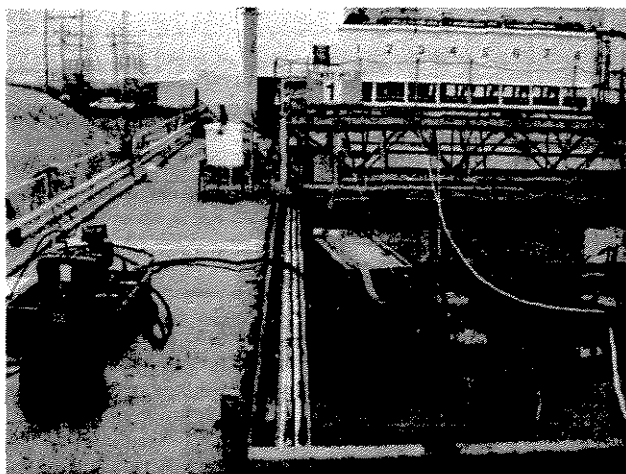FIGURE 2. PHOTO OF BOOM TRIANGLE AND DESMI TERMINATOR SKIMMER IN WATER.

FIGURE 3. PHOTO SHOWING POWER PACK ON DECK,
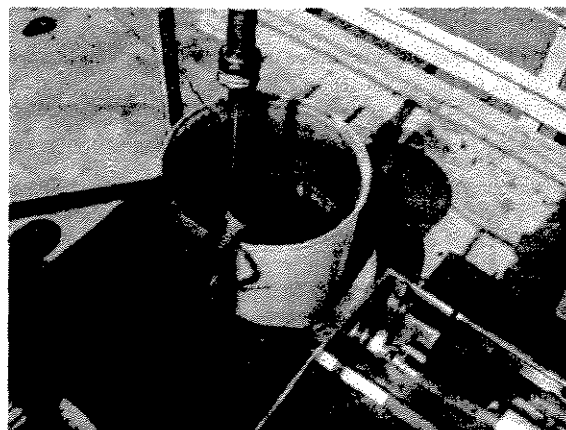SKIMMER DISCHARGE HOSE TO RECOVERY TANKS
AND INLINE MIXER.

FIGURE 4. TEMPORARY HOLDING TANK FOR
DECANTED WATER SAMPLING.

At the beginning of the tests, and subsequently as required, batches of emulsion were prepared. A gear pump was used to prepare the emulsion, since large quantities of a consistent quality were required on a daily basis. A blend of 80% Hydrocal 300/5% IFO 380/15% automotive diesel was used as the parent oil for most of the tests. Fresh Endicott crude was used as the parent oil for two tests. A sample of the first batch of Hydrocal blend emulsion prepared was allowed to sit for 24 hours, and showed no signs of breaking.

For a typical test, a pre-determined volume of emulsion was added to the test triangle, the waves were started, then the skimmer was started and make-up emulsion added to the triangle at a rate approximating the skimmer removal rate. Demulsifier was then added to the weir of the skimmer. The recovered fluids from the skimmer were directed to fill different cells in the Recovery Tank sequentially. The time required to fill each cell and its volume was recorded. At selected times after each cell had been filled, they were decanted, and measured to determine the volume of oily phase remaining. A sample of the oily phase was then taken to determine its water content. The decanted water was directed to a temporary holding tank on the deck beside the Auxiliary Bridge. When all water from a selected cell was transferred, the contents of the temporary holding tank were thoroughly mixed with a bladed impeller and allowed to settle for five minutes to permit large droplets of oil, from the end of the decanting process, to surface. The surface oil was removed with a sorbent pad and then the temporary holding tank was drained. Two small water samples, one for oil content analysis and one for IFT analysis to determine its demulsifier content, were taken when half the water had been drained from the temporary holding tank.

The complete results for the Ohmsett tests can be found in the final report (SL Ross 2004). The ability of emulsion breaking chemicals to resolve water-in-oil emulsions is highly parent oil/surfactant specific. The results are strictly valid only for the combinations of demulsifiers (Alcopol O 70% PG, aka Drimax, and Unichem RNB-60425) and emulsions used (50% salt water in either a blend of 80% Hydrocal 300/5% IFO 380/15% diesel, or fresh Endicott crude). The following summarizes the key findings.

Primary Break

In most cases, primary break was achieved in 30 minutes or less. This is entirely consistent with the results of both previous decanting test series at Ohmsett (SL Ross 1999 and 2002).

Partitioning of the Demulsifiers

It was not possible to discern any trends in the partitioning of the demulsifiers between the decanted water and the oily phase due to the limitations of the analytical technique. The same general observations as were noted in the lab-scale tests were evident in the results from the Ohmsett tests, namely:

- A large fraction of the demulsifier injected into the recovered fluid stream appears to end up in the decanted water.
- The concentrations of demulsifier in the decanted water are well in excess of 100 ppm and could be as high as in the 1000's of ppm.

Effectiveness of the Two Demulsifiers in Breaking Emulsions of the Two Oils

Without the addition of demulsifier, there was no dehydration in the emulsions recovered in Wave 1 conditions (length = 11.3 m, $H^{1/3}$ = 42 cm), and an increase in the water content of the untreated emulsions (from 50% at 2 min. to 65% at 60 minutes) in the steeper Wave 2 conditions (length = 4.6 m, $H^{1/3}$ = 38 cm). The extra mixing energy added to the slick by the steeper Wave 2 conditions caused additional emulsification of the oil (as observed in the previous tests—SL Ross 2002).

The addition of demulsifier caused significant amounts of water to separate from the treated emulsions. In Wave 1 conditions almost _[rds] of the emulsion water was removed and decanted; in Wave 2 conditions, a lesser degree of emulsion dehydration was calculated; however, these calculations are based on the assumption that the emulsion has an initial water content of 50%. If, as is likely, the emulsion water content was upwards of 65% by the end of a test in Wave 2 conditions, the dehydration efficiencies would be closer to 60%, rather than 36% and 46%. The best dehydration obtained was for a run in Wave 2 with the lowest dose rate of Alcopol of all, but with a recovery rate almost twice that of any other test. The 60-minute dehydration result of 64% (72%, if a 65% water content emulsion was being skimmed) was a testament to the fact that mixing energy is very important for effective emulsion breaking, even more so than demulsifier dose rate. The results obtained at Ohmsett were consistent with those from the lab tests with free water contents of less than 50%.

The efficiency of the Unichem demulsifier on the emulsions of fresh Endicott crude was not as high as the Alcopol with the Hydrocal blend emulsions, but the results were encouraging nonetheless. This is because the demulsifier is not an oil spill demulsifier, but a product designed for oil field production purposes (and hence, stored in large quantities in Alaska at the oil fields).

In Wave 1 conditions, 44% dehydration was achieved in the 60-minute sample. In Wave 2, 20% dehydration was calculated after 60 minutes (40%, if the emulsion was 65% water, not 50%).

Oil Content of the Decanted Water

In general, the concentration of oil in the decanted water declined from values in the thousands of ppm after two minutes, to the high hundreds of ppm after 60 minutes. The baseline results were generally similar to those obtained in the previous test series, with Total Petroleum Hydrocarbon (TPH) values determined by gas chromatography in the 200 to 1000 ppm range. The TPH values measured with tests involving demulsifier on Hydrocal blend emulsions were general higher than those obtained in the previous demulsifier test series. This was likely due to the addition of 15% diesel to the parent oil blend for the present test series. This would make the parent oil significantly less viscous, and hence easier to shear into very small droplets that take longer to rise out of the water. The TPH results for the Endicott emulsions treated with the Unichem demulsifier were in the same range as the results for the Hydrocal emulsion treated with the Alcopol demulsifier.

CONCLUSIONS

- The use of a demulsifier injected into a recovery system, combined with decanting, substantially reduced the volume of water in temporary storage tanks and the water content of emulsions for disposal/recycling.
- The formation of micelles by the demulsifier surfactants in the water at high concentrations and the resulting limitations of the analytical technique used to measure the concentration of the demulsifiers in the decanted water make definitive conclusions about the partitioning of the demulsifier between oily and water phases impossible. The following general conclusions could be made:
  1. A large fraction of the demulsifier injected into the recovered fluid stream appears to end up in the decanted water.
  2. The concentrations of demulsifier in the decanted water are well in excess of 100 ppm and could be as high as in the 1000's of ppm.
- The efficacy of the demulsifier was a strong function of free water content. In these tests, if the free water content exceeded about 55%, the effect of the surfactant was substantially reduced.
- The degree of emulsion breaking achieved increased with increasing mixing energy applied to the recovered fluids. Increasing the flow rate (and hence turbulence level) and increasing the length of the flow path both resulted in increased emulsion breaking.
- Primary break occurred in only a few minutes (2 to 5 in the lab tests, less than 30 for the Ohmsett tests). The application of demulsifier did not appear to affect the time required.
- The Ohmsett results indicated that the use of a demulsifier increased TPH concentrations in the decanted water.
- The efficiency of the Unichem demulsifier on the emulsions of fresh Endicott crude was not as high as with the Alcopol, but the results were encouraging nonetheless. This is because the demulsifier is not an oil spill demulsifier, but a product designed for oil field production purposes (and hence, stored in large quantities in Alaska at the oil fields).

The major implication of this research for oil spill response is that it may be possible to greatly reduce downtime for offshore skimming operations caused when the available onsite temporary storage systems are filled with fluids containing large amounts of water; however, it is likely that much of the demulsifier used will be contained in the decanted water. Knowing that the separated water can be decanted quickly will optimize onsite recovery operations and greatly reduce the volume of fluids requiring disposal. In fact, the removal of most of the free and emulsified water from the recovered product would greatly enhance the likelihood that it could be recycled, as opposed to requiring disposal.

ACKNOWLEDGEMENTS

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1 The opinions, conclusions, and recommendations contained in this report are those of the authors and do not necessarily reflect the views and policies of the U.S. Minerals Management Service. The mention of a trade name or any commercial product in this report does not constitute an endorsement or recommendation for use by the U.S. Minerals Management Service.