THE USE OF SYNTHETICS IN WELL DRILLING FLUIDS FOR THE FOR OFFSHORE OIL FIELD

Burney Lee
Amoco Chemicals
Building 503-1330
150 West Warrenville Road
Naperville, IL 60563-8460

KEYWORDS: Synthetic Based Mud, Drilling Mud, Offshore Drilling

ABSTRACT

As Gulf of Mexico offshore drilling moves into deeper water and into more demanding conditions in terms of the depth and type of wells (deviated and horizontal), drilling muds providing higher lubricity and better hole stability are needed. Previously, oil based muds (OBMs) which are primarily based on diesel oil met this need. However, the on site discharge of cuttings from wells drilled using OBMs was banned in the early 1990's. At this time, synthetic based muds (SBMs) were introduced that are prepared using synthetically derived base fluids. SBMs were developed to provide an environmentally safe alternative drilling mud that would meet both the severe drilling mud requirements and the need for cuttings discharge into the ocean. These base fluids are chemically synthesized from the reaction of specific purified chemical feedstocks to give readily characterized products. The synthetic fluids used in the Gulf of Mexico today are linear alpha olefins (LAOS), isomerized olefins (IOs), polyalphaolefins (PAOs) and esters. A description of their chemistry, the benefits they provide and the regulatory issues surrounding their use is discussed.

INTRODUCTION

Oil exploration and production offshore continues at high rates today all around the globe. It is expected to continue at these rates for the next 5 years. In the Gulf of Mexico, this activity has moved out onto the continental slope and beyond to water depths over 6000 feet at locations that are many miles from shore support. These severe conditions coupled with difficult drilling through water sensitive formations push drilling technology to the limit and demand maximum performance in all aspects of the oil exploration process. To minimize difficulties encountered from drilling through water sensitive formations, invert emulsion based drilling muds are often used today.

Drilling muds are materials that are pumped through the rig's drill string and drill bit to remove drill cuttings from the bore hole during drilling operations. They also clean the bit, maintain desired pressure differential between the formation and mud and serve to stabilize the hole. For most drilling, the muds used are prepared by dispersing finely divided clays in water and are called water based muds (WBMs). These solids provide the desired suspending power to assist with cuttings removal and mud density to control pressure. However, WBMs tend to interact with water sensitive formations leading to bit balling and hole stability problems. These conditions can lead to a variety of costly difficulties for operators such as stuck pipe and reduced drilling rates.

To combat these problems when drilling through difficult or unknown formation conditions, an invert emulsion based mud is used. In an invert emulsion mud an organic based fluid forms a continuous outer phase surrounding an internal aqueous phase of finely dispersed droplets (an emulsion). The mud solids and other additives are also suspended in the organic phase. Because the external phase is insoluble in water, interactions with water sensitive formations are reduced. For this reason invert muds reduce sloughing problems, form better filter cakes and produce more stable bore holes. These attributes lead to formation of in-guage holes that provide higher space velocity of the mud and thus better removal of cuttings. Cutting fines are also less likely to disperse in an organic phase, leading to fewer solids control problems. Lubricity, heat transfer and bit wear performance are also improved leading to enhanced drilling rates.

Invert muds are generally based on diesel or mineral oil and called oil base muds (OBMs). In the early 1990's, however, the discharge of drill cuttings into the ocean from wells drilled using
OBMs was prohibited. The inability to discharge cuttings greatly increased cost as they now had to be transported to a safe disposal site. This quickly produced a need for a high performance environmentally safe mud to allow for cuttings discharge. To meet this need, alternative inverse emulsion muds were developed using less toxic synthetic based organic fluids so that drill cuttings discharge would be allowed. These synthetic based muds (SBMs) are produced using synthetic fluids prepared from specific purified starting materials, and they lead to defined products that are essentially free of undesirable polycyclic aromatic hydrocarbons (PAHs). These materials are less toxic and more biodegradable than refined mineral oil products such as diesel oil. Synthetic fluids used today in the Gulf of Mexico to make SBMs include linear alpha-olefins, isomerized olefins, polyalphaolefins, and esters.

EXPERIMENTAL

In this section a brief description is given of the various chemistries used to produce synthetic fluids.

Synthesis of Linear Alpha Olefins (LAOs) and Isomerized Olefins (IOs)

Linear alpha olefins (LAOs) are prepared from the catalytic chain growth of ethylene on triethyl aluminum. After the chain growth step the larger alkyl groups are displaced from the aluminum either simultaneously with the chain growth step or in a separate step to give even numbered linear olefin products with carbon numbers from C4-C20+ (Figure 1). The olefin double bond is formed between the first and second carbons of the alkyl chain (the alpha position) during the displacement step. Distillation provides clean cuts of the desired olefin products.

Isomerized Olefins (IOs) are produced from LAOs using an isomerization catalyst to move the olefin double bond from the alpha position to an internal position along the carbon chain (Figure 1). The internal double bond is distributed throughout the linear chain. Isomerizing an LAO lowers the pour point of the fluid.

Synthesis of Polyalphaolefins (PAOs)

Polyalphaolefins are prepared by the catalytic oligomerization of LAOs followed by hydrogenation of the material to remove the double bond (Figure 2). The oligomerization reaction produces dimers, trimers, tetramers, ... of the LAO. These oligomers have many different types of branched structures due to olefin rearrangements occurring during the oligomerization reaction. The structure in Figure 2 represents one possibility for a dimer oligomer.

Synthesis of Esters

Esters are prepared from the condensation reaction of alcohols and organic acids generally under acid catalysis conditions (Figure 3). Because the alkyl group associated with the alcohol or acid can be obtained from a variety of sources, many structures of esters are possible. For drilling mud applications the starting materials generally come from vegetable oils.

Refining of Mineral Oils

In contrast to the synthesis of organic fluids for invert emulsions, diesel and mineral oils are refined from crude oil (Figure 4). These traditional fluids are produced solely through physical separation processes and/or minor chemical reactions such as cracking and hydrotreating. Refining eliminates most of the undesirable components of these mixtures but they still can contain significant amounts of PAHs.

DISCUSSION

The different chemistries available for making SBMs allows the operator choices when using the muds for drilling a well. The properties of synthetic fluids used in the Gulf of Mexico today to make drilling muds are given in Table I. The first generation of synthetic fluids were PAOs and esters. These materials provided technical performance that was equal to or better than that of an OBM, and because of their low toxicity, the drill cuttings could be discharged into the ocean. A second generation of synthetic fluids, LAOs and IOs, are used singularly or as blends with other synthetics. Cuttings produced when using these muds can also be discharged on site.
The lower viscosity of the second generation synthetic fluids leads to better rheological control in the muds and they have become the preferred materials of use. The ability to control low temperature viscosity becomes more important at deeper water depths where temperatures are in the low 30's (°F). Low temperature results in viscosity increases in the mud as it travels through the water column to the surface. IOs have lower pour points than LAOs (Table I) which allows for more rheological flexibility at lower temperatures.

SBMs are invert emulsion muds and thus are less reactive to water sensitive formations providing better hole stability, filter cake formation and drill rates. Enhanced hole stability provides better solids removal because of better mud velocities due to in-gauge hole and reduces maintenance time while tripping (moving in and out of the hole), casing and cementing. Stable filter cake provides lower drag and torque and less stuck pipe particularly while drilling deviated wells.

These benefits result in less nonproductive down time during drilling which can lower costs more than the enhanced rate of penetration SBMs provide. Operators choose SBMs to reduce risks and save time when drilling offshore through difficult water sensitive formations. With expensive drill rig day costs for these offshore operations, SBMs have proven themselves to have substantial economic benefits.

The environmental properties of synthetic fluids used in SBMs are excellent because of their low toxicity and biodegradability. This is due to their controlled synthesis from purified feedstocks to provide products that are typically free of PAHs. Removal of these priority pollutants greatly reduces fugitive emissions and worker exposure.

The use of SBMs and cuttings discharge criteria are currently piggy backed onto EPA regulations governing WBMs. Because of this, SBM well drill cuttings can be discharged at the well site provided they pass the mysid shrimp toxicity test and are free of crude and diesel oil contaminates. The EPA has now defined synthetics as materials produced by the reaction of specific purified chemical feedstocks, as opposed to traditional base fluids obtained through refining processes. Also the EPA is working to develop regulations specific to their use.

All synthetic materials used to produce SBMs meet the EPA's current toxicity effluent limit guideline for cuttings disposal with a mysid shrimp LC50 of 30,000 ppm suspended particulate phase. Because SBMs are invert emulsions, the organic phase tends to stick to the drill cutting's surface and can be carried to the sea floor. This changes the focus of toxicity concerns to the benthic communities that are exposed to these cuttings. There is currently no test accepted by the EPA to measure benthic toxicity of SBMs in the Gulf of Mexico.

The invert emulsion nature of SBMs also causes a problem measuring crude oil contamination in drilling muds using the current static sheen test developed for WBMs. The synthetic itself is lighter than water and can form a sheen giving a false positive, or stick to the cuttings and carry crude oil contamination to the sea floor producing a false negative. In contaminated SBM lab samples crude levels of up to 20 wt% have passed the sheen test.

The EPA recognizes the problems with the current regulatory toxicity and compliance monitoring tests developed for WBMs do not adequately address SBMs. The EPA is now working with the National Oceans Industry Association and the American Petroleum Institute to develop tests to measure the benthic toxicity for muds and crude oil contamination.

Synthetic fluids are biodegradable as measured by the difficult BODIS marine aerobic assay test. These studies show a trend that generally follows the molecular weight (MW) of the fluids for LAOs and IOs. The order of biodegradability generally increases as the MW decreases from that of PAOs to LAOs and IOs, PAOs<LAOs/IOs<esters (Figure 5). This trend is opposite that for mysid shrimp toxicity where toxicity tends to increase as MW decreases. When choosing a synthetic fluid for preparing a drilling mud a balance between biodegradability and toxicity must be reached. This balance is set by regulations governing the drilling area.

Other trends that follow the MW of synthetic fluids are skin compatibility and flash point, which increase as MW increases, and pour point and viscosity both decrease with decreasing MW.
CONCLUSIONS

Synthetic fluids have excellent physical properties suitable for producing invert emulsion based muds, SBMs. Their low toxicity provides improved worker safety, reduces environmental hazards and lessens fugitive emissions of PAHs. The number and type of synthetic fluids available give operators choices of performance when considering the use of SBMs for drilling wells. These materials are also marketed globally to meet drilling needs in the Gulf of Mexico and around the world.

REFERENCES


Figure 1: Synthesis of LAOs and IOs

Figure 2: Synthesis of Polyalphaolefins

Figure 3: Synthesis of Esters

R₁ and R₂ represent different hydrocarbon side chains
Figure 4: Refining of Diesel and Mineral Oils

![Diagram of oil refining process](image)

Table I: Physical Properties of Synthetic Fluids

<table>
<thead>
<tr>
<th>Fluid Type</th>
<th>Viscosity (cSt) @ 40°C</th>
<th>Viscosity (cSt) @ 100°C</th>
<th>Pour Point (°C)</th>
<th>Flash Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAO 2 cSt</td>
<td>5.50</td>
<td>1.80</td>
<td>&lt;-65</td>
<td>155</td>
</tr>
<tr>
<td>PAO 4 cSt</td>
<td>16.8</td>
<td>3.90</td>
<td>&lt;-65</td>
<td>215</td>
</tr>
<tr>
<td>Ester</td>
<td>5.13</td>
<td>1.82</td>
<td>-33</td>
<td>170</td>
</tr>
<tr>
<td>C1416 LAO</td>
<td>2.09-2.11</td>
<td>0.97</td>
<td>-12 to -9</td>
<td>114</td>
</tr>
<tr>
<td>C1618 IO</td>
<td>3.09-3.37</td>
<td>1.30-1.39</td>
<td>-24 to -14</td>
<td>134-137</td>
</tr>
<tr>
<td>C1618 LAO</td>
<td>2.98-3.08</td>
<td>1.27-1.29</td>
<td>3-9</td>
<td>146</td>
</tr>
</tbody>
</table>

Figure 5: Trends in Synthetics for Biodegradability and Toxicity with Carbon Number

- **Increasing Carbon Number**
  - C12, C14, C16, C18, C20
- **Lower Toxicity**
- **Better Skin Compatibility**
- **Lower Bioaccumulation Potential**
- **Higher Flash Point**
- **Improved Biodegradability**
- **Lower Viscosity**
- **Lower Pour Point**