RESEARCH STUDY ON FINDING A NEW SYNTHETIC OIL BASED MUD FROM ORGANIC MATERIAL (METHYL ESTER OF CASTOR OIL)

by

Umdao Nopparat

A dissertation submitted in partial fulfilment of
the requirement for the
Bachelor of Engineering (Hons)
(PETROLEUM ENGINEERING)

SEPTEMBER 2012

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CERTIFICATION OF APPROVAL

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Approved by,

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TRONOH, PERAK
SEPTEMBER 2012

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

UMDAO NOPPARAT

ABSTRACT

Oil based mud is a fluid used in modern day drilling. It is preferred compared to water based mud because it can be used in high pressure high temperature wells, doesn’t react with clay formations, provides better wellbore stability and reduces differential sticking in the hole. Though it has a lot of it benefits, its negative points are known for its high initial costs and harmful towards the environment. Nevertheless the use of oil based mud is proved harmful to the environment, it is still being used with the help of solids control and drilling waste management’s technology which leads to high cost of maintaining the mud. The need of drilling fluid to be environmentally friendly is important in the sense of not being harmful to the environment and reducing the cost impact. The study would be on developing a synthetic base mud using organic biodegradable based oil where methyl ester of castor oil will be used for this study. The final outcome expected is to have a synthetic based mud which is less harmful to the environment and user while competent with the current’s market base oil’s synthetic based mud. The study will be done in Universiti Teknologi PETRONAS’s lab and Scomi Global Research and Training Centre (GRTC) depending on availability of tools and technology.

ACKNOWLEDGEMENT

Firstly, author would like to thank Universiti Teknologi PETRONAS for supporting and providing all necessary resources in ensuring this project is successfully done. The author has gained a lot of experiences and knowledge from working on this project.

Next, the author would like to express gratitude towards project supervisor, Mr.Ali Fikret Mangi Alta'ee who kindly provides guidance and encouragement from the beginning of the study till end. He puts his trust in the author for every job assigned while spending a considerable time to share and discuss about every process of project.

The author would also like to thank Dr. Sonny Irawan and Mr. Jukhairi for their technical support and great advices from their area of expertise.

The author also would like to give a mention to Mr.Erwin Ariyanto, Scomi GRTC Technical Head and Manager, for all the support in providing the facilities and experiences into this project to help enhance the final outcome of the project.

Last but not least, the author would like to thank to all fellow Final Year Project colleagues, friends and families for their encouragement and support throughout this project period.

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CHAPTER 1
INTRODUCTION

1.1 Background of Study

The main target of drilling and production operations are to drill the wells and bring the wells to life. One of the important roles needed to achieve the target is the use of drilling fluids. The effectiveness of drilling fluids will be measured by providing enough pressure to maintain wellbore stability, providing good rate of penetration and transmit hydraulic horsepower to bit while drilling process, ability to transport cuttings from the well to surface, ability to isolate fluid from formation and wellbore, able to cool and lubricate drill bit and drilling assembly, not causing formation damages and borehole problems in order to operate at the lowest overall cost.

Oil based mud and synthetic based drilling fluid are preferred because they have many inherent advantages over water based drilling fluid including wellbore stability, tolerance to contamination, not reactive with clay formation and corrosion protection. Nevertheless, oil based mud from highly aromatic oil (e.g.diesel) which can pollute environment has been replaced by lower aromatic mineral oils and synthetic oils but still not suitable as its low biodegradability property. An average well can produce 1000-1500 tons of cuttings, while a shaker is able to separate the cuttings from the mud system leaving the oil on cuttings 14% to 15% by weight, meaning the amount of oil will be dumped into the sea can reach to 150 – 225 tons per well causing a large area around the drilling site being affected (Dosunmu and Joshua 2010).

Although unfriendly to the environment, synthetic oil based mud is still being used with help of solids control and drilling waste management’s technology even though it is proven to be harmful to the environment. As for some countries, the practice of using a dryer is used to reduce the oil on cuttings percentage to lower than 6% before dumping. Some countries impose a zero discharge law, where all cuttings need to be transported back onshore for treatment before disposing. This leads to high cost of maintaining the mud. In order to reduce cost impact and meet the technical and environmental criteria, the need of drilling fluid to be environmentally friendly is important and base fluid from organic material comes into consideration.

1.2 Problem Statement

1.2.1 Problem Identification

Even though oil based drilling fluids offer more advantages but there is a limitation of applying this drilling fluid which is its toxicity which causes harm to the environment. Moreover, it has a big impact on user's health. Also, handling and initial costs of oil base mud are high, which includes the solids control equipment and drilling waste management equipment.

1.2.2 Significant of the Project

This project will focus on research study information and the effect of the developed old based mud from organic materials towards the environment. Lab tests for properties and environment impact will be done to obtain results. Comparison of results will be done between the developed oil based mud and the current oil based mud in market based on the impact towards the environment.

1.3 Objectives

To develop a stable and environmentally friendly drilling fluid which has less harmful effect toward environment and user, and cost saving under required pressure and temperature condition compared to the conventional drilling fluid.

1.4 Scope of Study

The scope of work are to run a lab test on new organic oil based mud which will measure the effect of additives concentration which need in fewer amounts of additives as possible and a test on mud properties, rheology and impacts on the environment in order to meet the objective of project.

1.5 Relevancy of Project

The reason of having an environmental friendly oil based mud is to reduce the impact on the environment. For the current practice in Malaysia, only 6.9% oil on cuttings by weight is allowed to be dumped to the sea. Anything higher than that will be needed to be treated through the cutting dryer. That will increase the cost of drilling. With an environmental friendly oil based mud, the amount of oil able to dump to the sea can be increased as it is less harmful thus saving on the cost of the equipment as well.

1.6 Feasibility of Project

A proper planning and good background research of current product is needed to successfully achieve the objective of the project. A collaboration or memorandum of understanding will be done with mud servicing company for their knowledge and advice. Proper planning and discipline towards the project timeline is needed to achieve each progress of the project.

CHAPTER 2
LITERATURE REVIEW

2.1 Drilling Fluid Overview

Drilling fluids are fluids used during drilling and production operations. This drilling fluid better known as “drilling mud” is a one of the important role in drilling and production operation in order to drill the well and bring the well to life. The effectiveness of drilling fluids will be measured by providing enough pressure to maintain wellbore stability, providing good rate of penetration and transmition hydraulic horsepower to bit while drilling process, ability to transport cuttings from the well to surface, ability to isolate fluid from formation and wellbore, able to cool and lubricate drill bit and drilling assembly, not causing formation damages and borehole problems in order to operate at the lowest overall cost.

2.2 Drilling Fluid Functions

Following are the functions of drilling fluids towards drilling:

a) Control formation pressure
b) Transport or suspend cuttings
c) Maintaining wellbore stability
d) Sealing permeable formations
e) Minimising reservoir damage
f) Coolant and lubricator to the drill bit and drilling assembly
g) Ensure good data recovery
h) Control corrosion
i) Facilitate cementing
j) Minimising HSE risks

Drilling fluid manage to control formation pressure by providing hydrostatic pressure which is a force exerted by a fluid column together with density property and true vertical depth (TVD). Drilling fluid must overcome both borehole instability due to unequal mechanical stress and pressure created by physic-chemical interaction when surfaces are exposed in the process of drilling a well.

As drilled cuttings are generated by the bit, they must be removed from the wellbore. Drilling fluid is created to this purpose by circulating down the drill string and through the bit, transporting the cuttings up the annulus to the surface.

Wellbore stability is a complex balance of mechanical (pressure and stress) and chemical factors. The chemical composition and mud properties must combine to provide a stable wellbore until casing can be run and cemented. Regardless of the chemical composition of the fluid and other factors, the weight of the mud must be within the necessary range to balance the mechanical forces acting on the wellbore. Drilling fluid helps to maintain stable wellbore by supporting borehole pressure. Pore pressure was predicted before drilling operation. Mud weight planning is based on the predicted pore pressure gradient plus, typically, 200 to 500 psi.

2.3 Type of Drilling Fluid

2.3.1 Water Based Mud

Water based mud is a mud in which the continuous phase is water.

- **Advantage**

  This type of drilling fluid is environmentally friendly and users' friendly as the base fluid itself is a water. The handling cost of this water based mud is lesser than oil based mud as it does not require advance equipment and processes to manage the cuttings.

- **Disadvantage**

  In shale formations, if the mud weight is sufficient to balance formation stresses, wells are usually stable - at first. With water-base muds, chemical differences cause interactions between the drilling fluid and shale, and these can lead (over time) to swelling or softening. This causes other problems, such as sloughing and tight hole conditions. Highly fractured, dry, brittle shale formations, with high dip angles, can be extremely unstable when drilled. The failure of these dry, brittle formations is mostly mechanical and not normally related to water or chemical forces.

Water based mud provide less mud density which means it can be used at the limited formation depth range as the deeper formation require suitable mud weight to provide enough pressure in order to control well pressure.

2.3.2 Oil Based Mud

Oil based mud and synthetic based drilling fluid are preferred because they have many inherent advantages over water based drilling fluid including wellbore stability, tolerance to contamination, not reactive with clay formation and corrosion protection.

The oil used in this oil base mud can range from crude oil, refined oils such as diesel or mineral oils, or non-petroleum organic fluid.

A. Mineral Oil/ Synthetic Oil

Oil based mud from highly aromatic oil (e.g. diesel) which can pollute environment has been replaced by lower aromatic mineral.

- **Advantage**
  - Used for High Pressure High Temperature (HPHT) wells to stand the downhole high temperature.
  - Does not react with clay formation in shale formation
  - Creates sludge cake cutting where it reduces the risk of pipe stalemate
  - Able to be treated through Solids Control and Drilling Waste Management systems to be able for reuse.
- **Disadvantage**
  - Cannot be directly dispose into the ocean or land due to environment issue.

- People’s healths are compromised without proper safety Personal Protective Equipment (PPE). It releases bad odour and very acidic to the skin without proper gloves
- Handling costs of oil based mud is more for the chemicals and equipment used.
- Long-term legal liability has been imposed in many countries.

As per mention above, even though, oil based mud have many advantages over other type of base fluid, unfortunately environmental concerns make the use of oil based muds increasingly more difficult, costly and risky.

There are many groups and organizations concerned about this environmental issue as it is mentions in many articles, research paper and books.

As per mention by Joseph (2012) “Oil based mud is most certainly not environmentally friendly and great efforts are made to ensure it doesn't get into the oceans/environment. I should know, I work with the stuff. It's used a lot on Oil rigs, taken out there in sealed containers or pipelines, pumped down a borehole (sealed off from the sea), and when it's back, it either stays on the rig, or is sent back to shore for cleaning and decontamination (again, sealed containers/pipelines) and used again. Only when all the oil is gone, will any of it be put back into the environment. Workers cannot get it on our skin; we're covered in protective gear to work with it. Any samples of rock that have it on are washed before anything else is done to them”

Moreover there also a website said “Believe it or not, drilling for oil can be a definite source of waste that can harm the environment. The most common problem comes in the drilling fluids that are used. In the past, oil drilling sites have used oil-based-muds, OBMs, as drilling fluid to keep cuttings from the drill cleared away. The problem is that in the mud there is both diesel fluid and mineral oil. Both of these are harmful to the environment. While water-based-muds are available and provide a much more environmentally safe solution, they simply do not work as well for the drillers. Companies are working on creating more environmentally friendly drilling fluids. As of the 1990’s, companies began making SBMs, or synthetic-based-muds. These have the desired effect of OBMs with a much lower threat to the environment. Still, the perfect drilling solution beneficial to both man and planet has yet to be found"(Oil Industry 2012).

Besides , a study on the topic of Toxicity Study on Marine Organisms due to drilling fluid shown that oil base mud (diesel has proved to be most toxic) has a negative impact on marine organisms. The toxicity was due mainly to its base oil that was diesel. The result suggest that drilling fluid systems should be carefully formulated to minimize the effect to pollution to the environment.(Ismail, Ahmad, and Anam. 2012)

According to the reason that oil base mud has bad impact to environment, so that the drilling fluid need to be managed following the rules and regulations of each particular production area.

The Department of Industry and Resources (2012) have established Petroleum Guideline for Drilling Fluids Management which the operators in that development area need to follow.

The guideline mentioned regulating the use of drilling fluids by the Department of Industry and Resources (DoIR) assesses the use of drilling fluids in perspective with environmental risks associated with the whole operation. This holistic assessment approach takes into account the technical justification for the proposed use of the drilling fluid, environmental sensitivities of the proposed drilling location, the method of cuttings disposal and the drilling fluid environmental performance under standard test protocols. Criteria for assessing the environmental performance of drilling fluids include the eco-toxicity, biodegradation and bioaccumulation properties of the whole and base fluid.

- **Long Term Issue Due to Oil Base Mud**

  Existing cuttings piles contain a mixture of rock formation cuttings of varying sizes and drilling fluids that adhere to the rock cuttings. The size and nature of these cuttings piles vary according to the amount of cuttings discharged to the seabed, the platform configuration, oceanographic conditions and the type of drilling fluid used. In shallower waters cutting piles tend not to accumulate for individual exploration wells due to oceanographic condition, whereas cuttings piles are known to persist beneath some production platforms in deeper waters offshore Western Australia.

The burial of OBF's and SBF's discharged on cuttings limits the rate of natural biodegradation and there are indications that the residual oil in the sediments is not substantially biodegraded in the long term. Large cuttings piles are considered likely to be a source of chronic low level hydrocarbon seepage into the marine environment and may be taken up by sediment reworked species (Daan et. al., 1994; Munroe 1997). The Dutch North Sea study of the environmental impact of OBF cuttings discharges around wellsites in the Dutch sector demonstrated that the discharge of OBF cuttings involves high disturbance of benthic fauna up to hundreds of metres from platforms and that smaller effects can be detected up to a few kilometres (Daan et. al., 1996). Oil concentrations in deeper sediment layers (> 10 cm) of a large cutting pile have shown to be high eight years after the completion of OBF cuttings discharges.

The issue of removal and disposal of cuttings piles needs to be carefully considered. A comprehensive risk assessment of the options should be supplemented by environmental monitoring data to support the best approach to treatment. Decommissioning of WA production platforms in deeper water is unlikely to occur in the next decade. It may however, be prudent to consider this issue for current platform developments in the light of changing environmental awareness and the potential future cost of removing cuttings piles at the time of facility decommissioning.

B. Organic Oil

Esters

Esters are synthesized from fatty acids and alcohols. Fatty acid is derived from vegetable oils. Proper selection on the hydrocarbon chain length will minimize viscosity. Ester has general structure as adjacent figure. To form an ester, an alcohol is reacted with fatty acid, under acidic condition using acid catalyst

Ethers

Ethers are a class of organic compounds that contain an ether group — an oxygen atom connected to two alkyl or aryl groups — of general formula R–O–R'. Ethers can be prepared in the laboratory in several different ways. Ethers are also categorized as a broad range of materials which are usually synthesized from alcohols (Md, Amanllah, 2005).

- **Advantage**
  - This organic oil based mud is environmentally friendly as it is readily biodegradable. So that, there will be no environmental impact at the control concentration.
  - Less initial and management cost compare to conventional oil based mud and synthetic based mud.
- **Disadvantage**
  - Experiments need to be done in order to optimize properties of organic oil based fluid.
  - Limited resources of the organic oil, so that alternative organics oil should be studied.

2.4 Drilling Fluid Properties/ Selection Criteria

Selection of the best fluid to meet anticipated conditions will minimize well costs and reduce the risk of catastrophes such as stuck drill pipe, loss of circulation, gas kick, etc. Consideration must also be given to obtain adequate formation evaluation and maximum productivity. Some important considerations affecting the choice of mud’s to meet specific conditions are location, pressured, high temperature, hole instability, rock salt, hole inclination, formation and productivity impairment (Chapter -2 Drilling Fluids 2012).

Basic requirements of base oil properties discussed by Johan Scvik and Grieve (1987) are nontoxic and low aromatic content as should be non-acutely toxic in a standard 96 hr LC 50 toxicity test, as low kinematic viscosity as possible, higher flash point in order to minimize fire hazards which should be greater than 100degFand must be able to form a stable emulsion.

Base Fluid Properties

There are certain requirements to identify whether the oil can be used as base fluid in drilling fluid. The requirements are as follows;

- Non-toxic and low aromatic content

  Base oil should have total aromatic hydrocarbon content of less than 5%. It should be non-acutely toxic in a standard 96 hr LC 50 toxicity test, performed using 100% water soluble fraction of the base.

- Kinematic Viscosity

  It should be as low as possible. This allows the oil based mud to be formulated at lower oil/water ratio and gives better rheology (lower plastic viscosity) especially at lower mud temperature.

- Flash Point

  It should be greater than 100°F. Higher flash point will minimize fire hazards as less hydrocarbon vapours is expected to generate above the mud.

- Pour Point

  It should be lower than the ambient temperature to allow pump ability of mud from storage tanks.

2.5 Mud Additives

There are many additives in drilling fluid industry which are used to develop the key properties of the mud. The functional group of additives may contain several alternative materials with slightly different properties although more than 1,000 trade name or generic additives are available for drilling mud formulation. Most additives are added in small amounts to change mud properties to solve specific down-hole problems.

Table 1: Functional categories of materials used in drilling fluids, their functions, and examples of typical chemicals in each category from Boehm et al. (2001).

Functional Category	Function	Typical Chemicals
Weighting Materials	Increase density (weight) of mud, balancing formation pressure, preventing a blowout	Barite, hematite, calcite, ilmenite
Viscosifiers	Increase viscosity of mud to suspend cuttings and weighting agent in mud	Bentonite or attapulgite clay, carboxymethyl cellulose, &other polymers
Thinners, dispersants, & Temperature stability agents	Deflocculate clays to optimize viscosity and gel strength of mud	Tannins, polyphosphates, lignite, ligrosulfonates
Flocculants	Increase viscosity and gel strength of clays or clarify or de-water low-solids muds	Inorganic salts, hydrated lime, gypsum, sodium carbonate and bicarbonate, sodiumtetraphosphate, acrylamide-based polymers
Filtrate reducers	Decrease fluid loss to the formation through the filter cake on the wellbore wall	Bentonite clay, lignite, Nacarboxymethyl cellulose, polyacrylate, pregelatinized starch

Alkalinity, pH control additives	Optimize pH and alkalinity of mud, controlling mud properties	Lime (CaO), caustic soda (NaOH), soda ash (Na_2CO_3), sodium bicarbonate ($NaHCO_3$), & other acids and bases
Lost circulation materials	Plug leaks in the wellbore wall, preventing loss of whole drilling mud to the formation	Nut shells, natural fibrous materials, inorganic solids, and other inert insoluble solids
Lubricants	Reduce torque and drag on the drill string	Oils, synthetic liquids, graphite, surfactants, glycols, glycerin
Shale control materials	Control hydration of shalesthat causes swelling and dispersion of shale, collapsing the wellbore wall	Soluble calcium and potassium salts, other inorganic salts, and organics such as glycols
Emulsifiers & surfactants	Facilitate formation of stable dispersion of insoluble liquids in water phase of mud	Anionic, cationic, or nonionic detergents, soaps, organic acids, and water-based detergents
Bactericides	Prevent biodegradation of organic additives	Glutaraldehyde and other aldehydes
Defoamers	Reduce mud foaming	Alcohols, silicones, aluminum stearate ($C_{54}H_{105}AlO_6$), alkyl Phosphates
Pipe-freeing agents	Prevent pipe from sticking to wellbore wall or free stuck pipe	Detergents, soaps, oils, surfactants
Calcium reducers	Counteract effects of calcium from seawater, cement, formation anhydrites, and gypsum on mud properties	Sodium carbonate and bicarbonate (Na_2CO_3 & $NaHCO_3$) , sodium hydroxide (NaOH), polyphosphates

Corrosion inhibitors	Prevent corrosion of drill string by formation acids and acid gases	Amines, phosphates, specialty mixtures
Temperature stability agents	Increase stability of mud dispersions, emulsions and rheological properties at high temperatures	Acrylic or sulfonated polymers or copolymers, lignite, lignosulfonate, tannins

Oil based muds required special product to ensure that the emulsion is extremely stable and can withstand conditions of high temperature (HT) and contaminants. Every single product must be dispersible in the external oil phase (OLD-BASED MUDS & SYNTHETIC-BASED MUDS 2012).

- Emulsifying System

Calcium soaps are the primary emulsifier in oil muds. These are made in the mud by reaction of lime and long-chain fatty acid. Soap emulsion are strong emulsifying agent but may take reaction time before emulsion is actually formed.

Thus secondary emulsifiers are used: they consist in very powerful oil-wetting chemical which generally do not form emulsions but wet solids before the emulsion is formed. Also use to prevent from any water intrusion.

- Lime (Calcium Hydroxide)

Lime is essential in OBMs. It neutralizes fatty acids in the fluid, stabilizes the emulsion when present in excess, and controls alkalinity. In the field, it also neutralizes acid gases (H_2S and/or CO_2). Moreover it also can be corrosion control agent. Lime is a safer alternative to Caustic Soda to provide alkalinity for corrosion protection.

- Fluid Loss Reduction Additives

Many types of chemicals can be used as Fluid Loss control agents. They are usually organophiliclignites (amine-treated lignites), Gilsonite or Asphalt derivatives, or special polymers.

The reasons for fluid loss control are to maintain hole integrity, to protect water sensitive shales, to minimize hole washout to achieve better casing cement jobs, to reduce fluid loss to productive formation and to minimize formation damage and to reduce log analysis problems.

Bentonite is a multipurpose additive that aids in fluid loss control, barite suspension, viscosity, generator for hole cleaning purposes. It is not suitable for use in environments high in concentration of sodium, calciumor potassium without pre-hydration. It may contaminate formations such as salt or anhydrite. Slurries are susceptible to the effect of high temperature gelation which could cause an increase in the fluid loss.

XC Polymer builds viscosity. It increases gel structure, has low viscosity at high shear rates, has high viscosity at low shear rates and suspends barite.

Lignites and Tannins have good temperature stability in the range of 300°F to 350°F. They have colloidal structure that aids in fluid-loss control. The dual action of fluid loss control and dispersing tendencies makes these products suitable for single-product usage in some cases. They are susceptible to calcium-ion contamination and subsequent mud flocculation due to sequestering nature of the additive.

The impacts of such products on rheology depend on their nature. For instance, lignites do not affect viscosity, whereas asphalt derivatives can cause excessive viscosity and/or gelation.

- Wetting Agents

Supplemental additives to quickly and effectively oil-wet solids that became water-wet.

- Rheology Control Materials

When efficient control of viscosity and gel development cannot be achieved by control of viscosifier concentration, materials called "thinners", "dispersants", and/or "deflocculants" are added. These materials cause a change in the physical and chemical interactions between solids and/or dissolved salts such that the viscous and structure forming properties of the drilling fluid are reduced.

Thinners are also used to reduce filtration and cake thickness, to counteract the effects of salts, to minimize the effect of water on the formations drilled, to emulsify oil in water, and to stabilize mud properties at elevated temperatures.

Materials commonly used as thinners in clay- based drilling fluids are classified as: (1) planttannins, (2) lignitic materials, (3) lignosulfonates, and (4) low molecular weight, synthetic, water soluble polymers.

- Weighting Agents

They are substances with high specific gravity which can be added to the mud to increase its density, usually to control formation pressure. Barite is by far the most common weighting material used in drilling fluids. It has an API defined specific gravity of 4.2, which makes it possible to increase mud weight up to 21 ppg. It is cheap and readily available. However, suspension of barite requires high gel strength and viscosity. Hematite is sometimes used depending on the availability. Calcium Carbonate is an additive used in drilling mud’s, work over fluids and packer fluids to increase the fluid density. It has a specific gravity of 2.7, therefore, the fluid density can be increased up to 12 ppg. It is more economical than other agents, and can be suspended easier than barite. Also it is acid soluble (Chapter -2 Drilling Fluids 2012 ; OIL-BASED MUDS & SYNTHETIC-BASED MUDS 2012; Rabia 2012).

2.6 Mud Rheological Properties and Filtration Characteristics Measurement

Rheology is defined as the study of the deformation and flow of matter. In drilling operations, the term rheology refers to the use of the shear stress, shear rate and time relationships of drilling fluids. Rheological properties are used to design and evaluate the hydraulics and to assess the functionality of the mud system. Muds behave with non-Newtonian fluid flow properties as their viscosity is not only influenced by temperature and pressure but are also strongly related to the velocity at which the mud flows through the hydraulic system.

The drilling fluid velocity and the resulting rate of shear at the walls of the conduits play an important role on the viscosity of the fluid pumped. For this reason, it is important to know the viscosity in the full range of shear rate usually considered for hydraulic calculations. There is a well characterized minimum stress, called yield point, below which flow does not occur. At low shear rates there is a typical non-linear relationship between shear stress and shear rate, which tends to be attenuated with the increase of shear rate (Rheology of Drilling Muds 2012).

Rheological models (Figure 1) are mathematical equations used to predict fluid behavior across a wide range of shear rates and provide practical means of calculating pumping (pressure) requirements for a given fluid. Most drilling fluids are non-Newtonian and pseudo plastic and, therefore, hydraulic models use a number of approximations to arrive at practical equations (Rabia 2012).

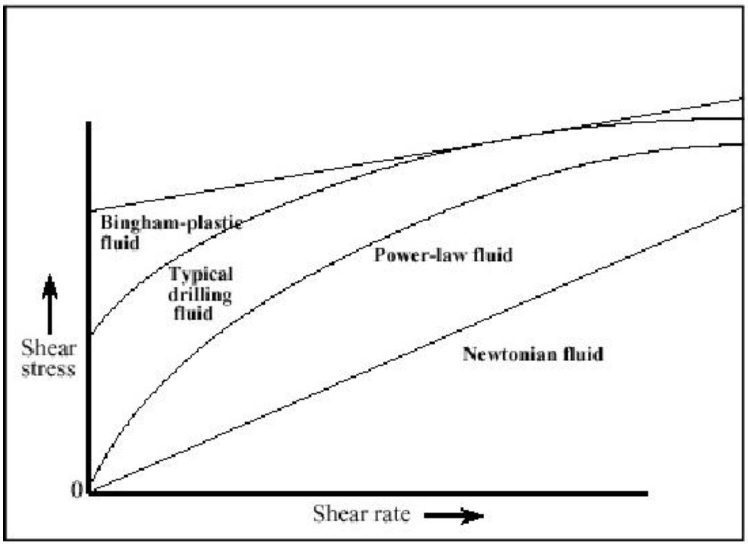


Figure 1: Rheological models

The three rheological models that are currently in use are:

- Bingham Plastic model

The Bingham Plastic model describes laminar flow using the following equation:

$$T = YP + PV \times (\gamma)$$

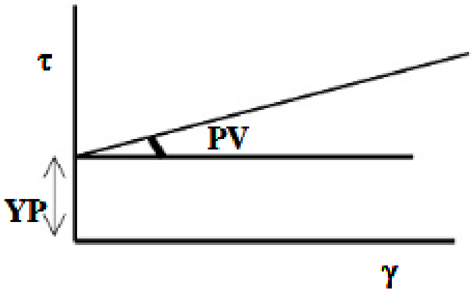


Figure 2: Bingham Plastic model(1)

Where T = measured shear stress in lb/100 ft2

YP = yield point in lb/100 ft2

PV = plastic viscosity in cP

γ = shear rate in sec–1

The values of YP and PV are calculated using the following equations:

$$PV = \theta 600 - \theta 300$$

$$YP = \theta 300 - PV$$

$$YP = (2 \times \theta 300) - \theta 600$$

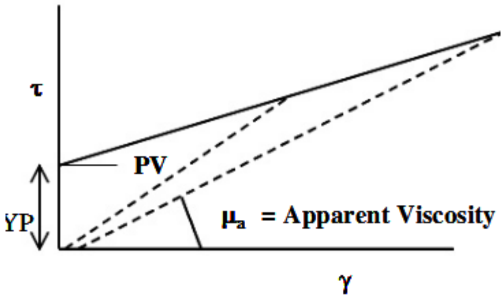


Figure 3: Bingham Plastic model(2)

The slope of a line connecting any point on the straight line to the origin is described as the apparent viscosity at that particular shear rate.

The Bingham Plastic model usually over predicts yield stresses (shear stresses at zero shear rates) by 40 to 90 percent.

The following equation produces more realistic values of yield stress at low shear rates:

$$YP\ (\text{Low Shear Rate}) = (2 \times \theta 3) - \theta 6$$

This equation assumes the fluid exhibits true plastic behavior in the low shear-rate range only.

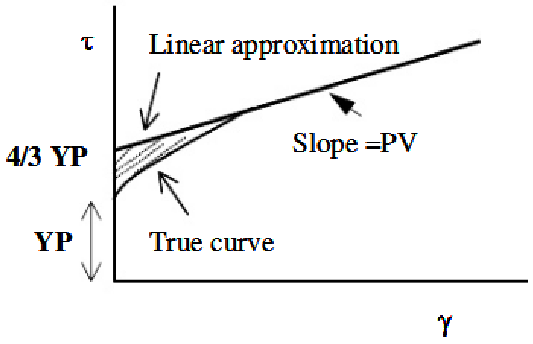


Figure 4: Bingham Plastic model(3)

- Power Law model

The Power Law model assumes that all fluids are pseudo plastic in nature and are defined by the following equation;

$$T = K\ (\gamma)n$$

Where

T =Shear stress (dynes / cm2)

K =Consistency Index

γ =Shear rate (sec-1)

n =Power Law Index

$n = 3.321 \log(\theta 600/\theta 300)$

$K = \theta 300/(511)n$

The constant “n” is called the POWER LAW INDEX and its value indicates the degree of non-Newtonian behavior over a given shear rate range. If 'n' = 1, the behavior of the fluid is considered to be Newtonian. As 'n' decreases in value, the behavior of the fluid is more non-Newtonian and the viscosity will decrease with an increase in shear rate. The constant “n” has no units. The “K” value is the CONSISTENCY INDEX and is a measure of the thickness of the mud. The constant 'K' is defined as the shear stress at a shear rate of one reciprocal second. An increase in the value of 'K' indicates an increase in the overall hole cleaning effectiveness of the fluid. The units of 'K' are either lbs/100ft2, dynes-sec or N/cm2.

The constants n and K can be calculated from Fann VG meter data obtained at speeds of 300and 600 rpm through the use of equations above.

Hence the Power Law model is mathematically more complex than the Bingham Plastic model and produces greater accuracy in the determination of shear stresses at low shear rates. The Power Law model actually describes three types of fluids, based on the value of 'n':

i) $n = 1$: The fluid is Newtonian
ii) $n < 1$: The fluid is non-Newtonian
iii) $n > 1$: The fluid is Dilatent

- Herschel-Bulkley (yield-power law:YPL) model

The Herschel-Bulkley (yield-power law [YPL]) model describes the rheological behavior of drilling muds more accurately than any other model using the following equation:

$$T = \tau o + K \times (\gamma) n$$

Where

τ = measured shear stress in lb/100 ft2
τo=fluid's yield stress (shear stress at zero shear rate) in lb/100 ft2
K = fluid's consistency index in cP or lb/100 ft sec2
n = fluid's flow index
γ=shear rate in sec-1

The YPL model reduces to the Bingham Plastic model when n = 1 and it reduces to the Power Law model when $\tau o= 0$.

The YPL model is very complex and requires a minimum of three shear-stress/shear-rate measurements for a solution.

Density or mud weight

Report in g/ml or in lb/gal, lb/cu ft, or psi/1000 ft of depth. Instrument should be calibrated once a day when weight is critical. Mud weight is measured by means of a mud balance. The weight of water is 8.33 ppg. The mud weight can be increased by adding barite (barium sulphate). Barite has a specific gravity of between 4.2 – 4.3. Other materials can be used to increase mud weight such as ilmenite (S.G of 4.58) (Drilling Fluids 2012).

Plastic Viscosity (PV)

It is a parameter of the Bingham plastic rheological model. PV is the slope of the shear stress/shear rate line above the yield point as mentioned earlier. Mud viscosity is difficult to measure but in the field the Marsh funnel and the Fann V-G meter is commonly used. The Marsh Funnel is filled with mud, the operator then notes the time, removes his finger from the discharge and measures the time for one quart (946 cm^3) to flow out. Marsh funnels are manufactured to precise dimensional standards and may be calibrated with water which has a funnel viscosity of 26 ± 0.5 sec.

In using Fann V-G (Viscosity-gel) meter, readings are taken at 600 rpm and 300 rpm.

The viscosities are defined as follows:

$$\mu_p = \phi_{600} - \phi_{300}$$

$$\mu_{aF} = \tfrac{1}{2}\,\phi_{600}$$

$$Y_b = \phi_{300} - \mu_p$$

Where μ_p = plastic viscosity, cp

μ_{aF} = apparent viscosity, cp

Y_b = Bingham yield point, lb/100 ft^2

ϕ = Torque readings from instrument dial at 600 and 300 rpm.

From these relationships:

$$Y_b = 2(\mu_{aF} - \mu_p)$$

$$\mu_{aF} = \mu_p + \tfrac{1}{2} Y_b$$

True yield point: $Y_t = \tfrac{3}{4} Y_b$

Yield point is influenced by the concentration of solids, their electrical charge, and other factors. If not at the proper value, it can also reduce drilling efficiency by cutting penetration rate, increasing circulating pressure, and posing the danger of lost circulation (Drilling Fluids 2012).

Gel strength

The gel strength is the shear stress of drilling mud that is measured at low shear rate after the drilling mud is static for a certain period of time. The gel strength is one of the important drilling fluid properties because it demonstrates the ability of the drilling mud to suspend drill solids and weighting material when circulation is ceased (Gel Strength of Drilling Mud 2012). We use the 3-rpm reading which will be recorded after stirring the drilling fluid at 600 rpm from a rheometer. Normally, the first reading is noted after the mud is in a static condition for 10 second. The second reading and the third reading will be 10 minutes and 30 minutes, respectively. You may wonder why we need to record the 3-rpm reading after 30 minutes. The reason is that the 30 minute-reading will tell us whether the mud will greatly form the gel during an extensive static period or not. If the mud has the high gel strength, it will create high pump pressure in order to break circulation after the mud is static for long time. Furthermore, increasing in a trend of 30-minute gel strength indicates a buildup of ultra-fine solid. Therefore, the mud must be treated by adding chemicals or diluting with fresh base fluid (GEL STRENGTH 2012).

The following causes will result in the high gel strength in the water base mud.

- Bacteria
- Drill solid
- Salt
- Chemical contamination as lime, gypsum, cement, and anhydrite
- Acid gases as Carbon Dioxide (CO2), and Hydrogen Sulphide (H2S)

For an oil base drilling fluid, there are several points that will cause the high gel strength in the mud system as follows.

- Over treatment with organic gelling material
- Buildup of fine solid particles in the mud

Operational impacts of the gel strength are as follows:
Cutting suspension ability - Low get strength drilling mud will not be able to efficiently suspend cuttings; therefore, the cutting will quickly drop once pumps are shut down. This can lead to several problems such as stuck pipe, hole pack off, and accumulation of cutting beds.

Barite sag - The barite sag issue mostly occurred because of low gel strength drilling fluid. Hence, the mud weight in the hole will not be constant. You will see that the lower mud weight will be seen at the shallow depth but the heavier mud weight will be noticed at the deeper section of the well. This situation could possibly lead to a well control incident because of insufficient mud weight to balance formation pressure at the shallow section of the wellbore.

Break circulation pressure - If you have highly progressive gel strength fluid, there will be a lot of pressure required to break circulation. Once high pumping pressure is applied, it could lead to break formation and results in lost circulation issue (Gel Strength of Drilling Mud 2012).

Yield Point (YP)

It is a parameter of the Bingham plastic rheological model. Yield Point is the yield stress extrapolated to a shear rate of zero. As shown in figure 1, a Bingham plastic fluid plot as a straight line on a shear rate (x-axis) versus shear stress (y-axis) plot, in which YP is the zero-shear-rate intercept. (PV is the slope of the line). Yield Point is calculated from 300- and 600-rpm viscometer dial readings by subtracting PV from the 300-rpm dial reading, as follow

$$YP = \theta 300 - PV$$

Yield Point is used to evaluate the ability of a mud to lift cuttings out of the annulus. A high YP implies a non-Newtonian fluid, one that carries cuttings better than a fluid of similar density but lower YP. YP is lowered by adding deflocculant to a clay-based mud and increased by adding freshly dispersed clay or a flocculant, such as lime. YP is measured in unit of lbf/100ft2.

When plastic viscosity rises, this is usually an indication that the solids control equipment are running inefficiently. Ideally, the yield point should be just high enough to suspend the cuttings as they are circulated up the annulus.

Yield Point is characterized also as resistance of initial flow of fluid or the stress required in order to move the fluid. The YP indicates the ability of the drilling mud to carry cuttings to surface. Moreover, frictional pressure loss is directly related to the YP. Higher YP will result in higher pressure loss while drilling mud is being circulated. In oil-based mud, the causes of increasing in YP are listed from Rabia (2012)

- Drill solid – the higher content of drill solid, the higher YP will be.
- Treatment CO_2 in the mud with lime (CaO) – The lime (CaO) will chemically react with CO_2 to form Calcium Carbonate ($CaCO_3$) which will increase the YP.
- Low temperature – in the oil base system, the low temperate will increase the viscosity and the YP.
- Operational impacts of the YP are as follows.

- Equivalent Circulating Density (ECD) – The ECD typically increases when the YP increases.
- Hole Cleaning – in drilling a large diameter hole, the YP in the drilling mud must be high in order to help hole cleaning efficiency.

Fluid Loss and Filter Cake

The fluid loss gives a representation of the fluids interaction with the wellbore under simulated pressure and temperature conditions. Ideally the fluid should form athin, flexible, impermeable layer (filter cake) against the wall and prevent fluid (filtrate) from entering the rock and reacting with the formations. A mud system with a low value of filtrate loss cause minimum swelling of clays and minimum formation damage. The filter cake should be in the region of 1 to 2 / 32" and should never be greater than 3/ 32”, even in an HPHT test with WBM (Rabia 2012) .

Both tests work on filling a cell with drilling fluid, and sealing it shut. Inside the cell is a filter paper that has been placed between the mud and the aperture in the cell. Pressure is applied to the cell which forces the mud and solids through the filter paper. The solids accumulating on the filter paper form a filter cake and the filtrate passing through the paper is collected in a graduated cylinder. The mud in the cell is pressurized for 30 minutes the fluid or filtrate is collected and measured. The filter paper is also collected, washed, then examined and the deposited filter cake is measured. HPHT tests with the cell put under heat are usually carried out on wells where the temperature is greater than 200^{o}F.

Unit: ml / 30 minutes at100 psi (for API test) or 500 psi and BHT (F) for high temperature/high pressure (HTHP).

Filtration control additives include:

- Starch
- Carboxymethylcellulose (CMC)
- Polyanionic Cellulose (PAC)

Alkalinity and pH Test

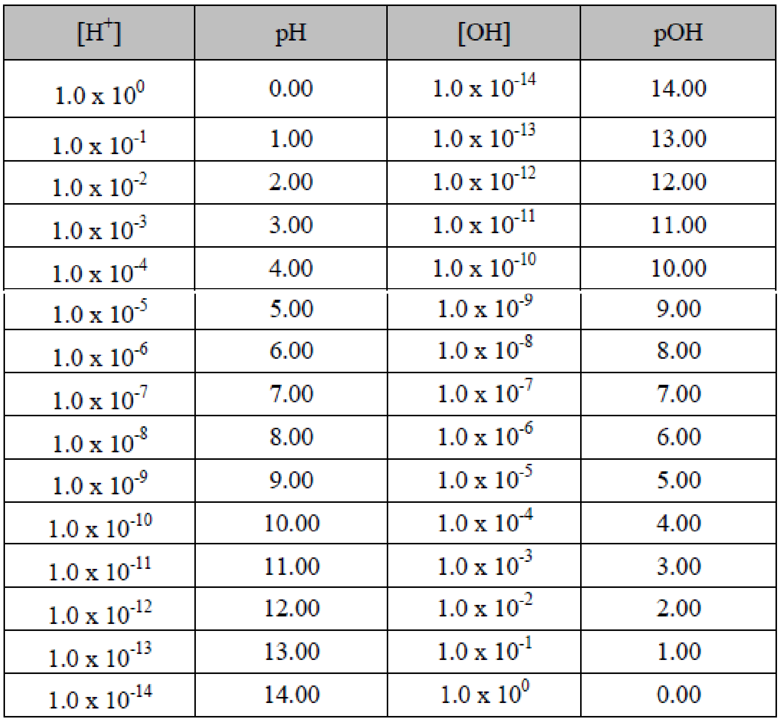
The pH affects several mud properties including:

- detection and treatment of contaminants such as cement and soluble carbonates
- solubility of many thinners and divalent metal ions such as calcium and magnesium
-

Alkalinity and pH control additives include: NaOH, KOH, Ca(OH)2, NaHCO3 and Mg(OH)2. These are compounds used to attain a specific pH and to maintain optimum pH and alkalinity in water base fluids (Drilling Fluid Functions 2012).

The term pH is used to express the concentration of hydrogen of hydrogen ions in an aqueous solution. pH is defined by pH = log [H+], Where [H+] is the hydrogen ion concentration in moles per litter. At room temperature, the ion product constant of water, Kw, has a value of 1.0 x 10-14 mol/L.

Table 2: Relations between pH, [H+] and [OH-] in water solutions



$[H^+]$	pH	[OH]	pOH
1.0×10^{0}	0.00	1.0×10^{-14}	14.00
1.0×10^{-1}	1.00	1.0×10^{-13}	13.00
1.0×10^{-2}	2.00	1.0×10^{-12}	12.00
1.0×10^{-3}	3.00	1.0×10^{-11}	11.00
1.0×10^{-4}	4.00	1.0×10^{-10}	10.00
1.0×10^{-5}	5.00	1.0×10^{-9}	9.00
1.0×10^{-6}	6.00	1.0×10^{-8}	8.00
1.0×10^{-7}	7.00	1.0×10^{-7}	7.00
1.0×10^{-8}	8.00	1.0×10^{-6}	6.00
1.0×10^{-9}	9.00	1.0×10^{-5}	5.00
1.0×10^{-10}	10.00	1.0×10^{-4}	4.00
1.0×10^{-11}	11.00	1.0×10^{-3}	3.00
1.0×10^{-12}	12.00	1.0×10^{-2}	2.00
1.0×10^{-13}	13.00	1.0×10^{-1}	1.00
1.0×10^{-14}	14.00	1.0×10^{0}	0.00

$$\mathbf{H2O = H^{+} + OH^{-}}$$

$$\mathbf{Kw = [H^{+}][OH^{-}] = 1.0 \times 10^{-14}}$$

For pure water, $[H^+] = [OH^-] = 1x10^{-7}$, and the pH is equal to 7, since in any aqueous solution the product $[H^+][OH^-]$ must remain constant, an increase in $[H^+] > [OH^-]$ is said to be acidic, and a solution in which $[OH^-] > [H^+]$ is said to be alkaline. The relation between pH, $[H^+]$, and $[OH^-]$ is summarized in table above.

The pH of a fluid can be determined using either a special pH paper or a pH meter. The pH paper is impregnated with dyes that exhibit different colors when exposed to solutions of varying pH. The pH is determined by placing a short strip of the paper on the surface of the sample. After the color of the test paper stabilizes, the color of the upper side of the paper, which has not contacted the mud, is compared with a standard color chart provided with the test paper. When saltwater muds are used, caution should be exercised when using pH paper. The solutions present may cause the paper to produce erroneous values.

The pH meter is an instrument that determines the pH of an aqueous solution by measuring the electro potential generated between a special glass electrode and a reference electrode. The electromotive force (EMF) generated across the specially formulated glass membrane has been found empirically to be almost linear with the pH of the solution. The pH meter must be calibrated using buffered solutions off known pH.

An electrical stability (ES)

It is a test for oil-base and synthetic-base muds that indicates the emulsion and oil-wetting qualities (stability) of the sample. The electric stability is read as an voltage reading from 0 to 2000 volts, which indicates the easiness of electric current to pass the mixture of liquid which results in the higher value will indicate that the emulsion is stable or more compacted, on the contrary if the voltage level is low, it indicates the emulsion stability is weak or not stable. The API standard for good emulsion of synthetic based mud (SBM) or oil based mud (OBM) is above 400 volts of ES value. Below this value, it is said that the emulsion is not good and the mud is not recommended to be used in drilling circulation system in drilling operations (Drilling Fluid Functions 2012).

2.7 Alternatives Base Fluid

There are some studies according to alternative fluid base mud which have some properties close to oil based mud but more environmental friendly.

Oil based mud developed using Palm oil and groundnut oil should be encouraged since its highly biodegradable, have better eco-toxicological properties and the cost of treatment of the cuttings are lower compared to Oil-based drilling mud formulated with diesel, mineral and conventional synthetic oil (Dosunmu and Joshua.O 2010).

There is a possibility of replacing oil-based mud with water-based glycol drilling mud which is environmental friendly and totally nontoxic. There are also done shale inhibition test, water-based glycol mud gives inhibition performance close to OBM. As well as rheology test which shows glycol mud can perform rheological properties close to OBM. Glycol mud also has a better quality under HTHP compared to water-base mud (Samaei and Tahmasbi 2007).

There is some issue concerned about existed palm oil based drilling fluid which is also used for human consumption. There will be not enough palm oil to supply the drilling operations and the price will become more expensive due to the competition which is not meet the objective of developing new oil based mud which means to reduce the cost.

2.7.1 Castor Oil

The castor oil plant, Ricinuscommunis, is a species of flowering plant in the spurge family, Euphorbiaceae. It belongs to a monotypic genus, Ricinus, and subtribe, Ricininae. Ricinoleic acid, a monounsaturated, 18-carbon fatty acid, is unusual in that it has a hydroxyl functional group on the 12th carbon. This functional group causes ricinoleic acid (and castor oil) to be unusually polar, and also allows chemical derivatization that is not practical with most other seed oils. It is the hydroxyl group which makes castor oil and ricinoleic acid valuable as chemical feedstocks.

Castor seed is the source of castor oil, which has a wide variety of uses. The seeds contain between 40% and 60% oil that is rich in triglycerides, mainly ricinolein (90 percent of fatty acid chains). The seed contains ricin, a toxin, which is also present in lower concentrations throughout the plant (Castor oil plant, Wikipedia 2012; Castor oil, Wikipedia 2012).

Castor oils unsaturated bond, high molecular weight (298), low melting point (5ºC) and very low solidification point (-12ºC to -18ºC) make it industrially useful, most of all for the highest and most stable viscosity of any vegetable oil. Moreover castor oil is currently less expensive vegetable oils. (Castor Oil as Biodiesel & Biofuel 2012).

Castor oil has better high temperature lubrication than most vegetable oils. Castor oil is the preferred lubricant for bicycle pumps, most likely because it does not dissolve natural rubber seals. Biodegradability results in decreased persistence in the environment in case of an accidental release. From these properties, the lubricants company Castrol took its name from castor oil. (Castor oil, Wikipedia 2012).

Figure 5: Seed and oil of castor

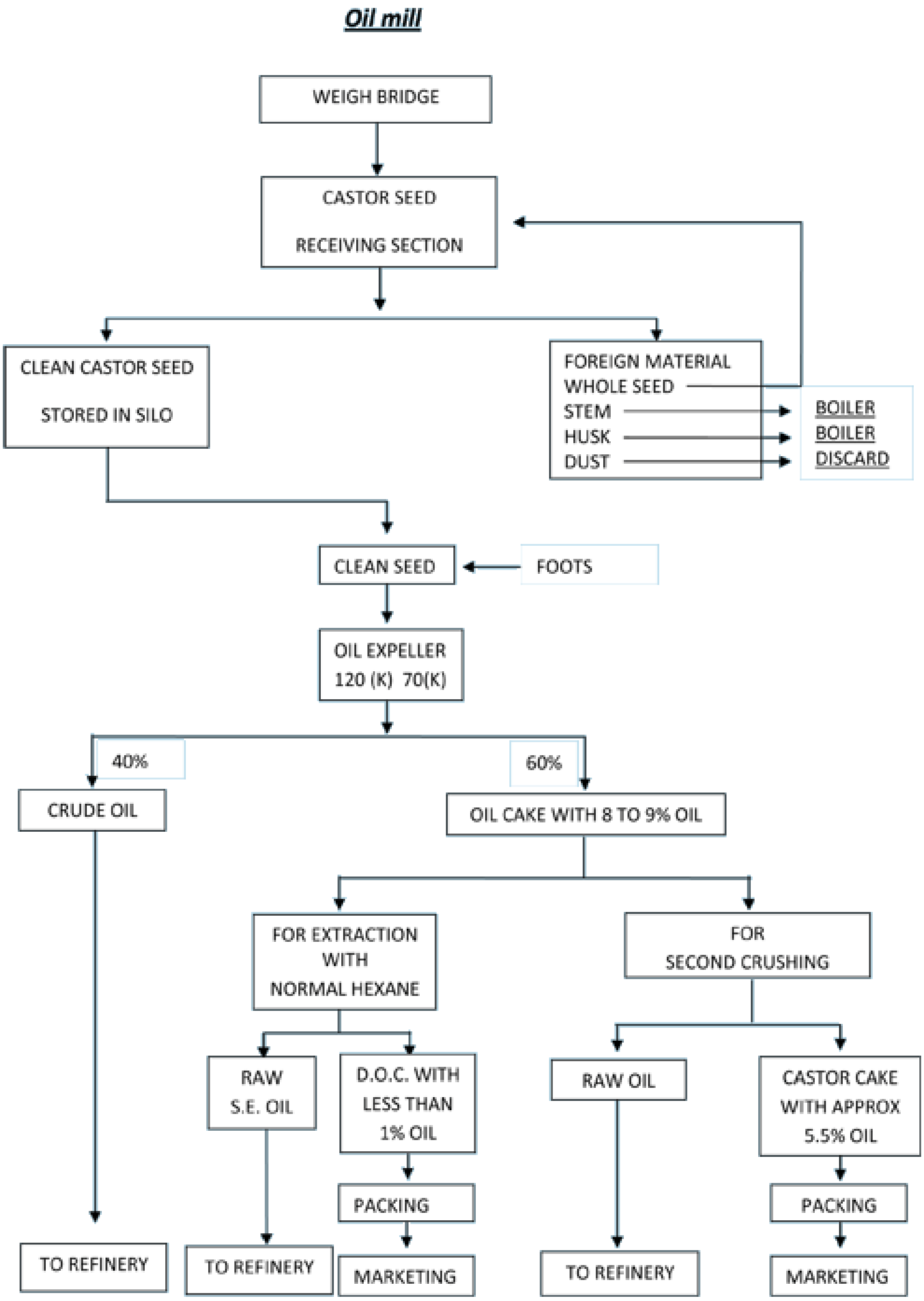


Figure 6: Extraction process of raw oil from castor seeds

Figure 6 shows the extraction process of oil from castor seeds. Initially, each seed will go through a separation process to discard all unknown and unwanted materials leaving out only clean seeds. It will then go through an Oil Expeller which is some kind of heating crusher to heat out crude oil from the seeds. Crude oils will be sent to the refinery while the remains of the extraction or cake will go through a second stage of processing due to high content of oil in the cake. Depending on the end product of cake desired, the second stage will be either extraction with hexane, a chemical used to extract oil for food processing, or crushing. Each process produces raw oil which will be sent to the refinery while the different type of cakes produced will be packed and sent for marketing.

Table 3: Castor oil production 2010 data (Tones) from FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS (2012) :

Country	**Production (Tones)**
India	1150000
China	180000
Brazil	93025
Thailand	12197
Vietnam	6000
South Africa	5500
Philippines	77
Brunei	-
Burma	-
Cambodia	1600
East Timor	-
Indonesia	1900
Laos	-
Malaysia	-
Singapore	-

From this table we can conclude that India is the biggest supplier of castor oil. Thailand produces the most castor oil per year (2010) among Southeast Asia countries.

2.7.2 Cow Fat

Animal fats and oils are lipid materials derived from animals. Physically, oils are liquid at room temperature, and fats are solid. Chemically, both fats and oils are composed of triglycerides (Animal fat 2012). Flesh and animal fat have a melting temperature of 184 °C, a boiling point of around 200 °C and an ignition point of 280 °C where it will burst into flames without spark (Mattogno 2012).

Tallow is a rendered form of beef or mutton fat, processed from suet. It is solid at room temperature. Unlike suet, tallow can be stored for extended periods without the need for refrigeration to prevent decomposition, provided it is kept in an airtight container to prevent oxidation (Tallow 2012).

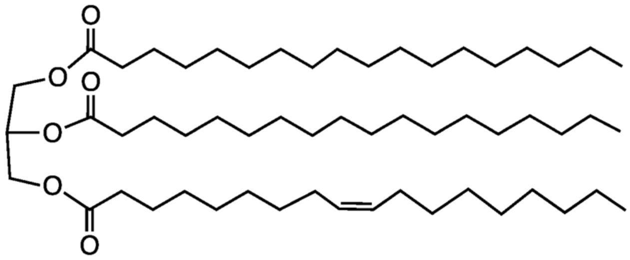


Figure 7: Tallow consists mainly of triglycerides (fat)

from TriglycerideTallow.png 2012)

Processed of animal fats

Oil is made by removing waste fat from animal carcasses using a rendering process. Rendering is a process that converts waste animal tissue into stable, value-added materials. Rendering consists of grinding the animal by-products to a fine consistency and cooking them until the liquid fat separates and pathogens are destroyed. This cooking process also removes water, which makes the fat and solid material stable against rancidity. The end products are fat, and a high-protein feed additive known as “meat and bone meal” (Gerpen 2012)

Property which may useful for based fluid: Lubrication

During developing of steam-driven piston engines, the hot vapors and liquids washed away most lubricants very quickly. It was found that tallow was quite resistant to this washing. Tallow and compounds including tallow were widely used to lubricate locomotive and steamship engines at least until the 1950s (Tallow 2012). As well as drilling fluids which are provide lubrication for drill bit and drill string while doing operation.

2.7.3 Jatropha

Jatrophacurcus (Linnaeus) is a multipurpose bush/small tree belonging to the family of Euphorbiaceae. The name Jatrophacurcus is derived from a Greek word “Jatros” meaning “Doctor” “and trophe” meaning ‘nutrition’ because of the potential of this plant for medicinal purposes (Patil and Singh 1991) It is believed to be a native of South America; but today it is found in almost all the tropical and sub-tropics in Africa/Asia. InIndia, Jatrophacurcus known as ratanjyote or seemaikattamanakku is found almost in all the states and is generally grown as a live fence for protection of agricultural fields from damage by livestock as it is not eaten by cattle because it is non-edible and also poisonous.(Jatropha oil 2012; Jatropha Oil 2012).

Jatropha oil cannot be used for nutritional purposes without detoxification; hence its use as energy or fuel source is attractive. In one hectare can yield up to 3500 litters of Jatropha extracted oil. (Anand et al. 2011).

Propose of extracting oil from the seeds is to prepare high quality bio-fuel an alternative source that can be used in diesel car which its properties similar to diesel fuel. It is a oxygenated fuel and is also a eco-friendly. While the remaining part after extracting oil is also can be used as a biomass feedstock to produce electricity and used as a fertilizer. (Jatropha Oil 2012).

Fadairo,Tozunku and Kadiri (2012) discussed about advantages and disadvantages of Jatropha oil as a based drilling fluid as following;

Advantages

- Environmental friendly. Considered as a one of renewable energy where it is part of vegetable oil.
- Can yield out to 3500 liters/hectare or 925 gallons/hectare. This shows that the continuity of Jatropa oil production. Refer to table in paper 11140 for reference table comparing it to other plants.
- Easy to be planted anywhere and most of the condition.
- Has better PH and density variation with temperature compared to diesel-oil.

Disadvantages

- The apparent viscosity of the Jatropha oil is higher under ambient temperature compared to the diesel oil based mud, caused by the highly viscous property of the oil.
- Salinity and temperature have bad effects on the rheological properties of the Jatropha oil.
- Needs other additives to make the oil’s properties balance and suitable for drilling. This will increase the cost of the project.

2.8 Selected Vegetable Oil

The selected base fluid in this research study is castor oil. Castor seeds are the source of castor oil. The seeds contain between 40% and 60% oil that is rich in triglycerides, mainly ricinolein (90 percent of fatty acid chains). The castor oil plant, Ricinuscommunis, is a species of flowering plant in the spurge family, Euphorbiaceae. It belongs to a monotypic genus, Ricinus, and subtribe, Ricininae. Ricinoleic acid, a monounsaturated, 18-carbon fatty acid, is unusual in that it has a hydroxyl functional group on the 12th carbon (Castor oil plant, Wikipedia 2012; Castor oil, Wikipedia 2012). Castor oils unsaturated bond, high molecular weight (298), low melting point (5ºC) and very low solidification point (-12ºC to -18ºC) make it industrially useful, most of all for the highest and most stable viscosity of any vegetable oil. Moreover castor oil is currently less expensive vegetable oils (Castor Oil as Biodiesel & Biofuel 2012). From FOOD AND AGRICULTURE

ORGANIZATION OF THE UNITED NATIONS (2012), India is the castor oil biggest supplier in Asian countries which can produce 1,150,000 tons per year in 2010 following by China, Brazil and Thailand.

Some important properties of castor oil are shown as tables below,

Table 4: Kinematic viscosity of castor oil

	Temperature		Kinematic Viscosity	
Castor oil	(^{o}F)	(^{o}C)	CentiStokes (cSt)	Seconds Saybolt Universal (SSU)
	100	37.8	259-325	1200-1500
	130	54.4	98-130	450-600
	Absolute Viscosity (at a temperature of *300 K*)			
	(N s/m^2, Pa s)		(cp)	
	0.650		650	

Table 5: Fatty acid composition of castor oil

Fatty acid	Composition (%)
ricinoleic acid	87
linoleic acid	5
oleic acid	4
palmitic acid	2
estearic acid	1
linoleic acid	1

Table 6 :castor oil properties

Properties	Value
free fatty acid (%)	0.63
flash point (°C)	230
smoke point (°C)	200
viscosity at 40 °C (mm 2/s)	227
water content (ppm)	367
iodine value (g I2/100 g sample)	85.5
auto-ignition temperature (°C /°F)	449/840.2
boiling point (°C)	313
pour point (^{o}C)	-24
melting point (^{o}C)	-18
dispersion properties	see solubility in water, methanol, diethyl ether
solubility	soluble in methanol, diethyl ether, chloroform, glacial acetic acid, benzene, carbon disulfide insoluble in cold water

Standards for industrial quality castor oil as specified by the ASTM are given in table 7 :

Table 7: industrial castor oil standards property

acid value,max	2
clarity	clear
Gardner color,max	2
hydroxyl value	160-168
loss on heating ,wt % max	0.2
refractive index ,25 C	1.4764-1.4778
saponification value	176-184
solubility in alcohol	complete
specific gravity 25/25C	0.957-0.961
unsaponifiablematter,wt % max	0.7
viscosity,mm^s	6.5-8.0
iodine value	84-88

2.9 Viscosity Dilution

Castor oil is vegetable oil which is readily biodegradable and non-toxic toward environment and user provided high flash point at 446degF (230 degC) which greater than the requirement makes castor oil seems suitable to be one of the alternative base fluids. However, viscosity of raw castor oil is still too high to use as a base for drilling fluid, further studies have been done to reduce viscosity of castor oil.

2.9.1 Toluene

Toluene has low kinematic viscosity which is 0.68 cSt at 20degC and it miscible with alcohol, it can be used as a diluter to reduce viscosity of base oil. In order to save time and cost, toluene is the suitable solvent for this study.

2.9.2 Transesterification

One of the chemical processes to reduce viscosity of castor oil is transesterification process. In organic chemistry, transesterification or alcoholysis has been widely used to reduce the high viscosity of triglycerides. The process is to exchange the organic group R″ of an ester with the organic group R′ of an alcohol. These reactions are often catalyzed by the addition of an acid or base catalyst (Burno et al. 2009).

The transesterification reaction can be expresses by the following equation:

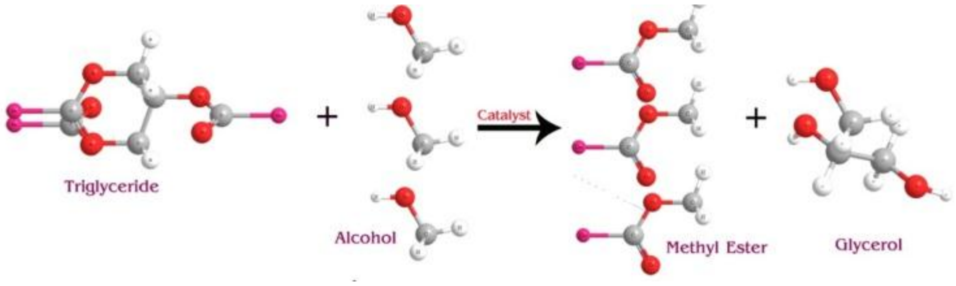


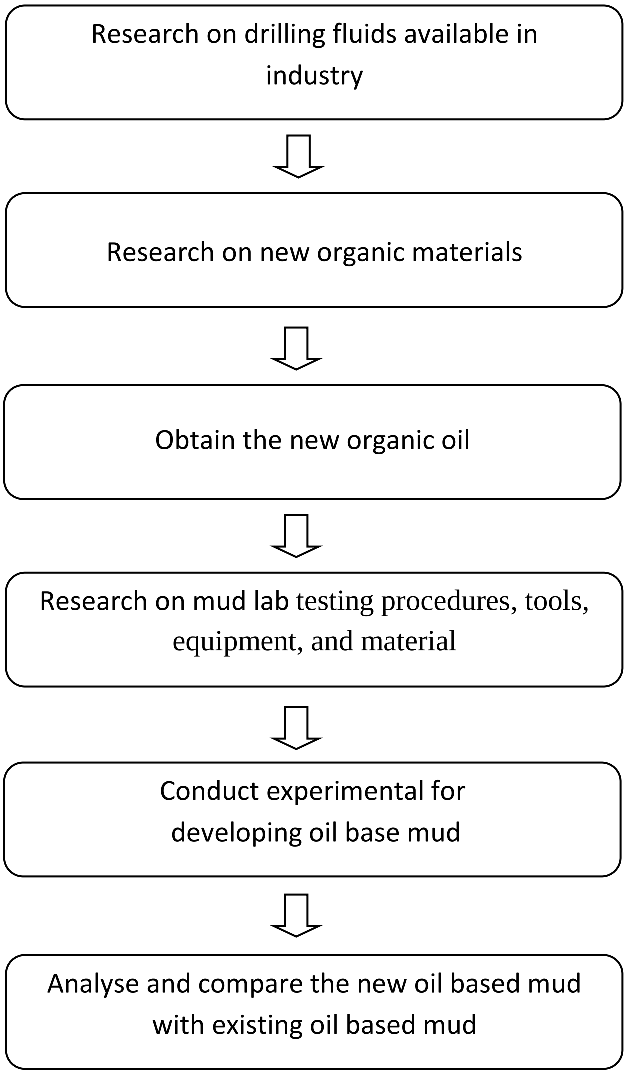
Figure 8: Overall reaction of triglyceride transesterification

from Transesterification (2012)

CHAPTER 3
METHODOLOGY

3.1 Research Methodology

The assessment of this research is to develop new oil base mud to achieve mud properties which required by industry:



3.2 Project Activities

Steps of project activities are as following:

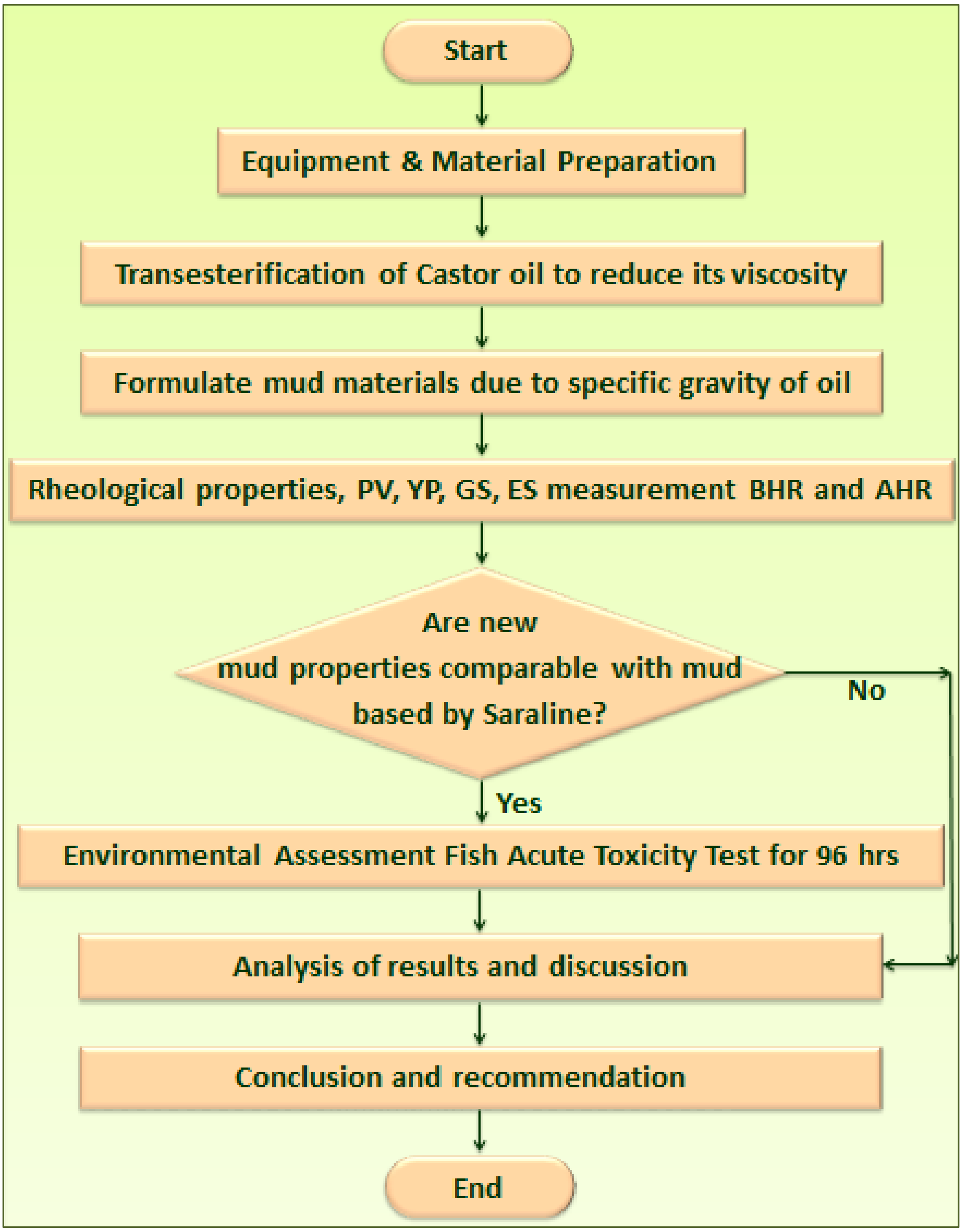


Figure 9: Project activities

3.3 Gantt Chart and Key Milestone

Gantt chart and Key Milestone for the project:

NO	Activities in FYP I / Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1	Selection of project topic	🟦	🟦					SEM BREAK								STUDY WEEK	EXAMINATION	
2	Preliminary research work (Literature review)		🟦	🟦	🟦	🟦												
3	Submission of proposal defense report						🟥											
4	Proposal defense (Oral Presentation)								🟦	🟦								
5	Project work continues										🟦	🟦	🟦					
6	Submission of Interim draft report													🟥				
7	Submission of interim report														🟥			

NO	Activities in FYP II / Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1	Material preparation and lab booking	🟧	🟧					SEM BREAK								STUDY WEEK	EXAMINATION	
2	Pre-test analysis		🟧	🟧														
3	Project run				🟧	🟧	🟧											
4	Progress report submission								🟥									
5	Pre-test analysis									🟧	🟧	🟧						
6	Pre-EDX										🟧	🟧	🟧					
7	Draf report submission											🟧	🟧					
8	Dissertation submission (Softbound)													🟥				
9	Technical paper submission													🟧				
10	Oral presentation													🟧	🟧			
11	Dissertation submission (Hardbound)														🟥			

🟥 Key Milestone

Table 8: Final year project gantt chart and key milestone

3.4 Tools Required

Following tools are required in order to follow mud lab testing procedures and environmental impact:

Testing Equipment

Property	Equipment/Materials
Mud density	- Standard Mud Balance
Funnel Viscosity	- Thermometer - Stopwatch - Marsh funnel
Rheology (PV,YP,GS)	- Rheometer - Mud cup - Stopwatch - Thermometer
An electrical stability (ES)	- OFI testing equipment
Oil, water and solid content	- Retort
HPHT Filtration loss	- HPHT Filter press unit
Mud property after hot rolling	- Hot rolling test unit
Environment Assessments	- Aquarium - Fish - Mud sample

3.5 Tranesterification and Mud Formulation

To start this research study in experimental process, equipment and material preparation must be done followed by trasesterification of castor oil. The experiment in this research study follows the process of tranesterification done by Deshpande et al. (2012) in order to obtain methyl ester at 14.10 cSt of kinematic viscosity. Castor oil of measured 100ml was added to the batch reactor and heated to 30degC while stirring at 460rpm. Dissolved solution of methanol (oil to alcohol mole ratio is 1:9) and potassium hydroxide which is a catalyst (1wt. % catalyst concentration) added into batch reactor at constant temperature and stirring rate. The reaction time is 45 minute. After this process done, it requires one night for glycerol to settle down. At that time, methyl ester separated from glycerol. Tranesterification process of castor oil can be shown in the diagram below:

Figure 10: Overall transesterification reaction of castor oil

To formulate mud material by using Scomi's mud formulator, specific gravity of the methyl ester measured by hydrometer is required which is equal to 0.925 at 25degC. Specific gravity of basic additives for synthetic based mud which are primary emulsifier, secondary emulsifier, viscosifier, fluid loss agent, lime, brine and barite added to formulator to calculate appropriate additives concentration in order to mix one lab barrel of mud, 350ml in the laboratory. The samples of mud were mixed by using Saraline (branch mark) and methyl ester of castor oil as base fluids by having mud weight which is 10ppg, oil-water ratio at 85to15, primary and secondary emulsifier concentration, fluid loss agent concentration and lime concentration as control parameters.

Each additive has its own functions. Primary emulsifier produces stable emulsions which are resistant to high temperatures and contamination, and imparts good fluid loss properties to the mud while secondary emulsifier offers emulsion stability as well as high temperature tolerance and resistance to contamination. It has secondary wetting agent capacities and helps maintain HTHP fluid loss in a water-free state. Viscosifier is used to increase the viscosity and gel strength in invert oil base or synthetic base mud. It provides suspension capability of weighting materials, increases hole-cleaning capacity and improves filter cakes quality. Fluid loss agent causes minimal viscosity increase, effective in controlling HTHP filtration in the invert oil/synthetic base systems over a wide range of temperatures and enhances emulsion stability in the same time. Lime is the common name for calcium hydroxide, $Ca(OH)_2$ which is used as a source of calcium and alkalinity in water and oil-based drilling fluids. It is used to increase pH for improving hole cleaning and controlling corrosion. Brine helps to increase emulsified water phase salinity which provides inhibition of shales and reactive solid. Barites used as the primary weight material in both water based and non-aqueous fluids with the purpose of increasing mud density (Scomi, 2012).

Methyl ester of castor oil is more viscous compared to Saraline which its kinematic viscosity is equal to 2.6 cSt at 40 deg C. As toluene has low kinematic viscosity which is 0.68 cSt at 20degC and it miscible with alcohol, it is used as a diluter to reduce viscosity of methyl ester. Same control parameters as mentioned above, toluene was mixed with methyl ester in ratio of 20:80 and 40:60, toluene to methyl eater. Specific gravity of each solution was measured to calculate additives concentration.

Mud materials were mixed using FANN multi mixer for 60 minute for a sample.

Steps of mud mixing are shown in table below;

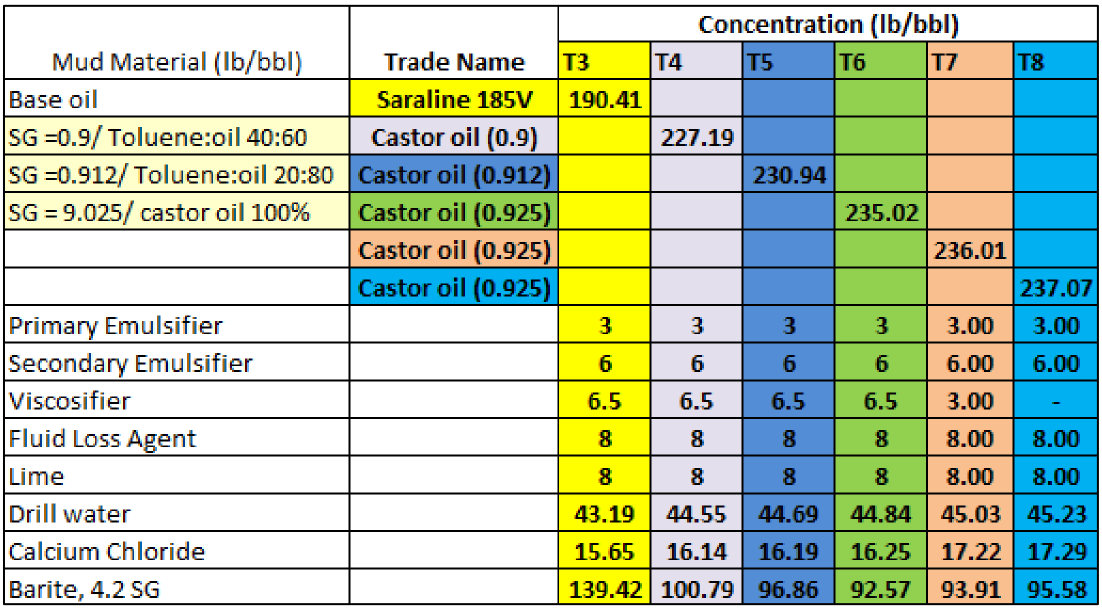
Table 9: Order and duration of mixing mud

Mud Material	1 lab bbl = 350ml at constant high speed	
	Order	Time (minutes)
Base oil	1	start
Primary Emulsifier	2	2
Secondary Emulsifier	3	2
Viscosifier	4	5
Fluid Loss Agent	5	2
Lime	6	2
Drill water	7	15
Calcium Chloride		

Barite, 4.2 SG	8	5
	Additional time	27
	Total time	60

The concentration of each mud material is now formulated. Each of samples will be tested for rheological and electric stability properties in order to identify whether the mud is suitable to use as a good drilling fluid or not. The samples formulation and additive concentration of this study are show in Table 10.

Table 10: Mud samples formulation for performance test
and comparison study



Mud Material (lb/bbl)	Trade Name	Concentration (lb/bbl)					
		T3	T4	T5	T6	T7	T8
Base oil	**Saraline 185V**	**190.41**					
SG =0.9/ Toluene:oil 40:60	**Castor oil (0.9)**		**227.19**				
SG =0.912/ Toluene:oil 20:80	**Castor oil (0.912)**			**230.94**			
SG = 9.025/ castor oil 100%	**Castor oil (0.925)**				**235.02**		
	Castor oil (0.925)					**236.01**	
	Castor oil (0.925)						**237.07**
Primary Emulsifier		**3**	**3**	**3**	**3**	**3.00**	**3.00**
Secondary Emulsifier		**6**	**6**	**6**	**6**	**6.00**	**6.00**
Viscosifier		**6.5**	**6.5**	**6.5**	**6.5**	**3.00**	**-**
Fluid Loss Agent		**8**	**8**	**8**	**8**	**8.00**	**8.00**
Lime		**8**	**8**	**8**	**8**	**8.00**	**8.00**
Drill water		**43.19**	**44.55**	**44.69**	**44.84**	**45.03**	**45.23**
Calcium Chloride		**15.65**	**16.14**	**16.19**	**16.25**	**17.22**	**17.29**
Barite, 4.2 SG		**139.42**	**100.79**	**96.86**	**92.57**	**93.91**	**95.58**

Mud samples:

- T3 Saraline base
- T4 Toluene40%-Castor oil60% base
- T5 Toluene20%-Castor oil80%
- T6 Castor oil with 6.5g viscosifier base
- T7 Castor oil with 3.0g viscosifier base
- T8 Castor oil with none viscosifier

CHAPTER 4

RESULT AND DISCUSSION

4.1 Experimentation

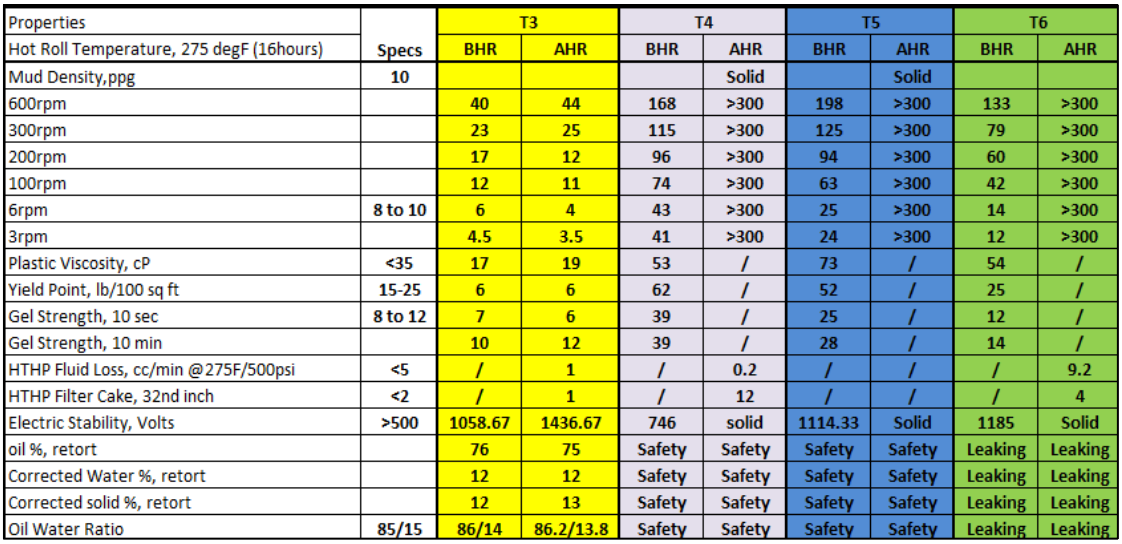
The mud samples: T3 Saraline base, T4 Toluene40%-Castor oil60% base, T5 Toluene20%-Castor oil80%, T6 Castor oil with 6.5g viscosifier base, T7 Castor oil with 3.0g viscosifier base and T8 Castor oil with none viscosifier base were tested for rheological, electric stability and HTHP filtration loss properties and measure oil, water, solid content by retort as a following procedures:

1. Rheology properties are determined by using Driven Fann 6 speed Viscometer. The six readings at speed of 3, 6, 100, 200, 300 and 600 rpm will be taken at 120degF. Plastic viscosity can be calculated by 600 reading - 300 reading (cps) and Yield point in Pounds / 100 ft2 = 300 reading - PV.
2. The gelling characteristics of the fluid will be determined by taking a 10 second and a 10 minute gel reading.
3. Electric stability (ES) measurement is measured out at 120degF, following rheology temperature in step 1 and step 2 by using ES digital meter in volts.
4. Fill the 50ml retort cup with mud sample in order to determine oil, water and solid content in the mud. Raise the temperature up to 950 degF, collect and measure condensed liquid, and calculate for solid portion.
5. Ageing or Hot-rolling is required to simulate reservoir environment to measure the stability of mud after 16hr operating at required condition.
6. Re-conduct step 1 to step 4 and continue at step 7.
7. Conduct HTHP filtration loss measurement for 30 minutes at 275degF and 500psi as a study condition. Fluid loss and filter cake thickness will be measured for further analysis.

4.2 Data Analysis

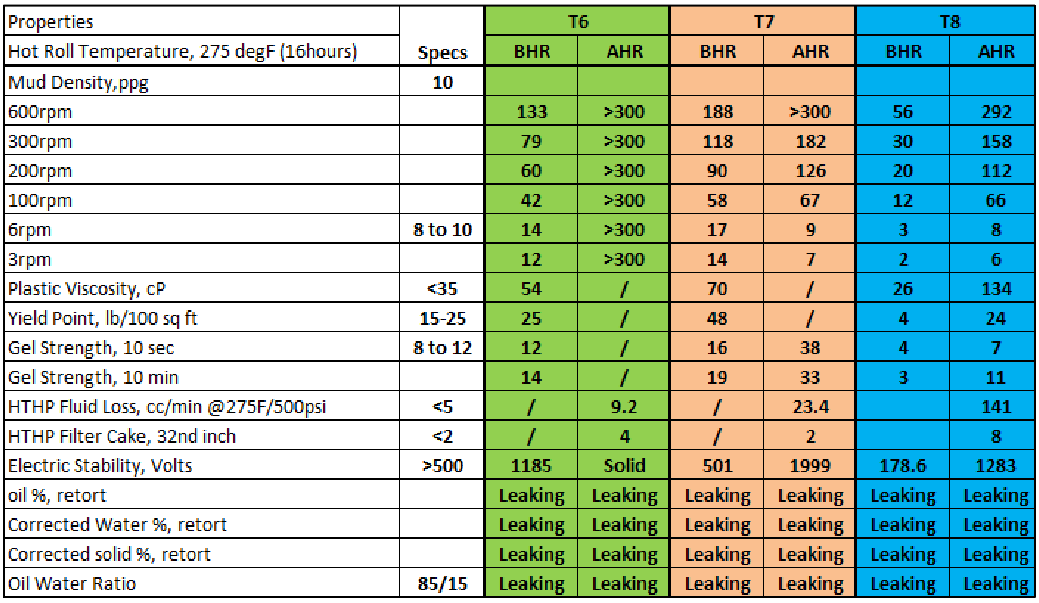
Mud properties of samples T3, T4, T5 and T6 are summarized in table 11 and mud properties of sample T6, T7, T8 are in table 12 ;

Table 11: Mud properties of samples T3, T4, T5 and T6



Properties		T3		T4		T5		T6	
Hot Roll Temperature, 275 degF (16hours)	Specs	BHR	AHR	BHR	AHR	BHR	AHR	BHR	AHR
Mud Density,ppg	10				Solid		Solid		
600rpm		40	44	168	>300	198	>300	133	>300
300rpm		23	25	115	>300	125	>300	79	>300
200rpm		17	12	96	>300	94	>300	60	>300
100rpm		12	11	74	>300	63	>300	42	>300
6rpm	8 to 10	6	4	43	>300	25	>300	14	>300
3rpm		4.5	3.5	41	>300	24	>300	12	>300
Plastic Viscosity, cP	<35	17	19	53	/	73	/	54	/
Yield Point, lb/100 sq ft	15-25	6	6	62	/	52	/	25	/
Gel Strength, 10 sec	8 to 12	7	6	39	/	25	/	12	/
Gel Strength, 10 min		10	12	39	/	28	/	14	/
HTHP Fluid Loss, cc/min @275F/500psi	<5	/	1	/	0.2	/	/	/	9.2
HTHP Filter Cake, 32nd inch	<2	/	1	/	12	/	/	/	4
Electric Stability, Volts	>500	1058.67	1436.67	746	solid	1114.33	Solid	1185	Solid
oil %, retort		76	75	Safety	Safety	Safety	Safety	Leaking	Leaking
Corrected Water %, retort		12	12	Safety	Safety	Safety	Safety	Leaking	Leaking
Corrected solid %, retort		12	13	Safety	Safety	Safety	Safety	Leaking	Leaking
Oil Water Ratio	85/15	86/14	86.2/13.8	Safety	Safety	Safety	Safety	Leaking	Leaking

Table 12: Mud properties of samples T6, T7 and T8



Properties		T6		T7		T8	
Hot Roll Temperature, 275 degF (16hours)	Specs	BHR	AHR	BHR	AHR	BHR	AHR
Mud Density,ppg	10						
600rpm		133	>300	188	>300	56	292
300rpm		79	>300	118	182	30	158
200rpm		60	>300	90	126	20	112
100rpm		42	>300	58	67	12	66
6rpm	8 to 10	14	>300	17	9	3	8
3rpm		12	>300	14	7	2	6
Plastic Viscosity, cP	<35	54	/	70	/	26	134
Yield Point, lb/100 sq ft	15-25	25	/	48	/	4	24
Gel Strength, 10 sec	8 to 12	12	/	16	38	4	7
Gel Strength, 10 min		14	/	19	33	3	11
HTHP Fluid Loss, cc/min @275F/500psi	<5	/	9.2	/	23.4		141
HTHP Filter Cake, 32nd inch	<2	/	4	/	2		8
Electric Stability, Volts	>500	1185	Solid	501	1999	178.6	1283
oil %, retort		Leaking	Leaking	Leaking	Leaking	Leaking	Leaking
Corrected Water %, retort		Leaking	Leaking	Leaking	Leaking	Leaking	Leaking
Corrected solid %, retort		Leaking	Leaking	Leaking	Leaking	Leaking	Leaking
Oil Water Ratio	85/15	Leaking	Leaking	Leaking	Leaking	Leaking	Leaking

To compare mud properties of methyl ester of castor oil based mud and saraline based mud, sample T3, T4, T5 and T6 were tested. The relationships of each mud properties and each sample before hot rolling (BHR) and after hot rolling (AHR) are shown in the following figures.

As mentioned by Rabia, Drilling Ahead groups and KMC Oiltools (2012), the main focus for mud rheology is 6 rpm reading because the initial gel strength will be more or less the same as the 6 rpm reading which Mud programs will specify a range for the 6 rpm reading. It is a good indicator of a colloidal solids build up that may not be detected by solids analysis.

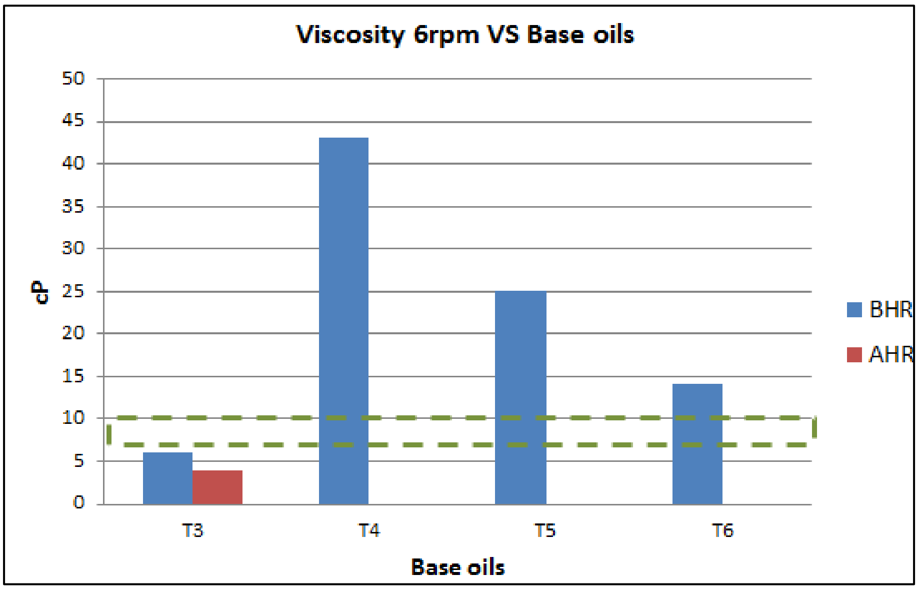


Figure 11: Viscosity reading at 6 rpm BHR and AHR of each base oils

Specific value of rheology reading at 6 rpm of this study is in the range of 8-10 cP which sample T3 seems to give the most satisfy value BHR and give too low value AHR. Sample T4, T5 and T6 give exceeded values from specific range BHR and give no value AHR because all sample could not be tested as all turned to solid phase. The most preferable sample is T3 which is Saraline based mud.

Plastic Viscosity (PV) is also known as resistance of fluid to flow. Any increase in solid content in drilling mud results in higher the plastic viscosity. One of the methods to reduced PV is diluting drilling mud with base fluid. In this study, toluene is added in sample in order to reduce samples' viscosity. In oil base mud, the emulsified water in oil base drilling fluid will act like a solid, and it will increase the plastic viscosity drastically so the high oil-water ratio at 85:15 is set to gain a lower viscosity value.

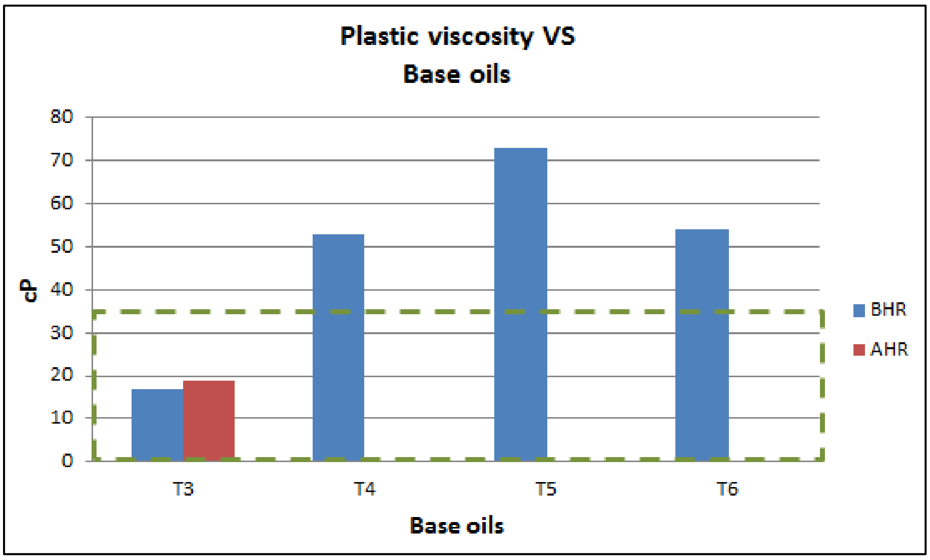


Figure 12: Plastic viscosity BHR and AHR of each base oils

Specific range value of PV in this study is lower than 35 cP. Sample T4, T5 and T6 give higher values BHR compare to specific range. Values of PV after hot rolling were not be able to obtained due to the muds turns to solid. Sample T3 is still the most suitable based mud which gives both PV values BHR and AHR in the specific range.

Yield Point (YP) is used to evaluate the ability of a mud to lift cuttings out of the annulus measured in unit of lbf/100ft2. YP is also a measurement of chemical bond which characterized as resistance of initial flow of fluid or the stress required in order to move the fluid so that it should be just high enough to suspend the cuttings as they are circulated up the annulus. Too high YP cause a pressure loss problem.

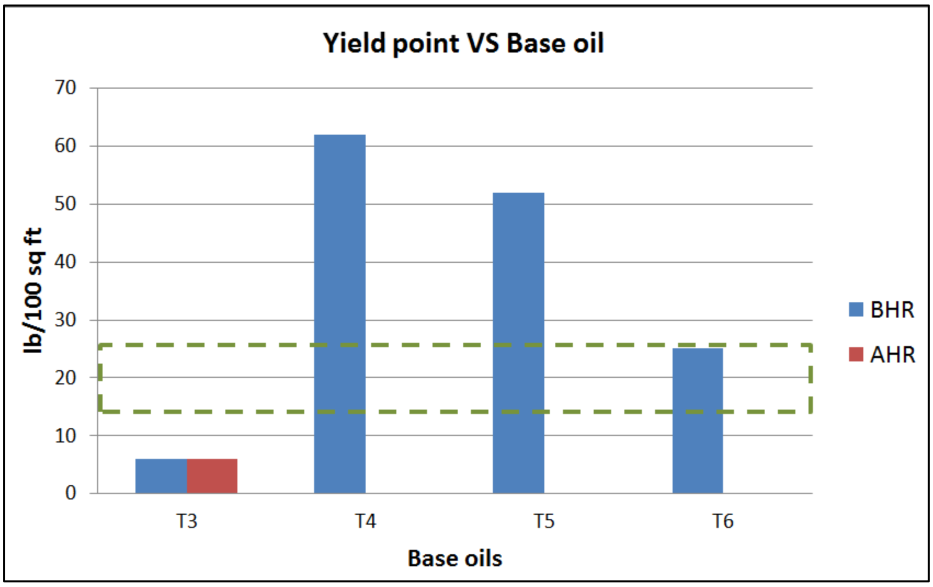


Figure 13: Yield point BHR and AHR of each base oils

Specific range of YP here is between 15-25 lb/100sqft. Sample T6 BHR give the satisfy value which is better than sample T3 which have very low YP. It is means that methyl ester of castor oil based mud in this study has a better YP property at lab condition compare to saraline base mud. But it is still not good enough to conclude that methyl ester of castor oil based mud is a suitable drilling fluid because the mud turn to be solid at reservoir condition.

There are two readings for gel strengths (GS), 10 second and 10 minute with the speed of the viscometer set at 3 rpm. Ideally the two values of gel strength should be close rather than progressively far apart. Measurement of GS is to measure attractive forces of chemical bond under static condition. The reason of the 10 minute reading will indicate whether the mud will greatly form the gel during an extensive static period or not. If the mud has the high gel strength, it will create high pump pressure in order to break circulation after the mud is static for long time.

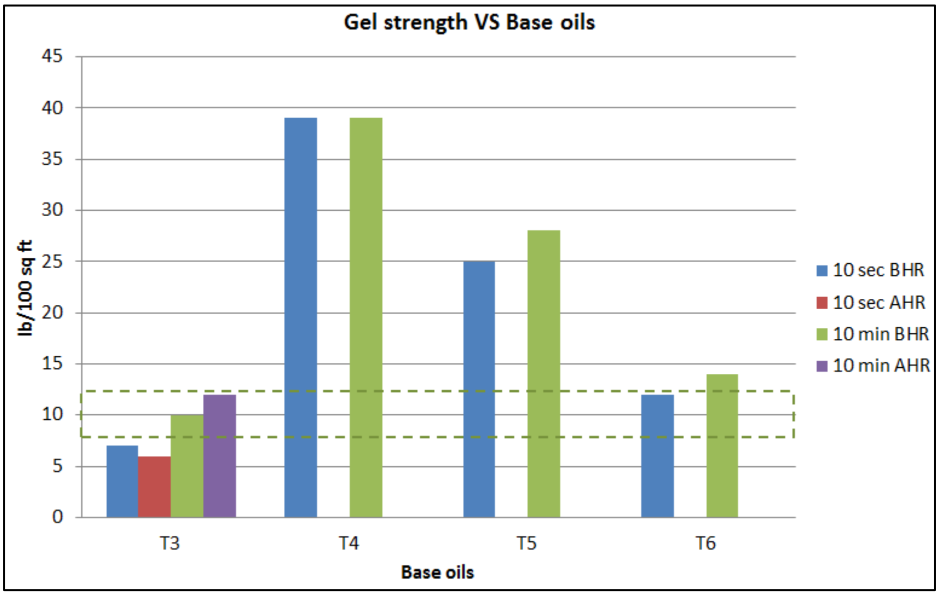


Figure 14: Gel strength BHR and AHR of each base oils at 10 sec and 10 min

Specific range of GS BHR is between 8-12 lb/100sqft which the value AHR also should be in this range. The sample T6 BHR still gives a better value compare to sample T3 which have lower GS. But overall comparison, T3 seems to be more satisfied as it did not turn to solid AHR and value of GS at 10sec and 10min not give much different which are also in the specific range at reservoir condition.

Electrical Stability (ES) test is a test for oil based and synthetic based muds that indicate the emulsion and oil wetting qualities (stability) of the sample. The electric stability is read as a voltage reading which indicates the easiness of electric current to pass the mixture of liquid which results in the higher value will indicate that the emulsion is stable or more compacted. . The API standard for good emulsion of synthetic based mud is above 400 volts of ES.

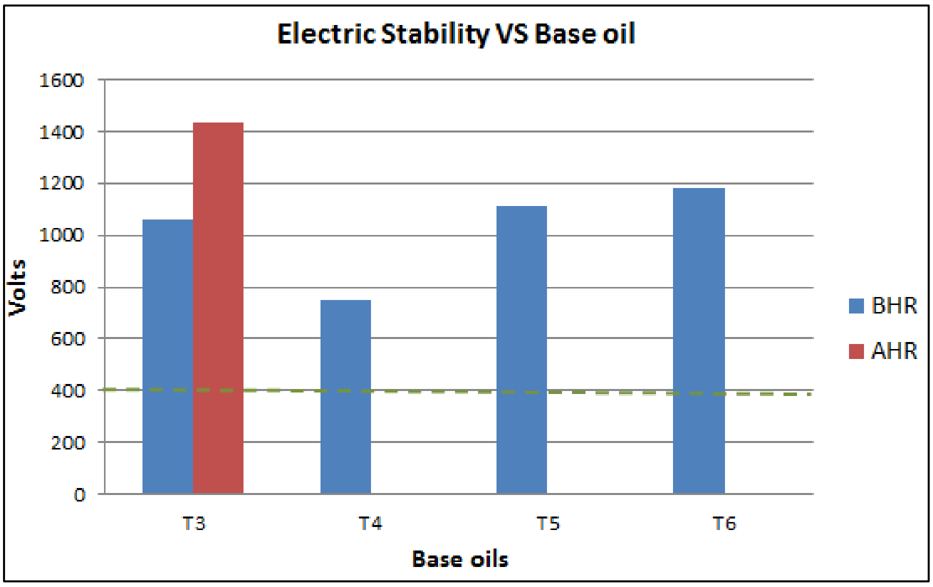


Figure 15: Electric stability (ES) BHR and AHR of each base oils

Specific value of ES must be above 400 volts following API standard. All samples provide a good ES at lab condition. Sample T3 give good readings both BHR and AHR condition which AHR values of T4, T5 and T6 could not be obtained as they are in solid phase.

Fluid Loss and Filter Cake are also measure after reservoir condition. Fluid loss is defined as the amount of water expelled from the drilling mud under particular pressure and temperature after 30 min. Filter cake is measured in 1/32” at bottom hole temperature 275degF in this study condition. The fluid loss gives a representation of the fluids interaction with the well bore under simulated pressure and temperature conditions. Ideally the fluid should form a thin and impermeable layer of filter cake against the wall and prevent fluid filtrate from entering the rock and reacting with the formations. A mud system with a low value of filtrate loss is more preferred which cause minimum swelling of clays and minimum formation damage.

As shown in table 4, High Temperature High Pressure (HTHP) filtration loss property of sample T3 is the most reasonable. Its fluid loss is lesser than 5cc and filter cake thickness is lesser than 2/32”. Sample T4 show the lowest fluid loss value which is 0.2cc but the cake thickness is too high. Both fluid loss and cake thickness of sample T6 are too high which is not suitable to use and drilling fluid under HTHP condition.

Retort study also done in order to measure water, oil and solid content and to calculate oil-water ratio at 950degF condition. As a concern for safety issue, sample T4 and T5 should not conduct retort study as they contain toluene which has low flash point (43degF). Sample T3 give a good retort reading which shows oil-water ratio BHR and AHR similar to set specific value which is 85 to 15. A lot of smoke and bad smell emerged from sample T6 which indicate that vapour is escaping through the threads connecting. In many cases, this situation happened because tube to condenser has been blocked and resulted in escaping of flaring from high pressure in the retort cup. This retort study of sample T6 could not give any accurate measurement.

From the above comparisons, saraline based mud give more preferred overall properties of drilling fluid compare to methyl ester of castor oil based mud. But methyl ester of castor oil based mud give a better properties compare to the samples which dilute with toluene. At lab condition, methyl ester of castor oil based mud shown the better YP and GS values compare to saraline based mud. From this information, further experiments will be conducted by reducing viscosifier. The objective of this further study is to study an effect of viscosifier toward methyl eater of castor oil based mud. Sample T7 which reduce viscosifier form 6.5 lb/bbl to 3 lb/bbl and sample T8 with no viscosifier were mixed to compare with sample T6. The following graph are to show the comparison and relationship of rheology reading at 6rpm, plastic viscosity, yield point, gel strength and electric stability BHR and AHR of sample T6, T7 and T8.

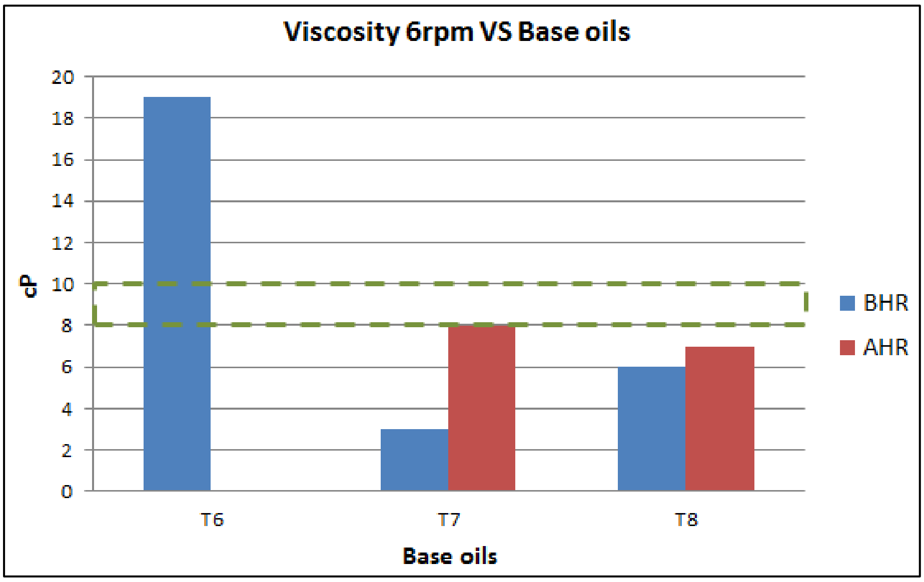


Figure 16: Viscosity reading at 6rpm BHR and AHR of each base oils

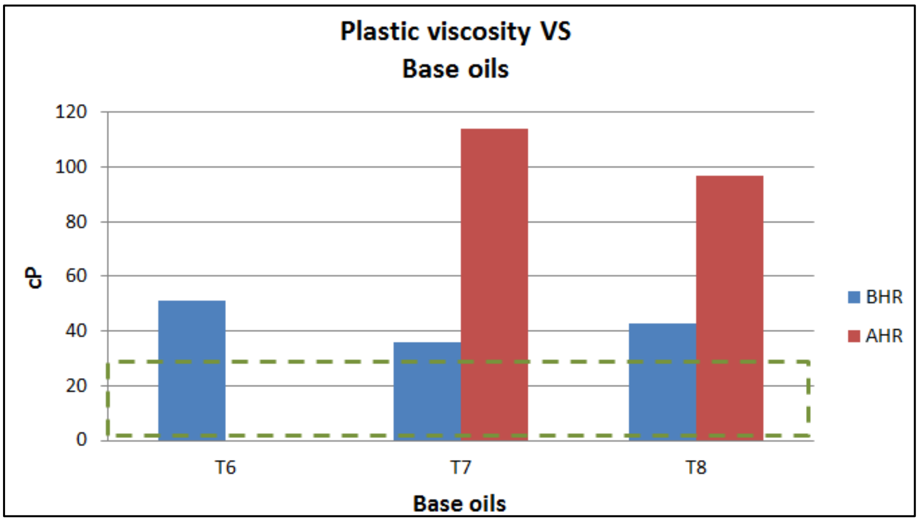


Figure 17: Plastic viscosity BHR and AHR of each base oils

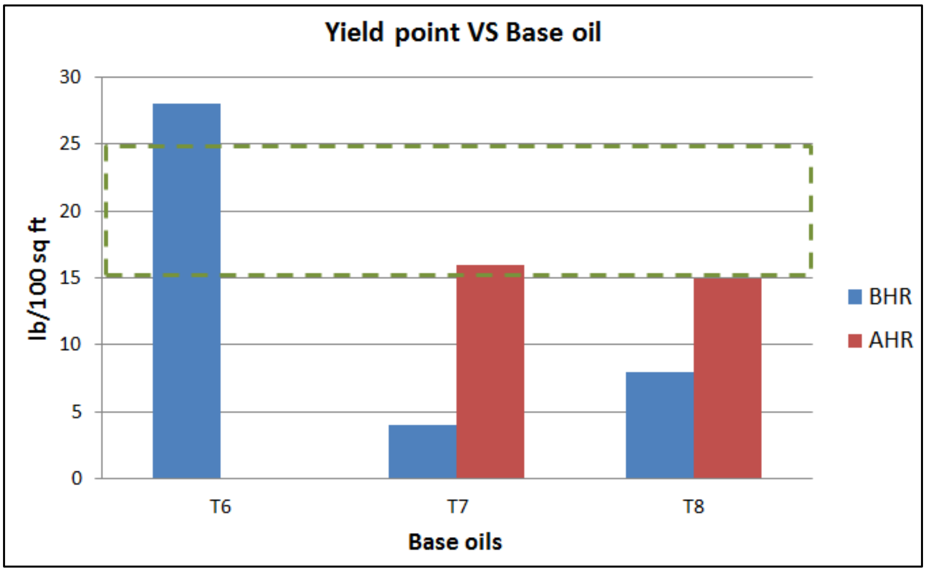


Figure 18: Yield point BHR and AHR of each base oils

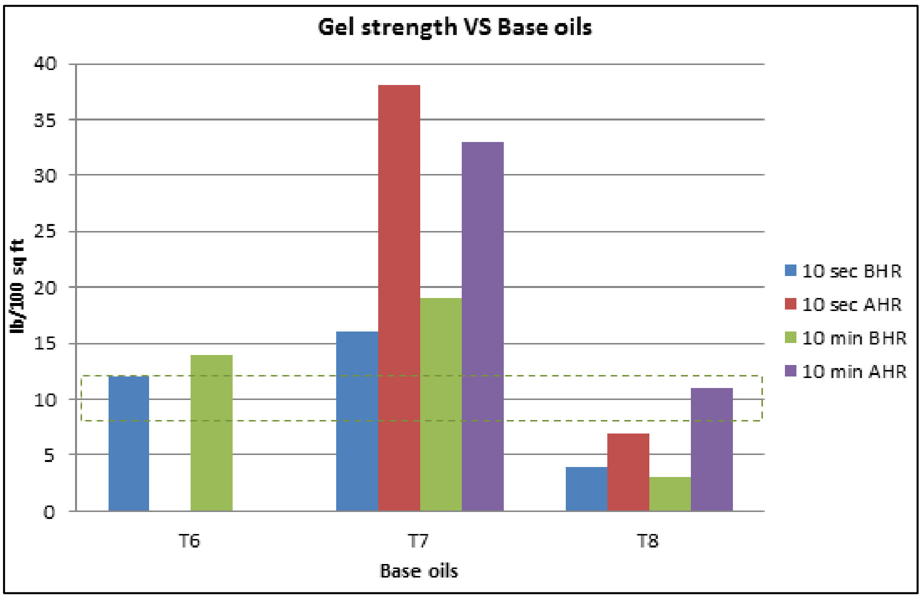


Figure 20: Gel strength BHR and AHR of each base oils at 10 sec and 10 min

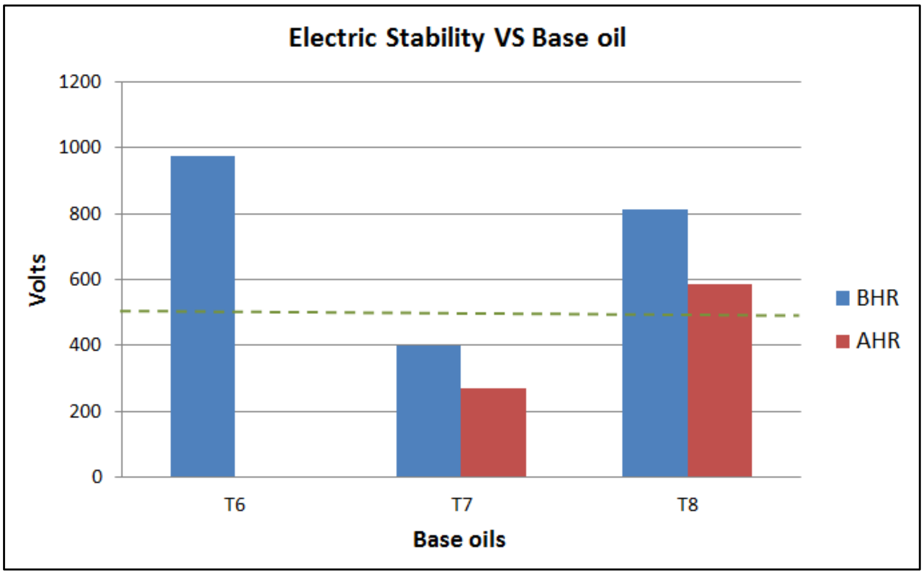


Figure 21: Electric stability (ES) BHR and AHR of each base oils

Viscosity of sample T7 AHR at 6rpm speed meet the specific value but the value BHR is too low. SampleT8 give too low value at both BHR and AHR condition while sample T6 give very high value BHR. PV of all samples give too high values compare to specific range which indicates too high solid content or too high viscosity of base fluid. YP values of samples were observed. Sample T7 and T8 shown satisfy values of YP AHR. In this case, it is still not good enough to say that sample T7 and T8 are good drilling fluid as YP value at BHR and AHR shown too much different. Same goes to GS value which BHR and AHR values show the big gap. The most preferred sample which shows the best gel property is sample T6 which can be measure only at BHR condition. ES properties of sample T7 is lower than specific value so it is not suitable to use as drilling fluid in this study condition while sample T8 shown satisfy value but still not stable as a big range different of BHR and AHR values were observed. HTHP fluid Loss and filter cake are also measure at reservoir condition. Sample T7 and T8 seems to lost this property as they give very high value of fluid loss and filter cake which are higher than value given by sample T6. Smoke can be observed from retort study of sample T7 and T8 both BHR and AHR condition.

4.3 Findings

1. Kinematic viscosity of castor oil is high.

Original → 259- 325 cSt (54.5 ^{o}C)

Methyl ester of castor oil → 14.10 cSt (37 ^{o}C)

2. Viscosity of castor oil become higher after aging (Hot Roll)

Evident:

1. Rheology: Rheology of methyl ester of castor oil based mud After Hot Rolling > Before Hot roling.
2. Retort: Observed based oil (methyl ester of castor oil) becoming thinker as grease and blocked off the spout after being heated at 950^{o}F.

Figure 22: Retort was leaking due to plugging of base fluid

3. Due to higher viscosity, it is not possible to add more solid (mud additives) to achieve mud specification.

All these concerns will not be observed, if the mud is built using current base oil available in the market (Ex. Saraline 185V).

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Relevancy to the Objectives

As the objective of this research study is to develop a stable and environmental friendly drilling fluid which has less harmful effect towards the environment and user, and cost saving at mud weight of 10ppg under 275degF and 500 psi high pressure high temperature condition comparing to saraline based fluid which is the conventional drilling mud.

Throughout the experiments and discussion, this research study can be concluded that Castor oil cannot be used as base oil under conventional formulation and condition compared to Saraline based mud at the same condition because even the viscosity of castor oil was reduced during transesterification process is still not low enough compared to saraline's viscocity.

From the conclusion above, environmental assessment fish acute toxicity test has not been done referring to the project activity in chapter 3.

5.2 Suggested Future Work for Expansion and Continuation

Further studies should be conducted before castor oil can be incorporated as the base oil in drilling fluid industry such as a study of effects of each additive towards castor oil's properties.

From this research study, fluid loss control additive should be increased since the fluid loss property decreases when viscosity was reduced.

The author recommends the use of organic additives to develop drilling fluid in order to be more environmental friendly and for the new mud to undergo environmental assessment before applying in the real field.

CHAPTER 6

REFERENCES

1. Anand A., ParameshM.H.N.,KrishnamurthyS.R.,and Mani S.R.1011. Compatibility of Metals in Jatropha Oil. Paper No. 11140. Government work published by NACE International.
2. Animal fat. Wikipedia, http://en.wikipedia.org/wiki/Animal_fat.Downloaded 6 August 2012.
3. Boehm, P.D., Turton D., Ravel A., Caudle D., French D., Rabalais N., Spies R., and Johnson J. 2001. Environmental Risks of Chemical Products Used in Gulf of Mexico Deepwater Oil and Gas Operations. Vol. 1.Technical Report. OCS Study MMS 2001-011. U.S. Dept. of the Interior, Minerals Management Service, Gulf of Mexico OCS Region, New Orleans, LA.
4. Burno B. Franca, Fabio M.Pinto ,Fernando Luiz P.Pessoa and Angela Maria C.Uller (2009),J.Chem Eng. Data, Liquid-Liquid Equilibria for Castor Oil Biodiesel + Glycerol + Alcohol ,pp 2354 -2369.
5. Castor oil. Wikipedia, http://en.wikipedia.org/wiki/Castor_oil. Downloaded 6 August 2012.
6. Castor oil plant.Wikipedia, http://en.wikipedia.org/wiki/Castor_oil_plant. Downloaded 6 August 2012.
7. Castor Oil as Biodiesel & Biofuel. Castor Oil.in, http://www.castor oil.in/uses/fuel/castor_oil_fuel.html. Downloaded 3 August 2012.
8. Chapter - 2 Drilling Fluids. Metu, http://www.metu.edu.tr/~kok/pete321 /PETE321_CHAPTER2.pdf. Downloaded 25 June 2012.
9. Daan,R., Muldar,M.& Van Leeuwen,A. 1994. Differential Sensitivity of Macrozoobenthic Species to Discharges of oil Contaminated Drill Cuttings in the North Sea. Netherlands Journal of Sea Research.33: 133-127.
10. Density, Vapor Pressure and Viscosity Data. Foodengineering, http://www.foodengineering.info/wp-content/uploads/2011/01/Density_data_ foodengineering.info_.pdf.Downloaded 3 August 2012.
11. Deshpande D.P[1], Haral S.S.[2], Gandhi S.S.[3] and Ganvir V.N.[4] . Received 21st

May 2012. Transeterification of Castor oil. ISCA Journal of Engineering Sciences. Vol. 1(1), 2-7, July (2012).

12. Dosunmu,A. and Joshua.O,O. “Development of Environmentally Friendly Oil Based Mud using Palm-Oil and Groundnut-Oil.2010” SPE paper 140720 presented at the 34th Annual SPE International Conference and Exhibition held in Tinapa – Calabar, Nigeria, 31 July- & August 2110.
13. Drilling Ahead groups. Drilling Ahead world oilfield network. http://www.drillingahead.com/groups .Downloaded 3 September 2012.
14. Drilling Fluids. http://www.google.com.my/url?sa=t&rct=j&q=&esrc=s&source=web&cd=2&ved=0CFYQFjAB&url=http%3A%2F%2Fmaterial.eng.usm.my%2Fstafhome%2Ftermizi%2FEBS418E%2520Petroleum%2520Eng%2F5_Drilling%2520Fluid.doc&ei=iSvzT5NNufZige5w4SkCQ&usg=AFQjCNF4zoqRw3RNRmV8JMKGFLbfUWgxvg&sig2=KuUFnWCUCeqCxuWWMTzkQ. Downloaded 22 June 2012.
15. Drilling Fluid, Amoco Production Company Drilling Fluid Manual (1994) pp.3-49
16. Drilling Fluid Functions. Scribd, http://www.scribd.com/doc/23326855/Drilling-Fluid-Functions.Chapter3.Downloaded 6 August 2012.
17. Dye,W.,K., d’ Augereau, N., Hansen, M., Otto, L., Shoulte,R., Leaper,D., Clapper and T. Xiang. “ New Water-based Mud balance high Performance Drilling and Environmental Compliance.2006”, paper SPE 92367 presented at the SPE/IADC Drilling Conference, Amsterdam, February 23-24,p.1.
18. Fadairo, A.S., Tozunku, K.S., Kadiri T.M. and Falode O.A. “Investigating the Effect of Electorlytes and Temperature on Rheological Properties of Gatropha oil based mud.2012”. paper SPE 163027 prepared for presentation at the 2012 SPE Nigerian Annual International Conference and Exhibition held in Abuja, Nigeria, 6-8 August 2012.
19. Fluids - Kinematic Viscosities. The Engineering ToolBox, http://www.engineeringtoolbox.com/kinematic-viscosity-d_397.html. Downloaded 2 August 2012.
20. FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS.FOASTAT,http://faostat.fao.org/site/567/DesktopDefault.aspx?PageID=567#ancor.Downloaded 6 August 2012.

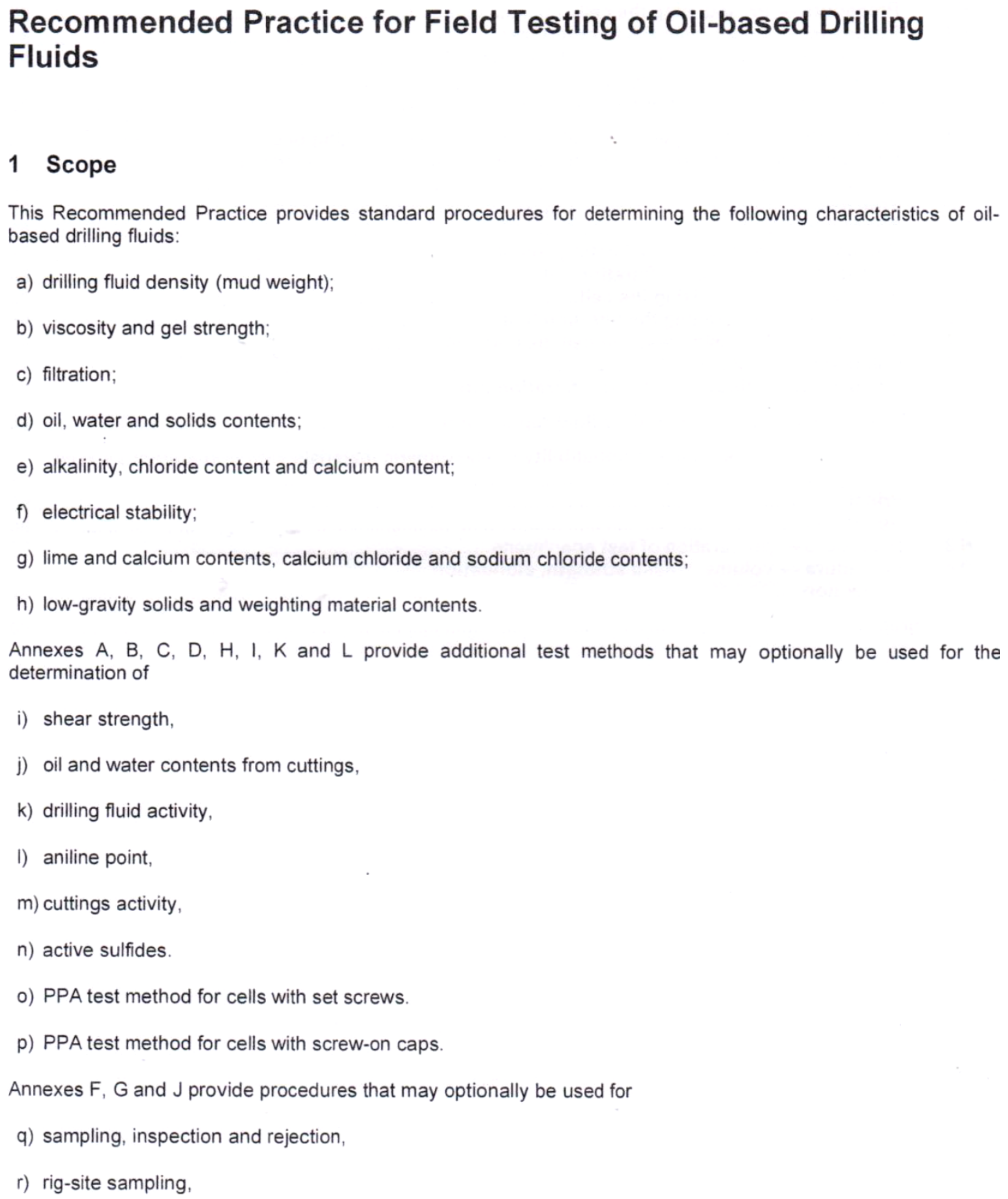
21. GEL STRENGTH. Drillingahead, http://www.drillingahead.com/profiles/blogs/gel-strength. Downloaded 3 August 2012.Gel Strength of Drilling Mud. civil-engg-world.blogspot, http://civil-engg-world.blogspot.com/2011/05/gel-strength-of-drilling-mud_08.html. Downloaded 3 August 2012.
22. Gerpen,J.V.Animal Fats for Biodiesel Production.Extension, http://www.extension.org/pages/30256/animal-fats-for-biodiesel-production.Downloaded 6 August 2012.
23. Ismail, A.R.,Ahmad,N.J. and Anam,M.N. Toxicity Study on Marine Organisms due to Drilling Fluid.eprints.utm,http://eprints.utm.my/4031/1/SKMBT_60007071715040.pdf. Downloaded 25 June 2012.
24. Jatropha Oil. Aumkiipure, http://www.aumkiipure.com/jatropha-oil.html.Downloaded 3 August 2012.
25. Jatropha oil. Wikipedia, http://en.wikipedia.org/wiki/Jatropha_oil.Downloaded 3 August 2012.
26. Johancsvik C.A and Grieve W.R. “Oil-based mud reduces borehole problems” Oil and Gas Journal, April 27, 1987 p.47.
27. Joseph and Bobby. Versaclean? How can an oil based mud be environmentally friendly? Is it?.YahooAnswer,http://uk.answers.yahoo.com/question/index?qid=20120129231139AAb6W5S. Downloaded 10 July 2012.
28. KMC Oiltools. mud testing procedures, section 3. Section 3b- naf testing procedures.Page 71-104.
29. Mattogno, C. Combustion Experiments with Flesh and Animal Fat. VHO, http://vho.org/tr/2004/1/Mattogno64-72.html.Downloaded 3 August 2012.
30. MCKENNA P.June 9, 2009 .ALL WASHED UP FOR JATROPHA? , The draught-resistant "dream" biofuel is also a waterhog.Technology review,http://www.technologyreview.com/news/413746/all-washed-up-for-jatropha/.Downloaded 6 August 2012.
31. Md, Amanullah. (2005): ―Physio-Chemical Characterisation of Vegetable Oils and Preliminary Test Results of Vegetable-Oil-Based Muds‖, paper SPE/IADC 97008 presented at SPE/IADC Middle East Drilling Technology Conference & Exhibition held in Dubai, U.E.A., September 12-14.pp1-9.

32. Munroe, P.D., Moffet, C.F., Couper, L., Brown, N.A. Croce, B. and Stagg,R.M. 1997. Degradation of Synthetic Mud Base Fluids in a Solid-Phase Test System. Fisheries Research Services Report No.1/97.
33. OIL-BASED MUDS & SYNTHETIC-BASED MUDS, Formulation, Engineering, Field habits and Recommendations. gilsonite-bitumen, http://www.gilsonitebitumen.com/Gilsonite_files/PDF/patent/oil%20based%20 muds.pdf. Downloaded 20 July 2012.
34. Patil.V and Singh.K. 1991. Oil Gloom to Oil Boom JatrophaCurcas: A Promising Agro-forestry Crop.India: Agro-Forestry Federation Maharashtra and Government of India, Ministry of Environment and Forests, National Wastelands Development Mission.
35. Rabia H. Well Engineering & Construction‖. Chapter 7: Drilling Fluids and Chapter 8: Practical Rig Hydraulics.
36. Rheology of Drilling Muds. rishibabuadari.tripod, http://rishibabuadari.tripod. com/MudRheology/Rheology.htm. Downloaded 6 August 2012.
37. RicinuscommunisL..Center for New Crops & Plant Products, at Purdue University,http://www.hort.purdue.edu/newcrop/duke_energy/ricinus_communis.html.Downloaded 3 August 2012.
38. Samaei, S.M.andTahmasbi,K. “ The Possibility of Replacing Oil Based Mud with the Environmentally Accepatable Water-Based Glycol Drilling Mud for the Iranian Fields.2007” SPE paper 106419 presented at the 2007 SPE E&P Environment and Safety Conference held in Galveston, Texas, U.S.A., 5-7 March 2007.
39. Scomi Group Bhd.Oilfield Services, Drilling Fluids. http://www. scomi.com.my/core/product_info.asp. Downloaded 11 October 2012.
40. Specific Gravity And Viscosity Of Liquids. CSG, Computer Support Group, Inc. and CSGNetwork.Com,http://www.csgnetwork.com/specific_gravity_ viscosity_ liquids.html.Downloaded 6 August 2012.
41. Tallow. Wikipedia, http://en.wikipedia.org/wiki/Tallow.Downloaded 3 August 2012.

42. The Department of Industry and Resources. Petroleum Guidelines , Drilling Fluids Management. Environment Division.Government of Western Australia, http://www.dmp.wa.gov.au/documents/ED_Pet_GL_DrillingFluidMgmt_Dec06.pdf.Downloaded 21 July 2012.
43. The Environmental Risks of Drilling and Transporting Oil: Are they Worth It?.Oil Industry, http://www.crudeoilbiz.com/oil-industry-environmental.shtml.Downloaded 12 July 2012.
44. Tranesterification. PSU, http://share.psu.ac.th/file/waraporn.ra/view/4640. Downloaded 11 October 2012.
45. TriglycerideTallow.png .Wikipedia,http://en.wikipedia.org/wiki/File:Triglyceride Tallow.png.Downloaded 3 August 2012.

APPENDIX

Appendix 1 – Recommended practice standard procedure for field testing oil-based drilling fluids(1998), American Petroleum Institute.



Recommended Practice for Field Testing of Oil-based Drilling Fluids

1 Scope

This Recommended Practice provides standard procedures for determining the following characteristics of oil-based drilling fluids:

a) drilling fluid density (mud weight);

b) viscosity and gel strength;

c) filtration;

d) oil, water and solids contents;

e) alkalinity, chloride content and calcium content;

f) electrical stability;

g) lime and calcium contents, calcium chloride and sodium chloride contents;

h) low-gravity solids and weighting material contents.

Annexes A, B, C, D, H, I, K and L provide additional test methods that may optionally be used for the determination of

i) shear strength,

j) oil and water contents from cuttings,

k) drilling fluid activity,

l) aniline point,

m) cuttings activity,

n) active sulfides.

o) PPA test method for cells with set screws.

p) PPA test method for cells with screw-on caps.

Annexes F, G and J provide procedures that may optionally be used for

q) sampling, inspection and rejection,

r) rig-site sampling,

s) calibration and verification of glassware, thermometers, viscometers, retort kit cups and drilling fluid balances.

Annex E provides examples of calculations for

t) lime, salinity and solids content.

Annex M contains an example of a drilling fluid report form.

2 Terms and definitions

For the purposes of this Standard, the following term and definition applies:

2.1
ACS reagent grade
grade of chemical meeting the purity standards specified by the American Chemical Society (ACS)

2.2
API
American Petroleum Institute, 1220 L Street NW, Washington, DC 20005

2.3
CAS
Chemical Abstracting Service

2.4
USC
United States Customary unit, shown in parentheses following SI unit

3 Abbreviations

ACS	American Chemical Society
BAD	Base alkalinity demand
EDTA	eithylenediaminetetraacetic acid
ES	electrical stability
HT/HP	high temperature, high pressure
OCMA	Oilfield Chemical Manufacturer's Association
PNP	propylene glycol normal-propyl ether
PTFE	polytetrafluoreoethylene, brand name Teflon®
TC	to contain
TD	to deliver
R_{300}	viscometer reading at 300 r/min
R_{600}	viscometer reading at 600 r/min
[illegible]	static filtration rate

m_1	mass of retort cup, lid and body with steel wool, g
m_2	mass of retort cup, lid, body and cuttings, g
m_3	mass of empty liquid receiver, g
m_4	mass of liquid receiver and fluid collected during solids analysis, g
m_5	mass of solids remaining in retort cup following solids analysis, g
R	static filtration rate
V	volume of liquid collected in receiver, ml
V_o	volume of oil, cm^3
V_s	volume of solids, cm^3
V_1	volume of filtrate after 7,5 min, cm^3
V_2	volume of filtrate after 30 min, cm^3
V_w	volume of water, cm^3
η_P	viscosity of plastic viscosity
η_Y	viscosity of yield point
η_A	appararent viscosity
φ_o	volume fraction of oil
φ_s	volume fraction of solids
φ_w	volume fraction of water
ρ	density
$\nabla\rho$	density gradient

4 Determination of drilling fluid density (mud weight)

4.1 Principle

A procedure is given for determining the mass of a given volume of liquid (= density). The density of drilling fluid is expressed as grams per cubic centimetre, kilograms per cubic metre, pounds per gallon or pounds per cubic foot.

4.2 Apparatus

a) Any **density-measuring instrument** having an accuracy of ± 0,01 g/cm^3, ± 10 kg/m^3, ± 0,1 lb/gal, or ± 0,5 lb/ft^3.

The mud balance is the instrument generally used for drilling fluid density determinations. The mud balance is designed such that the drilling fluid holding cup, at one end of the beam, is balanced by a fixed counterweight at the other end, with a sliding-weight rider free to move along a graduated scale. A level-bubble is mounted on the beam to allow for accurate balancing. Attachments for extending the range of the balance may be used when necessary.

The instrument should be calibrated frequently with fresh water. Fresh water should give a reading of 1,00 g/cm^3 or 1 000 kg/m^3 at 21 °C (70 °F). If it does not, adjust the balancing screw or the amount of lead shot in the well at the end of the graduated arm as required.

b) **Thermometer**, with a range of 0 °C to 105 °C (32 °F to 220 °F).

4.3 Procedure

4.3.1 The instrument base should be set on a flat, level surface.

4.3.2 Measure the temperature of the drilling fluid and record.

4.3.3 Fill the clean, dry cup with drilling fluid to be tested; put the cap on the filled drilling-fluid holding cup and rotate the cap until it is firmly seated. Ensure that some of the drilling fluid is expelled through the hole in the cap, in order to free any trapped air or gas.

4.3.4 Holding the cap firmly on the drilling-fluid holding cup (with cap hole covered), wash or wipe the outside of the cup clean and dry.

4.3.5 Place the beam on the base support and balance it by moving the rider along the graduated scale. Balance is achieved when the bubble is under the centreline.

4.3.6 Read the drilling fluid density at the edge of the rider toward the drilling-fluid cup. Make appropriate corrections when a range extender is used.

4.4 Calculation

4.4.1 Report the drilling fluid density, ρ_s, to the nearest 0,01 g/cm^3 , 10 kg/m^3, 0,1 lb/gal or 0,5 lb/ft^3.

4.4.2 To convert the reading to other units, use the following:

$$\rho_s = 1\,000 \times \text{g/cm}^3 \qquad (1)$$

$$\rho_s = 16 \times \text{lb/ft}^3 \qquad (2)$$

$$\rho_s = 119{,}8 \times \text{lb/US gal} \qquad (3)$$

where ρ_s is the density, expressed in kilograms per cubic metre.

$$\nabla\rho_s = 9{,}81 \times \text{g/cm}^3 \qquad (4)$$

$$\nabla\rho_s = 0{,}0226 \times \text{psi/1 000 ft} \qquad (5)$$

where $\nabla\rho_s$ is the drilling fluid density gradient, expressed in kilopascals per metre.

A list of density conversions from SI to USC units is given in Table 1.

Table 1 — Density conversions between SI and USC units

Grams per cubic centimetre[a] g/cm^3	Kilograms per cubic metre kg/m^3	Pounds per US gallon (lb/US gal)	Pounds per cubic foot (lb/ft^3)
0,70	700	5,8	43,6
0,80	800	6,7	49,8
0,90	900	7,5	56,1
1,00	1 000	8,345[b]	62,3
1,10	1 100	9,2	68,5
1,20	1 200	10,0	74,8
1,30	1 300	10,9	81,0
1,40	1 400	11,7	87,2
1,50	1 500	12,5	93,5
1,60	1 600	13,4	99,7
1,70	1 700	14,2	105,9
1,80	1 800	15,0	112,1
1,90	1 900	15,9	118,4
2,00	2 000	16,7	124,6
2,10	2 100	17,5	130,8
2,20	2 200	18,4	137,1
2,30	2 300	19,2	143,3
2,40	2 400	20,0	149,5
2,50	2 500	20,9	155,8
2,60	2 600	21,7	162,0
2,70	2 700	22,5	168,2
2,80	2 800	23,4	174,4
2,90	2 900	24,2	180,7

[a] Same value as relative density.

[b] Accurate conversion factor.

5 Alternative method for determination of drilling fluid density

5.1 Principle

5.1.1 The pressurized mud balance provides a more accurate method for determining the density of a drilling fluid containing entrained air or gas than does the conventional mud balance. The pressurized mud balance is similar in operation to the conventional mud balance, the difference being that the slurry sample is placed in a fixed-volume sample cup under pressure.

5.1.2 The purpose of placing the sample under pressure is to minimize the effect of entrained air or gas upon slurry density measurements. By pressurizing the sample cup, any entrained air or gas is decreased to a negligible volume, thus providing a slurry density measurement more closely in agreement with that obtained under downhole conditions.

5.2 Apparatus

a) Any **density-measuring instrument** having an accuracy of ± 0,01 g/cm^3, ± 10 kg/m^3, ± 0,1 lb/gal, or ± 0,5 lb/ft^3.

The pressurized mud balance is the instrument generally used for density determinations of pressurized drilling fluids. The pressurized mud balance is designed such that the drilling-fluid holding cup and screw-on lid, at one end of the beam, is balanced by a fixed counterweight at the other end, with a sliding-weight rider free to move along a graduated scale. A level-bubble is mounted on the beam to allow for accurate balancing.

Calibrate the instrument frequently with fresh water. Fresh water should give a reading of 1,0 g/cm^3 or 1 000 kg/m^3 at 21 °C (69,8 °F). If it does not, adjust the balancing screw or the amount of lead shot in the well at the end of the graduated arm as required.

b) **Thermometer**, with a range of 0 °C to 105 °C (32 °F to 220 °F).

5.3 Procedure

5.3.1 Measure the temperature of the drilling fluid and record.

5.3.2 Fill the sample cup to a level slightly (approximately 6 mm) below the upper edge of the cup.

5.3.3 Place the lid on the cup with the attached check-valve in the down (open) position. Push the lid downward into the mouth of the cup until surface contact is made between the outer skirt of the lid and the upper edge of the cup. Any excess slurry will be expelled through the check-valve. When the lid has been placed on the cup, pull the check-valve up into the closed position, rinse off the cup and threads with water, and screw the threaded cap on the cup.

5.3.4 The pressurizing plunger is similar in operation to a syringe. Fill the plunger by submersing its end in the slurry with the piston rod completely inside. Then draw the piston rod upward, thereby filling the cylinder with slurry. This volume should be expelled with the plunger action and refilled with fresh slurry sample to ensure that this plunger volume is not diluted with liquid remaining from the last clean-up of the plunger mechanism.

5.3.5 Push the nose of the plunger onto the mating O-ring surface of the cap valve. Pressurize the sample cup by maintaining a downward force on the cylinder housing in order to hold the check-valve down (open) and at the same time to force the piston rod inside. A force of approximately 225 N (50 lbf) or greater should be maintained on the piston rod.

5.3.6 The check-valve in the lid is pressure-actuated; when the inside of the cup is pressurized, the check-valve is pushed upward into the closed position. To close the valve gradually ease up on the cylinder housing while maintaining pressure on the piston rod. When the check-valve closes, release pressure on the piston rod before disconnecting the plunger.

5.3.7 The pressurized slurry sample is now ready for weighing. Rinse the exterior of the cup and wipe dry. Place instrument on the knife edge. Move the sliding weight right or left until the beam is balanced. The beam is balanced when the attached bubble is centred between the two black marks. Read the density from one of the four calibrated scales on the arrow side of the sliding weight. The density can be read directly in units of grams per cubic centimetre, pounds per gallon, and pounds per cubic foot, or as a drilling fluid gradient in pounds per square inch per 1 000 feet.

5.3.8 To release the pressure inside the cup, reconnect the empty plunger assembly and push downward on the cylinder housing.

5.3.9 Clean the cup and rinse thoroughly with base oil.

5.4 Calculation

Report the drilling fluid density to the nearest 0,01 g/cm^3 , 10 kg/m^3, 0,1 lb/gal, or 0,5 lb/ft^3.

For conversions, use the formulas given in 4.4.2.

6 Viscosity and gel strength

6.1 Principle

Viscosity and gel strength are measurements that relate to the flow properties (rheology) of drilling fluids. The following instruments are used to measure viscosity and/or gel strength of drilling fluids:

a) Marsh funnel — a simple device for indicating viscosity on a routine basis;

b) direct-indicating viscometer — a mechanical device for measurement of viscosity at varying shear rates.

NOTE Information on the rheology of drilling fluids can be found in API RP 13D.

6.2 Determination of viscosity using the Marsh funnel

6.2.1 Apparatus

a) **Marsh funnel**, calibrated to deliver 946 cm^3 (1 quart) of fresh water at a temperature of 21 ± 3 °C (70 ± 5 °F) in 26 ± 0,5 s, with a graduated cup as a receiver.

The Marsh funnel shall have the following characteristics:

1) **funnel cone**, length 305 mm (12,0 in), diameter 152 mm (6,0 in) and a capacity to bottom of screen of 1 500 cm^3 (1,6 quarts);

2) **orifice**, length 50,8 mm (2,0 in) and inside diameter 4,7 mm (0,185 in);

3) **screen**, with 1,6 mm (0,063 in) openings (12 mesh); fixed at 19,0 mm (0,748 in) below top of funnel.

b) **Graduated cup,** with capacity at least 946 cm^3 (1 quart).

c) **Stopwatch**.

d) **Thermometer**, with a range of 0 °C to 105 °C (32 °F to 220 °F).

6.2.2 Procedure

6.2.2.1 Cover the funnel orifice with a finger and pour freshly sampled drilling fluid through the screen into the clean, upright funnel. Fill until fluid reaches the bottom of the screen.

6.2.2.2 Remove finger and start the stopwatch. Measure the time for drilling fluid to fill to the 946 cm^3 (1 quart) mark of the cup.

6.2.2.3 Measure the temperature of the fluid, in degrees Celsius (degrees Fahrenheit).

6.2.2.4 Report the time (6.2.2.2), to the nearest second, with the volume, as the Marsh funnel viscosity. Report the temperature (6.2.2.3) of the fluid to the nearest degree Celsius (degree Fahrenheit).

6.3 Determination of viscosity and/or gel strength using a direct-indicating viscometer

6.3.1 Apparatus

a) **Direct-indicating viscometer,** powered by an electric motor or a hand crank.

Drilling fluid is placed in the annular space between two concentric cylinders. The outer cylinder or rotor sleeve is driven at a constant rotational velocity. The rotation of the rotor sleeve in the fluid produces a torque on the inner cylinder or bob. A torsion spring restrains the movement of the bob, and a dial attached to the bob indicates displacement of the bob. Instrument constants should be adjusted so that plastic viscosity and yield point are obtained by using readings from rotor sleeve speeds of 300 r/min and 600 r/min.

The components shall meet the following specifications.

1) **Rotor sleeve**

Inside diameter	36,83 mm (1,450 in)
Total length:	87,0 mm (3,425 in)
Scribed line:	58,4 mm (2,30 in) above the bottom of sleeve, with two rows of 3,18 mm (0,125 in) holes spaced 120° (2,09 rad) apart, around rotor sleeve just below scribed line.

2) **Bob**, closed, with flat base and tapered top

Diameter:	34,49 mm (1,358 in)
Cylinder length:	38,0 mm (1,496 in)

3) **Torsion spring constant:**

386 dyne-cm/degree deflection

4) **Rotor sleeve speeds**

High speed:	600 r/min
Low speed:	300 r/min

NOTE Other rotor speeds are available in viscometers from various manufacturers.

b) **Stopwatch.**

c) **Thermostatically controlled viscometer cup.**

d) **Thermometer**, with a range of 0 °C to 105 °C (32 °F to 220 °F).

6.3.2 Procedure

6.3.2.1 Place a sample of the drilling fluid in a thermostatically controlled viscometer cup. Leave enough empty volume (approximately 100 cm^3) in the cup for displacement of fluid due to the viscometer bob and sleeve. Immerse the rotor sleeve exactly to the scribed line. Measurements in the field should be made with minimum delay from the time of drilling fluid sampling. Testing should be carried out at either (50 ± 1) °C [(120 ± 2) °F] or (65 ± 1) °C [(150 ± 2) °F]. The place of sampling should be stated on the report.

The maximum recommended operating temperature is 90 °C (200 °F). If fluids have to be tested above this emperature, either a solid metal bob, or a hollow metal bob with a completely dry interior should be used.

CAUTION Liquid trapped inside a hollow bob may vaporize when immersed in high-temperature fluid and cause the bob to explode.

6.3.2.2 Heat (or cool) the sample to the selected temperature. Use intermittent or constant shear at 600 r/min to stir the sample while heating (or cooling) to obtain a uniform sample temperature. After the cup temperature reaches the selected temperature, immerse the thermometer into the sample and continue stirring until the sample reaches the selected temperature. Record the temperature of the sample.

6.3.2.3 With the sleeve rotating at 600 r/min, wait for the viscometer dial reading to reach a steady value (the time required is dependent on the drilling fluid characteristics). Record the dial reading R_{600} in pascals for 600 r/min.

6.3.2.4 Reduce the rotor speed to 300 r/min and wait for the dial reading to reach steady value. Record the dial reading R_{300} in pascals for 300 r/min.

6.3.2.5 Stir the drilling fluid sample for 10 s at 600 r/min.

6.3.2.6 Allow drilling fluid sample to stand undisturbed for 10 s. Slowly and steadily turn the hand-wheel in the appropriate direction to produce a positive dial reading. Record the maximum reading as the initial gel strength. For instruments having a 3 r/min speed, the maximum reading attained after starting rotation at 3 r/min is the initial gel strength. Record the initial gel strength (10-second gel) in pounds per 100 square feet.

NOTE To convert the dial reading to pounds per 100 square feet: 1 Pa = 0,48 lb/100 ft^2.

6.3.2.7 Restir the drilling fluid sample at 600 r/min for 10 s and then allow the drilling fluid to stand undisturbed for 10 min. Repeat the measurements as in 6.3.2.6 and report the maximum reading as the 10-minute gel in pascals (pounds per 100 square feet).

NOTE To convert the dial reading to pounds per 100 square feet: 1 Pa = 0,48 lb/100 ft^2.

6.3.3 Calculation

$$\eta_P = R_{600} - R_{300} \tag{6}$$

$$\eta_Y = 0{,}48 \times (R_{300} - \eta_P) \tag{7}$$

$$\eta_A = R_{600}/2 \tag{8}$$

where

η_P is the plastic viscosity, in millipascal seconds;

NOTE Plastic viscosity is commonly known in the industry by the abbreviation PV.

η_Y is the yield point, in pascals;

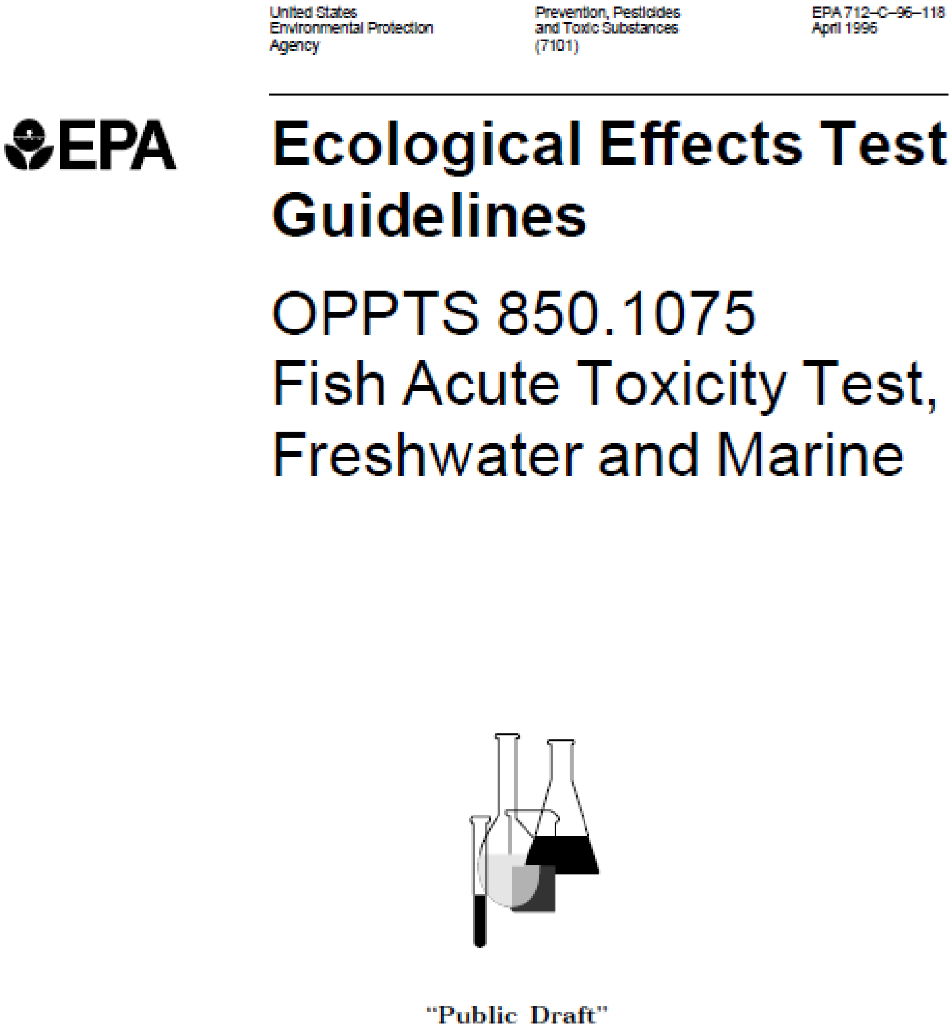
η_A is the apparent viscosity, in millipascal seconds;

R_{600} is the dial reading at 600 r/min, in pascals (pounds per 100 square feet);

R_{300} is the dial reading at 300 r/min, in pascals (pounds per 100 square feet).

NOTE 1 To convert to CGS units of centipoise, 1 mPa·s = 1 cP.

Appendix 2 - Ecological Effects TestGuidelines. OPPTS 850.1075 Fish Acute Toxicity Test,Freshwater and Marine.



United States
Environmental Protection
Agency

Prevention, Pesticides
and Toxic Substances
(7101)

EPA 712–C–96–118
April 1996

EPA

Ecological Effects Test Guidelines

OPPTS 850.1075
Fish Acute Toxicity Test, Freshwater and Marine

"Public Draft"

INTRODUCTION

This guideline is one of a series of test guidelines that have been developed by the Office of Prevention, Pesticides and Toxic Substances, United States Environmental Protection Agency for use in the testing of pesticides and toxic substances, and the development of test data that must be submitted to the Agency for review under Federal regulations.

The Office of Prevention, Pesticides and Toxic Substances (OPPTS) has developed this guideline through a process of harmonization that blended the testing guidance and requirements that existed in the Office of Pollution Prevention and Toxics (OPPT) and appeared in Title 40, Chapter I, Subchapter R of the Code of Federal Regulations (CFR), the Office of Pesticide Programs (OPP) which appeared in publications of the National Technical Information Service (NTIS) and the guidelines published by the Organization for Economic Cooperation and Development (OECD).

The purpose of harmonizing these guidelines into a single set of OPPTS guidelines is to minimize variations among the testing procedures that must be performed to meet the data requirements of the U. S. Environmental Protection Agency under the Toxic Substances Control Act (15 U.S.C. 2601) and the Federal Insecticide, Fungicide and Rodenticide Act (7 U.S.C. 136, *et seq.*).

Public Draft Access Information: This draft guideline is part of a series of related harmonized guidelines that need to be considered as a unit. *For copies:* These guidelines are available electronically from the EPA Public Access Gopher (gopher.epa.gov) under the heading ‘‘Environmental Test Methods and Guidelines’’ or in paper by contacting the OPP Public Docket at (703) 305–5805 or by e-mail: guidelines@epamail.epa.gov.

To Submit Comments: Interested persons are invited to submit comments. By mail: Public Docket and Freedom of Information Section, Office of Pesticide Programs, Field Operations Division (7506C), Environmental Protection Agency, 401 M St. SW., Washington, DC 20460. In person: bring to: Rm. 1132, Crystal Mall #2, 1921 Jefferson Davis Highway, Arlington, VA. Comments may also be submitted electronically by sending electronic mail (e-mail) to: guidelines@epamail.epa.gov.

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OPPTS 850.1075 Fish acute toxicity test, freshwater and marine.

(a) **Scope**—(1) **Applicability.** This guideline is intended to meet testing requirements of both the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) (7 U.S.C. 136, *et seq.*) and the Toxic Substances Control Act (TSCA) (15 U.S.C. 2601).

(2) **Background.** The source material used in developing this harmonized OPPTS test guideline are 40 CFR 797.1400 Fish Acute Toxicity Test; OPP 72–1 Acute Toxicity Test for Freshwater Fish and 72–3 Acute Toxicity Test for Estuarine and Marine Organisms (Pesticide Assessment Guidelines, Subdivision E—Hazard Evaluation; Wildlife and Aquatic Organisms) EPA report 540/09-82-024, 1982; and OECD 203 Fish Acute Toxicity Test.

(b) **Purpose.** The purpose of the acute toxicity test with fish species is to help in the assessment of possible risk to similar species in natural environments, as an aid in determination of possible water quality criteria for regulatory purposes, and for use in correlation with acute testing of other species for comparative purposes. Data on a cold and warm freshwater species are generally required. The rainbow trout, *Oncorhynchus mykiss*, and bluegill sunfish, *Lepomis macrochirus*, are preferred species to meet this requirement since they are sensitive indicator species and a large data base which characterizes the response to environmental contaminants is available. Other species as identified in paragraph (e)(4)(i)(A) of this guideline may be used. However, under certain circumstances, when potential environmental exposures may lead to significant risks, data on the preferred species may be required for risk assessment purposes so that the Agency can conduct comparative analyses with alternative chemical substances. Historically, it appears that many chemical classes are subject to comparative analyses. Development of a good data base could ultimately result in the use of other species in comparative analyses. In any case, the results of such a study should not be construed to represent behavior of the test material in the natural environment where other factors may come into play, but rather as a indicator of effects which might occur under comparable conditions as those utilized in the study.

(c) **Principle of the test**—(1) **Definitive test.** The goal of the definitive test is to determine concentration-response curves for fish mortality, the LC50's, and the 95 percent confidence intervals for each species tested at 24, 48, 72, and 96 h in a static, static-renewal, or flow-through system.

(2) **Range-finding or limit testing.** Definitive testing may be waived if limit testing with at least 30 organisms shows LC50 levels to be greater than 1,000 mg/L based on 100 percent active ingredients (AI), or the limits of water solubility or dispersibility. For pesticides, a lower level of 100 mg AI/L may be tested when estimated environmental concentrations are not expected to exceed 100 mg/L (ppm) as might occur with pesticide use. Prior to selection of definitive test concentrations it may be advisable

to conduct a range-finding test. Results of any range-finding and limit tests should be reported with results of the definitive test.

(3) **Information on the test substance.** The material to be tested should be technical grade unless the test is designed to test a specific formulation, mixture, or effluent. The degree of purity must be recorded for technical ingredients and mixtures. The percentage of each impurity should be reported and percentages should total 100 percent. A complete description of physicochemical characteristics (i.e. solubility, vapor pressure, hydrolysis in pH 5, 7, and 9) should be included with description of the AI used in specific chemical testing. A reliable analytical method for quantification of test substance concentrations must be available.

(d) **Validity of the test.** (1) Maximum-allowable control or solvent control mortality is 10 percent (or 1 mortality if 7 to 10 control fish are used) for a 96–h period of testing. If the test is continued past 96 h, the maximum-allowable additional mortality is 10 percent.

(2) Constant conditions must be maintained throughout the test period. Flow-through procedures are preferred over static-renewal or semistatic procedures and static-renewal procedures are preferred over a static test procedure.

(3) In static tests, the dissolved oxygen (DO) in each replicate should at all times be greater than 60 percent saturation. In flow-through tests, the DO should be maintained above 75 percent saturation.

(4) Measured concentrations are required if the test chemical is unstable or a flow-through diluter system is employed. Exception may be made in cases where hydrolysis studies indicate chemical to be stable (< 5 percent degradation) in 96 h at a pH comparable to test dilution water. In any case there must be evidence that test concentrations remained at least 80 percent of the nominal concentrations throughout the test or that mean measured concentrations are an accurate representation of exposure levels maintained throughout the test period.

(e) **Description of the method—(1) Apparatus.** Normal laboratory equipment and especially the following is necessary:

(i) Equipment for determination of water hardness, etc.

(ii) Adequate apparatus for temperature control.

(iii) Tanks constructed of chemically inert material and of suitable capacity to allow recommended loading levels.

(2) **Water.** (i) Clean surface or ground water, seawater (for estuarine or marine species), and reconstituted water are acceptable as dilution water. Dechlorinated water should not be used because some forms of chlorination are difficult to remove adequately. If dechlorinated tap water

is used, then daily chlorine analysis should be performed. Reconstituted or natural water is preferred.

(ii) Chemical analysis of water used in testing should include the following elements and limitations on maximum concentrations based on at least biannual testing:

Substance	Maximum concentration
Particulate matter	20.0 mg/L
Chemical oxygen demand (COD)	5.0 mg/L
Total organic carbon (TOC)	2.0 mg/L
Boron and fluoride	<100.0 mg/L
Residual chlorine	0.003 mg/L
Un-ionized ammonia	0.020 mg/L
Aluminum, arsenic, chromium, cobalt, copper, iron, lead, nickel, and zinc.	0.001 mg/L
Cadmium, mercury, and silver	<0.100 µg/L
Total organophosphorus pesticides	0.050 µg/L
Total organochlorine pesticides + PCBs or organic chlorine	0.050 µg/L
Specific conductivity	<1.0 µohms

(iii) Salinity should be 20 ± 5 ppt for estuarine species.

(iv) Hardness should range between 40 and 180 mg/L as $CaCO_3$ for freshwater species.

(v) Water hardness or salinity, as appropriate, should be measured at the beginning of each test.

(vi) In marine flow-through tests, salinity should be recorded at the beginning of the test, on day 4, and if extended, on days 7 and 14.

(3) **Solutions of test water.** (i) Distilled water should be used in making stock solutions of the test substance. If the stock volume is more than 10 percent of the test solution volume, dilution water should be used. If a carrier, i.e. a solvent and/or dispersant, is absolutely necessary to dissolve the test substance, the amount used should not exceed the minimum volume necessary to dissolve or suspend the test substance in the dilution water. If the test substance is a mixture, formulation, or commercial product, none of the ingredients is considered a carrier unless an extra amount is used to prepare the stock solution.

(ii) Solvent concentration may not exceed 0.5 mL/L in static-renewal or static testing, and 0.1 mL/L in flow-through testing.

(iii) Preferred solvents are dimethyl formamide, triethylene glycol, methanol, acetone, or ethanol. Solvent use should be avoided if possible.

(iv) Solvent concentrations selected should be kept constant in the solvent control and all test solutions. The concentration of solvent in highest treatment level should be used in the solvent control.

(v) The use of a solubility (saturation) column is permitted in the preparation of stock solutions. This may help to ensure the aqueous solubility limit is attained for poorly soluble test materials.

(vi) The pH should not be adjusted after the addition of the test chemical or stock solution into dilution water.

(vii) The pH should be measured in each replicate at the beginning of the test and every 24 h thereafter.

(viii) The pH must be monitored in low, medium, and high test concentrations and must remain > 6.0 and < 8.0 for freshwater testing and > 7.5 and < 8.5 for marine testing.

(ix) The pH may be adjusted in stock solutions to match the pH of dilution water if pH change does not affect stability of compound in water. HCl and NaOH may be used for this adjustment if warranted.

(4) **Selection of test species**—(i) **Test species.** One or more of the following species may be used:

(A) Freshwater species—Atlantic salmon, *Salmo salar*; bluegill sunfish, *Lepomis macrochirus*; brook trout, *Salvelinus fontinalis*; channel catfish, *Ictalurus punctatus*; coho salmon, *Oncorhynchus kisutch*; common carp, *Cyprinus carpio*; fathead minnnow, *Pimephales promelas*; guppy, *Poecilia reticulata*; rainbow trout, *Oncorhynchus mykiss*; red killifish, *Oryzias latipes*; threespine stickleback, *Gasterosteus aculeatus*; and zebrafish, *Brachydanio rerio*.

(B) Saltwater species—Atlantic silverside, *Menidia menidia*; sheepshead minnow, *Cyprinodon variegatus*; and tidewater silverside, *Menidia penisulae*.

(C) Data on both a warm and a cold freshwater species are generally required. The preferred warm water species is the bluegill sunfish. The rainbow trout is the preferred cold water species. When data on a marine or estuarine species is desired, the Atlantic silversides is preferred.

(ii) **Acclimation.** (A) A minimum 12–day acclimation period is required with 14 days recommended. A minimum of 7 days of the acclimation period must be performed in test dilution water.

(B) Holding water should come from the same source as the test dilution water, if not, acclimation to the dilution water should be done gradually over a 48–h period.

(C) No disease treatments may be administered within 48 h of test initiation or during testing.

(D) No feeding is permitted within 48 h of test initiation.

(E) Pretest mortality must be < 5 percent during acclimation. If pretest mortality is > 10 percent, then the entire batch must be rejected and a new batch begun in acclimation.

(F) Any changes in water temperature should not exceed 3 °C per day. Fish should be held for a minimum of 7 days at the test temperature prior to testing.

(G) During the final 48 h of acclimation fish should be maintained in facilities with background colors and light intensities similar to those of testing area.

(iii) **Age and size of test fish.** (A) Juvenile fish must be tested. Juvenile fish < 3.0 g should be used and the longest should not be more than twice the length of the shortest. The fish should be of normal size and appearance for their age. All fish must be of the same age.

(B) Wild caught fish may be used to satisfy testing guidelines if size, age, and source requirements are satisfied. Wild caught fish should be quarantined 7 days before acclimation procedures begin.

(C) Fish must originate from the same source and population. Records should be kept regarding the source of the initial stock and/or culturing techniques.

(D) Fish should not be used for a test if they appear stressed, or if more than 5 percent die during the 48 h immediately prior to the test, or if they were used in previous tests for treatments or controls.

(iv) **Temperature.** The recommended test temperatures are:

Species	Temperature, °C
Atlantic salmon	12±2.0
Atlantic silverside	22±2.0
Bluegill sunfish	22±2.0
Brook trout	12±2.0
Channel catfish	22±2.0
Coho salmon	12±2.0
Common carp	22±2.0
Fathead minnnow	23±2.0
Guppy	23±2.0
Rainbow trout	12±2.0
Red killifish	23±2.0
Sheepshead minnow	22±2.0
Threespine stickleback	10±2.0
Tidewater silverside	22±2.0
Zebra-fish	23±2.0

(v) **Feeding.** Feeding of test fish daily until 48 h prior to test initiation is suggested.

(f) **Performance of the test—(1) Test design—(i) Test duration.** Acute testing must be performed for a minimum of 96 h.

(ii) **Controls.** Every test should include controls consisting of the same dilution water, conditions, procedures, and test population, except that no test substance is added. Solvent (carrier) controls are also required if a solvent was used.

(iii) **Introduction of fish.** Fish should be added to test chambers within 30 min of addition of the test material to dilution water. Fish may be added prior to addition of test material. Fish should be introduced randomly to individual replicates.

(iv) **Number of test organisms.** A minimum of seven fish per replicate is required. The use of 10 fish per replicate is preferred to obtain a more statistically accurate representation of the dose-response curve, to allow for mortality which may occur, yet be unrelated to chemical effect, and to avoid unnecessary repetitions of the test due to excessive control mortality.

(v) **Replicates.** (A) Two replicates per test concentration are preferred to avoid test repetition due to system failures, and to provide a stronger statistical baseline.

(B) Each test chamber should contain an equal volume of test solution and equal numbers of test fish. Replicate test chambers should be physically separated.

(vi) **Loading.** (A) The number of fish placed in each replicate should not be so great as to affect the test results.

(B) In static or static-renewal tests, loading should not exceed 0.8 g (fresh weight) of fish per liter of test solution in a replicate at any one time.

(C) In flow-through tests, loading should not exceed 0.5 g fresh weight of fish (FWF) per liter of test solution passing through a replicate within 24 h.

(vii) **Test chambers and support equipment.** (A) Construction materials and equipment that contact the stock solution, test solution, or dilution water should not contain substances that can be leached or dissolved into aqueous solutions in quantities that can affect the test results. Materials and equipment that contact stock or test solutions should be chosen to minimize sorption of test chemicals. Glass, no. 316 stainless steel, nylon screen, and perfluorocarbon plastic (e.g. Teflon) are acceptable materials and should be used whenever possible. Concrete, fiberglass, or plastic (e.g. PVC) may be used for holding tanks, acclimation tanks, and water supply systems, but they should be thoroughly conditioned before use. Rubber, copper, brass, galvanized metal, epoxy glues, lead, and flexible tubing should not come in contact with the dilution water, stock solution, or test solution.

(B) Test chambers should be loosely covered to reduce evaporation and to minimize the entry of dust or other particulates into solutions and to prevent loss of test fish.

(C) Size. Many different sizes of test chambers have been used successfully. The size, shape, and depth of the test chamber is acceptable if the specified flow rate and loading requirements can be achieved. Test vessels must be of adequate size to maintain a load rate of FWF $>$ 0.8 g FWF/L for static or static-renewal tests, or FWF $>$ 0.5 g FWF/L for flow-through tests.

(D) Test substance delivery system. (*1*) In flow-through tests, proportional diluters, metering pump systems, or other suitable systems should be used to deliver the test chemical to the test chambers. The choice of a specific delivery system depends on the specific properties and requirements of the test substance.

(*2*) The system should be calibrated before and after each test. Calibration includes determining the flow rate and test concentration in each replicate. The apparatus used should accurately and precisely deliver the appropriate amount of stock solution and dilution water to each replicate.

(*3*) A closed flow-through system may be used to test volatile compounds when more than 20 percent of the test substance would be lost through volatility or the test substance would cause oxygen levels may fall below 60 percent of the saturation level. A design description of this type of system should be included in the study report.

(E) Aeration. Gentle aeration of test vessels used in static systems during the exposure period is permitted only in cases where oxygen levels are in danger of dropping below 60 percent saturation due to chemical characteristics of the test material. Test concentrations must be measured during the test if aeration is used. No aeration of actual test vessels may be utilized in flow-through tests.

(viii) **Light.** (A) The photoperiod with 15 to 30 min transition periods is suggested. Photoperiods may range from 12D/12N to 16D/8N, where D = day, and N = night.

(B) Light intensity should range from 30 to 100 lm at the water surface; the intensity selected should be duplicated as closely as possible in all replicates.

(ix) **Temperature.** (A) Temperatures must be recorded in all replicates at the beginning of the test and every 24 h thereafter. The temperature should be recorded at least hourly in one replicate throughout the test. Temperature should vary no more then 1.0 °C in any given 24–h period.

(B) The test system should be equipped with an automatic alarm system to alert staff of temperature changes in excess of 2.0 °C.

(C) If the water is heated, precautions should be taken to ensure that supersaturation of dissolved gases is avoided.

(x) **Dissolved oxygen.** DO concentrations should be measured in each replicate at the beginning of the test and every 24 h thereafter.

(xi) **Feeding.** Fish may not be fed during the treatment period.

(xii) **Disturbances.** Any disturbance which might change the behavior of the test fish should be avoided.

(2) **Test concentrations.** (i) A minimum of five test concentrations must be employed.

(ii) Five or more concentrations in a geometric series should be tested. Test concentrations must be at least 50 percent greater than the next lowest test concentration (not to exceed 120 percent). Range-finding studies prior to testing may allow more accurate selection of test concentrations.

(iii) No more than 25 percent variation is allowed between test concentrations within the same treatment during the test.

(iv) Concentration selection. (A) Test concentrations should be selected to produce a no-observable-effect concentration (NOEC) and, preferably, at least two partial mortalities, i.e. one greater than and the other less than 50 percent, after 96 h. The highest test concentration should not exceed the chemical's aqueous solubility limit if the chemical is not a surfactant or the chemical's self-dispersibility limit if the chemical is a surfactant or a charged polymer.

(B) Exceptions may be required in testing certain pesticide AIs as products. Product formulations may increase the solubility of the AI beyond its aqueous solubility limit.

(v) Concentration analysis. (A) Concentration analysis must be performed at initiation and every 48 h of the study thereafter.

(B) In static tests, the test substance concentration should be measured in each replicate minimally at the beginning (0–hour, before test organisms are added), at 48 h, and at the end of the test.

(C) In static-renewal tests, the test substance should be measured in each replicate at the beginning and end of test and just before and after each renewal.

(D) In flow-through tests, the test substance should be measured as follows:

(*1*) In each replicate at 0, 48, and 96 h, and every 96 h thereafter, as long as the test is continued.

(*2*) In at least one appropriate chamber whenever a malfunction is detected in any part of the test substance delivery system.

(3) **Collection of samples for measurement.** (i) Water samples must be removed from a central point within the test vessel, not from inflow or outflow points.

(ii) These samples should not contain any surface particulates or material dislodged from the bottom or sides. Samples should be analyzed immediately, or handled and stored in a manner which minimizes loss of test substance through microbial degradation, photodegradation, chemical reaction, volatilization, or sorption.

(iii) The test solution volume should not be reduced during the test by more than 10 percent as a result of sampling.

(iv) Samples from each test concentration replicate should not be pooled for analyses.

(v) Diluter systems must be monitored for proper adjustment, and operation every 24 h, and should be monitored during the first hour of operation.

(vi) Surface films and precipitates must be reported should they occur.

(vii) The flow rate to each replicate should be measured at the beginning and end of each test.

(viii) During a test, the flow rates should not vary more than a factor of 10 from any one replicate to another.

(ix) Minimum number of test vessel replacements should be 6 to 10 per 24–h period for flow-through testing.

(4) **Observations.** (i) Mortality observations should be recorded at 6, 24, 48, 72, and 96 h.

(ii) If the test is continued past 96 h, additional observations should be made every 24 h until termination.

(iii) In addition to mortality, any abnormal behavior should be recorded, such as, but not limited to, erratic swimming, loss of reflex, increased excitability, lethargy, and changes in appearance or physiology such as discoloration, excessive mucous production, hyperventilation, opaque eyes, curved spine, or hemorrhaging.

(g) **Data and reporting—(1) Treatment of results.** The cumulative percentage mortality for each exposure period is plotted against concentration on logarithmic paper. Normal statistical procedures are then employed to calculate the LC50 for the appropriate exposure period. Confidence limits (CI) with p = 0.95 for the calculated LC50 values are to be included.

(2) **Test report.** (i) The test report must include the following:

(ii) Test facilities, test dates, and personnel must be reported.

(iii) Identification of the test substance and purity.

(iv) Water quality characteristics as reported in the laboratory records for the study. These must include 24-h records of DO, pH, and temperature.

(v) Methods of stock solution preparation and the concentrations used in definitive testing.

(vi) All test concentrations measured during the test and at termination.

(vii) The number of test organisms in each replicate and/or test concentration.

(viii) The LC50 concentration-response curves, LC50 values, and associated 95 percent CI should be determined for 24, 48, 72 and 96 h, whenever sufficient data exist.

(ix) A graph of the concentration-mortality curve at test termination. Any control mortality observed during the acclimation or study period.

(x) An NOEL for the 96–h test should also be reported.

(xi) If no LC50 value is determined, but it can be demonstrated that the concentrations tested were the highest possible due to the test chemical's aqueous solubility limit, self-dispersibility limit, or other physicochemical limitations, then the data will be considered for acceptance. Explanation should include details of the solvents which were tried prior to initiation of the final study.

(xii) Any abnormal behavior displayed by the test fish.

(xiii) Any protocol deviations or occurrences which may have influenced the final results of the test.

(xiv) A quality control methods and quality assurance statement should accompany all final study reports.

(xv) Raw data must be available to support study author's conclusions and should be presented with the study report.

(xvi) Methods of statistical analysis should be reported.

(xvii) Methods used in analysis of test concentrations of the test chemical should be described. The accuracy of the method (i.e. detection limit and quantification limit) should be given.

(h) **References.** The following references should be consulted for additional background material on this test guideline.

(1) Standard Guide for Conducting Acute Toxicity Tests with Fishes, Macroinvertebrates, and Amphibians, E 729–88a. American Society Testing Materials, Philadelphia, PA. Approved Nov. 21, 1988.

(2) Organization of Economic Cooperation and Development, Guidelines for Testing of Chemicals, Guideline 203 ‘‘Fish Acute Toxicity Test.’’ Adopted July 17, 1992.

(3) Test Guideline EG–9, Fish Acute Toxicity Test, Office of Pollution Prevention and Toxics, Office of Prevention, Pesticides and Toxic Substances, U.S. Environmental Protection Agency, Washington DC.

(4) Standard Evaluation Procedure Acute Toxicity Test for Freshwater Fish, EPA–540/9–85–006, Office of Pesticide Programs, Office of Prevention Pesticides and Toxic Substances, U.S. Environmental Protection Agency, Washington DC. Revised June 1985.

(5) Acute Toxicity Test for Estuarine and Marine Organisms (Estuarine Fish 96–Hour Acute Toxicity Test), EPA 540/9–85–009, Office of Pesticide Programs, Office of Prevention, Pesticides, and Toxic Substances, U.S. Environmental Protection Agency, Washington DC. Revised June 1985.

(6) Federal Insecticide, Fungicide, Rodenticide Act, Subdivision E, Hazard Evaluation, Wildlife and Aquatic Organisms, U.S. Environmental Protection Agency. October 1982.

(7) Finney, D.J., Probit Analysis. 3rd Edition. Cambridge University Press: London and New York (1971).

(8) Stephen, C.E., ‘‘Methods for Calculating an LC50’’ Aquatic Toxicology and Hazard Evaluation, ASTM STP 634, American Society of Testing and Materials, Philadelphia, PA (1977).

(9) Canada, Environment Canada. Biological test method: acute lethality test using threespine stickleback (*Gasterosteus aculeatus*). Environmental Protection, Conservation and Protection, Environment Canada, Report EPS 1/RM/10 (1990).