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## **Innovation of Purified Glycerol Palm Oil in Drilling Fluid System**

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### **Abstract:**

Glycerol is by-product of palm oil biodiesel industry which potential to be applicable in drilling fluid system. With its characteristic; low price and low toxicity, glycerol application in drilling fluid is very beneficial compared with other materials which still widely used in drilling industries without considering toxicity and cumulative impact on terrestrial, coastal, and marine habitats. Thus, the development of sustainable material which could produce a highly biodegradable base fluid and act as an additive for drilling fluid was conducted.

This study focus on two types of glycerol utilization; as a new alternative base fluid for Synthetic-Based Mud (SBM) and lubricant for Water-Based Mud (WBM). In purpose to evaluate stability of glycerol as base fluid for SBM, an invert emulsion mud was developed and the study of emulsion stability, rheological properties, and thermal conditioning effect was conducted. On the other hand, study of lubrication properties, rheology, filtration loss, and its compatibility with other additives was evaluated in WBM which contain glycerol as lubricant.

The experiment was carried out by comparing performance of glycerol with other oil-based mud, such as saraline and biodiesel. The result showed a significant performance given by glycerol, especially its capability to lubricate drilling fluid without affecting other properties of drilling fluid. Thus, the glycerol characteristic and performance in drilling fluid system add up to be a potential innovation in drilling fluid.

**Keyword:** Glycerol, synthetic-based mud, water-based mud

### **1. Introduction**

Within the last few years, the development of the biodiesel industry as an alternative energy source to meet the challenges of the future energy needs in Indonesia is growing rapidly. Along with the increased production of biodiesel, the glycerol production is also increasing. Glycerol is by-product of transesterification process of vegetable oil to produce biodiesel. The average amount of crude glycerol produced from biodiesel production process is about 10% [1]. Lower prices and increased production quantities will cause glycerol be not worth selling, giving rise to environmental problems caused by glycerol waste. This can be overcome by processing glycerol into more useful products as an alternative solution to increase its commercial value.

Drilling fluid is one of the solution in glycerol application. A preliminary study [2] has shown the physio-characteristic of glycerol with satisfying result. According to this background, a study of glycerol application in drilling fluid was conducted with an objective to develop glycerol to be applied in drilling industries.

### 1.1. Glycerol

Glycerol (glycerin, glycol alcohol, or 1, 2, 3- propanetriol) is a substance with three hydroxyl group with characteristic of high viscosity, odorless, colorless, sweet flavored (0.6 times sucrose), and non-toxic material in its pure condition. Glycerol has three hydroxyl groups that are responsible for its solubility in water. Its hygroscopic nature makes glycerol absorb water from the air. Glycerol molecular formula is  $C_3H_8O_3$  with molecular weight of 92.

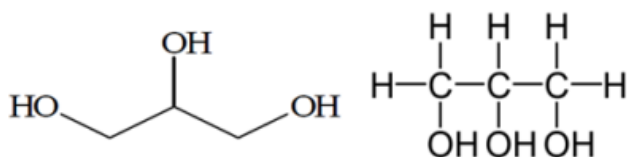


Figure 1. Glycerol molecular structure

Table 1. Physio-chemical properties of glycerol [3]

PROPERTY	VALUE
Physical form	Liquid
Purity	95 - 99.5% (water as an impurity with trace levels polyglycerol)
Melting point	18 deg C
Boiling point	290 deg C at 1013 hPa
Relative density	1.26 at 20 deg C
Vapor pressure	0.000106 hPa at 25 deg C (calculated) and 0.0033 hPa at 50 deg C (measured)
n-octanol -water partition coefficient	log Kow -1.76
Water solubility	Miscible
Dissociation constant	0.07E-13
Flash point	160 deg C
Autoflammibility	393 deg C
Viscosity	1410 mPa.s at 20 deg C
Surface tension	63.4 mN/m at 20 deg C

Commonly, glycerol production from fats can be generated through three methods, which are saponification, hydrolysis, and transesterification. The transesterification of triglycerides with

methanol is the current route to biodiesel production, generating fatty acid methyl esters (biofuel) and glycerol. It can be estimated that from biodiesel making process, around 10% of crude glycerol are produced [4].

In recent years biodiesel industry is growing rapidly due to the depletion of fossil fuels availability. Therefore, the world looking for alternative energy sources, one of which is biodiesel. In 2006, U.S. biodiesel production reached 30-40 million gallons. If assumed, an increase in the production of 50-80% per year, then in 2012 U.S. biodiesel production will reach 400 million gallons. Glycerol abundance due to increased production of biodiesel will cause world crude glycerol prices to drop dramatically, even reaching the lowest level of prices up to \$ 0.05 per lb [1]. According to Tyson (2003) [5], an increase in biodiesel production could increase production by 114% glycerol.

## **1.2. Drilling Fluid**

Drilling fluid or drilling mud is a component which was initially used to circulate cuttings from the borehole to the surface. Other functions of drilling fluid are maintain wellbore stability, prevent formation fluids flowing into the wellbore, and control formation pressure.

### **1.2.1. Water-Based Mud (WBM)**

Water itself can be used as a drilling fluid. However, to maintain a better circulation of the cuttings, WBM requires some degree of viscosity. The viscosity of WBM is generated by the addition of clay or polymers. There are two main purposes of adding clay which are first, increasing viscosity of the mud so that improves the lifting capacity of cuttings and second, building a filter cake (mud cake) in permeable zones to prevent fluid loss. [6]

### **1.2.2. Oil-Based Mud (OBM)**

Oil-based muds use crude or refined oils as the continuous phase and water as emulsified phase. Common types of OBM are oil mud which has less than 5% water and invert emulsion mud which has water concentration greater than 5%.

## **2. Methods**

The methodology proposed in this study is an experiment of purified glycerol processing, glycerol-SBM system formulation, and glycerol-WBM system formulation.

### **2.1. Glycerol Processing and Characterization**

Transesterification process is the first stage of glycerol processing to generate biodiesel as the main product and glycerol as the side product. This is the process of exchanging the organic group R" of an ester with the organic group R' of an alcohol. Usually these reactions are catalyzed by the addition of an acid or base catalyst.

Triglycerides contained in palm oil were reacted with an alcohol using alkaline catalyst to produce fatty acid alkyl esters (biodiesel) and glycerol. In this experiment, transesterification reaction was conducted by mixing 15% (v/v) methanol and 1% (v/v) KOH to form methoxide solution. Afterwards, the solution was mixed with a solution of methoxide transesterification reactor. Transesterification process lasted for 1 hour, stirring at a temperature of 55<sup>0</sup> C with 100 rpm. Then, settling process was performed to separate biodiesel and crude glycerol.

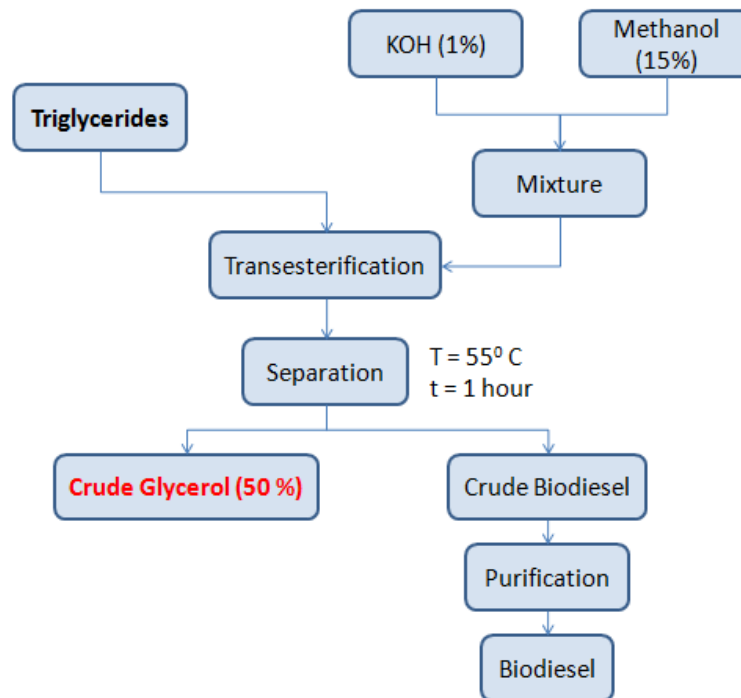


Figure 2. Flow diagram of the process of making biodiesel [5]

After crude glycerol was generated from transesterification reaction, glycerol processing entered the second stage, purification stage. Crude glycerol obtained directly from the separation of biodiesel contained many impurities, such as unreacted methanol, soaps, and potassium hydroxide (KOH) catalyst [8] [9]. Impurities in glycerol, especially matter organic non-glycerol (MONG) such as trimethylene glycol, give impact on the quality and quantity of generated glycerol. If level of MONG is high (3-5%), then problem of odor, color, and flavor will arise in the resulting product [10].

Separation of impurities of crude glycerol was conducted by mixing crude glycerol with 85% Phosphoric Acid (H<sub>3</sub>PO<sub>4</sub>) solution as much as 5% (v/v). The acid reacted with residual catalyst Potassium Hydroxide (KOH) to form Potassium Phosphate salts (K<sub>3</sub>PO<sub>4</sub>). In addition, phosphoric acid converted soaps to form free fatty acids. Expected glycerol purity obtained from this method of purification is 82.15% [7].

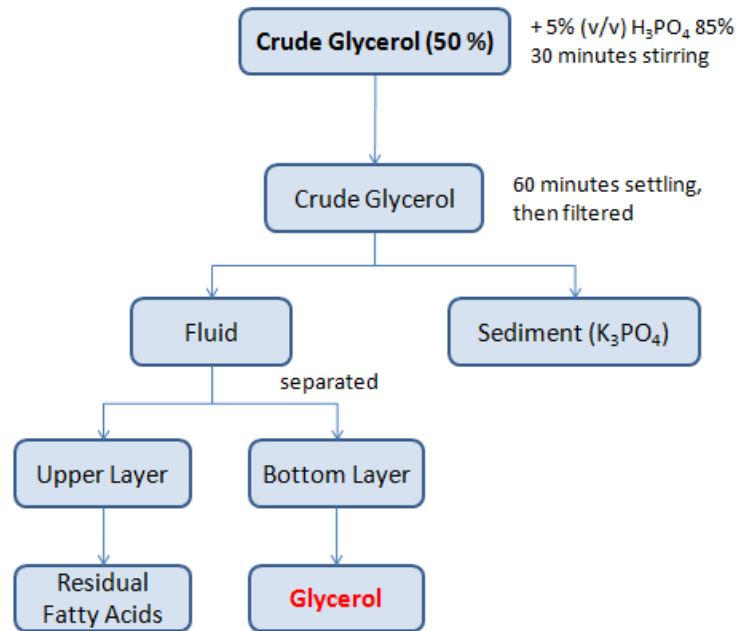


Figure 3. Flow diagram of crude glycerol purification

The physio-chemical test of crude and purified glycerol was conducted to obtain its characteristics; specific gravity, cloud point, pour point, and flash point, for further development of glycerol as base drilling fluid.

## 2.2. Synthetic-Based Mud Formulation with Glycerol as Base Fluid

Preliminary formulations of glycerol with certain additives for glycerol SBM were conducted in this study. The selected additives for the formulations, are primary emulsifier, secondary emulsifier, filtration control additive, viscosifier, lime, and potassium chloride. As comparison, mineral oil and palm oil biodiesel were formulated as base fluid with similar specification of additives. Mud formulation is shown in Table 2.

Table 2. Mud composition of glycerol, palm oil biodiesel, and saraline SBM

Mud Components	Glycerol	Palm Oil Biodiesel	Saraline	Mixing Duration (min)
Base Fluid (ml)	273	273	273	5
Primary Emulsifier (ml)	3	3	3	5
Secondary Emulsifier (ml)	2	2	2	5
Duratone (ppb)	4	4	4	5
Lime (ppb)	5	5	5	5
KCl (ppb)	17	17	17	10
Water (ml)	70	70	70	10
Geltone (ppb)	6	6	6	10

After the formulation, a study to evaluate the drilling fluids, such as emulsion stability, rheological properties, and thermal conditioning effect was conducted.

### **2.3. Water-Based Mud Formulation with Glycerol as Additives**

In this experiment, a standard WBM was formulated using bentonite as reactive clay. Then, glycerol was added as additive with various concentrations, ranged from 0% to 15%. Test parameters to evaluate WBM are lubricity testing, plastic viscosity, yield point, gel strength, density, filtration test, and acidity of mud filtrate.

## **3. Results and Analysis**

### **3.1. Glycerol Processing and Characterization Result**

Glycerol processing which include transesterification reaction and purification, has generated two types of glycerol, crude and purified glycerol. A distinct color difference of crude and purified glycerol is seen as crude glycerol has darker color than purified glycerol.



Figure 4. (A) Crude glycerol (B) Purified glycerol

The result of physio-chemical test for both crude and purified glycerol is shown in Table 3, as comparison with other base fluids.

Table 3. Comparison of glycerol physical properties with some base oils

Parameter	Unit	Crude Glycerol (Hutapea, 2013)	Glycerol After Purification (Hutapea, 2013)	Palm Oil Biodiesel (Hutapea, 2013)	Saraline (Setya wan et al, 2007) [11]	Sarapar (Setya wan et al, 2007) [11]
SG	-	1.09	1.24	0.9	0.78	0.76
Cloud Point	Celcius	24.4	< 0	21.4	N/A	N/A
Pour Point	Celcius	4.4	< 0	5.9	-16	-11
Flash Point	Celcius	82	99	250	81	112
Kinematic Viscosity	cSt	N/A	N/A	5	3.3	2.5

### 3.2. Glycerol as Base Fluid for Synthetic-Based Mud

At initial, viscosity test was conducted by using viscometer, to obtain viscosity characteristic among crude glycerol, purified glycerol, palm oil biodiesel, and saraline. The result shows that crude glycerol has the highest dial reading on viscometer, meanwhile purified glycerol has higher dial reading than saraline and palm oil biodiesel. High dial reading on viscometer indicates high fluid viscosity. This solubility cause viscosity of glycerol decreases significantly.

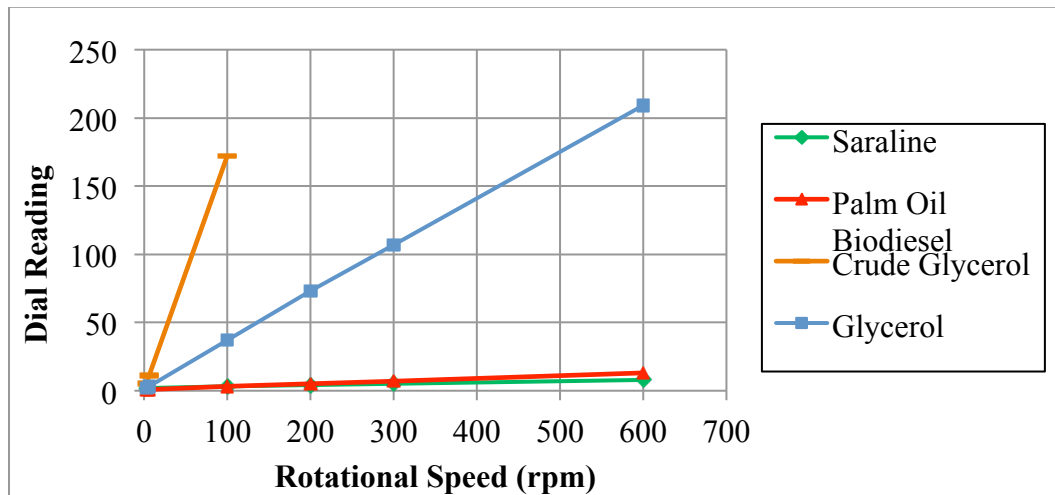


Figure 5. Viscosity characteristics of base fluids

Afterwards, SBM of purified glycerol, saraline, and biodiesel were formulated and the evaluation of SBM was performed before and after 20 hours thermal aging at 302 ° F, which summarized in Table 4.

Table 4. Rheological test results of base fluids

Parameters	Glycerol		Saraline		Biodiesel	
	BHR	AHR	BHR	AHR	BHR	AHR
600 rpm	42	25	22	13	51	34.5
300 rpm	24	20	13	9	29	22
200 rpm	16	17	10	6.5	21	17
100 rpm	9	10	6	4.5	13	10
6 rpm	2	5	2	2	3	2.5
3 rpm	2	3	2	1.5	3	2
10 sec, lb/100sqft	2	8	3	2	4	1
10 min, lb/100sqft	4	11	4	2.5	5	2
PV, cp	18	5	9	4	22	12.5
YP, lb/100sqft	6	15	4	5	7	9.5

\*) BHR = Before Hot Rolling, AHR = After Hot Rolling

### 3.2.1. Before Hot-Rolling

The result of viscosity and gel strength test of glycerol, saraline, and biodiesel SBM is shown in Figure 6 and 7. According to viscosity result, biodiesel SBM has the highest plastic viscosity (22 cp) and slight higher than glycerol SBM (18 cp). Although glycerol has higher viscosity than biodiesel, glycerol has better solubility with water during the formulation of SBM than biodiesel.

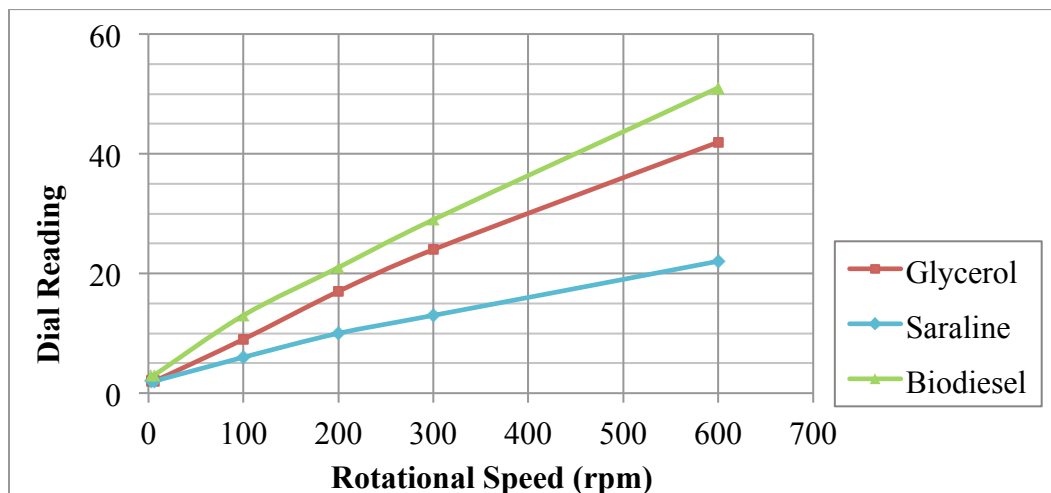


Figure 6. Viscosity characteristics of various SBM before hot rolling

The gel strength result shows that glycerol, saraline, and biodiesel SBM have relatively small number of gel strength. This indicates that those SBM have poor suspension capacity of the mud which lead to hole cleaning problem.



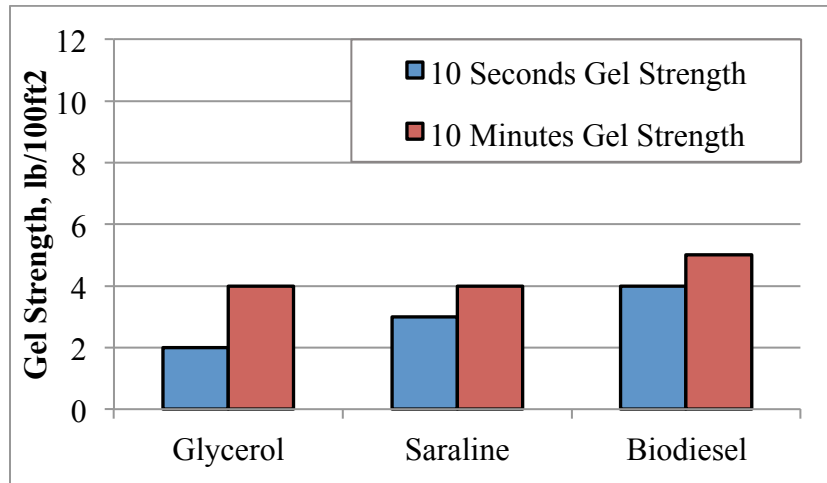


Figure 7. Gel strength of various SBM before hot-rolling

### 3.2.2. After Hot-Rolling

The result of viscosity test shows that plastic viscosity of glycerol, saraline, and biodiesel SBM after heating is lower than plastic viscosity, and difference ranged from 5 up to 18 cp. On the other hand, yield point of SBM after heating process is higher than before heating. The result of gel strength test shows that gel strength of glycerol SBM is increase after entered heating process; 10 seconds gel strength increases from 2 to 8 lb/100ft<sup>2</sup> and 10 minutes gel strength increases from 4 to 11 lb/100ft<sup>2</sup>. Meanwhile, saraline and biodiesel SBM after heating have lower gel strength value than before being heated.

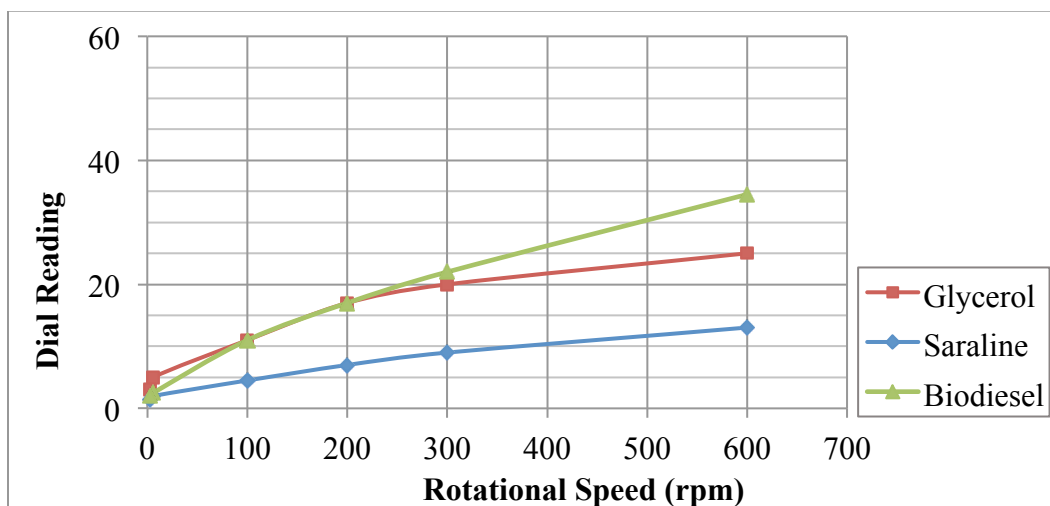


Figure 8. Viscosity characteristics of various SBM after hot-rolling

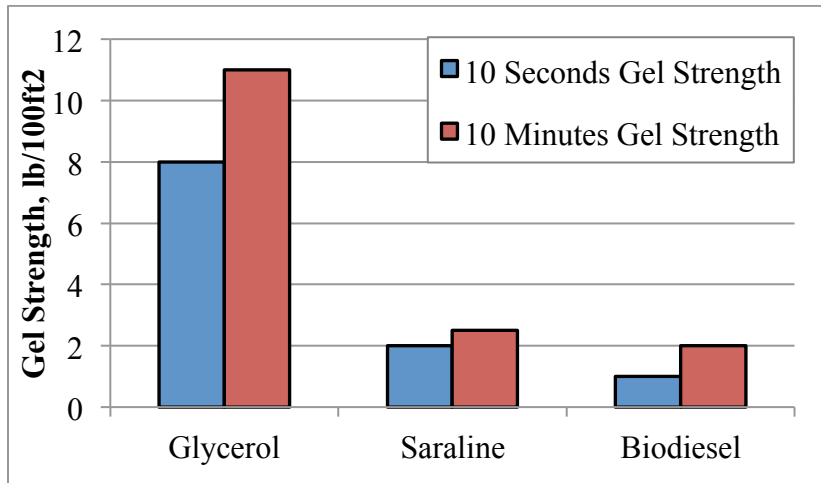


Figure 9. Gel Strength of glycerol, saraline, and biodiesel SBM after hot-rolling

The results indicate that heated glycerol SBM has a good shear thinning profile and good capacity in handling cutting suspension. In addition, the application glycerol SBM shall be accompanied with viscosifiers to increase the viscosity of glycerol SBM. Therefore, an experiment to generate the precise amount of water, glycerol, and viscosifiers shall be conducted in further development.

According to the experiment, glycerol application in drilling fluid could be divided into two treatment; as invert and non-invert emulsion. To produce an invert emulsion as SBM base fluid, glycerol is processed with fatty acid to generate glycerol ester or fatty acid which has an oil-like behavior because contains “hydrophobic” acid tail. On the other hand, the application of glycerol in drilling fluid could be performed without altering its characteristics. Because glycerol is soluble in water, glycerol is treated as a substitute of WBM base fluid by using water as media to carry clay and additives.

### 3.3. Glycerol as Additives for Water-Based Mud

The second experiment was conducted by adding glycerol as an additive for WBM with various concentrations; 0%, 2%, 5%, 10%, and 15%. The evaluation of this experiment covers rheological properties, lubricity, density, filtration loss, and filtrate acidity. The complete results of the tests is summarized in Table 5.

Table 5. Test results of WBM with various glycerol concentrations

Parameters	Test				
	1	2	3	4	5
<b>Glycerol Concentration (%)</b>	0	2	5	10	15
<b>Lubricity Test</b>					
Film Strength (psi)	2118	2492	4707	6051	7060
<b>Rheology</b>					
600 rpm	51	39	40	36	42
300 rpm	34	26	29	25	27
200 rpm	27	20	24	20	22
100 rpm	17	13	15	14	16
3 rpm	3	3	3	5	7
10 sec, lb/100sqft	3	4	4	5	8
10 min, lb/100sqft	19	14	21	23	24
PV, cp	17	13	11	11	15
YP, lb/100sqft	17	13	18	14	12
<b>LPLT Test</b>					
API Filtrate, ml	11.8	12	9.2	10.8	12
Filtrate pH	7.5	7	7	6	5.5
Mudcake Thickness, cm	0.19	0.143	0.097	0.092	0.107
<b>Density, ppg</b>	8.55	8.4	8.2	8.1	7.7

### 3.3.1. Lubricity

Lubricity test was conducted by using Baroid EP/Lubricity tester Model 212 to measure film strength of mud at extreme pressure (EP). The test were performed by applying a measured force with a torque arm to rotating ring with circulated mud. Higher film strength indicates a better lubricity. The result shows a significant increment of film strength as the glycerol concentration increase. The highest film strength was given by WBM with 15% glycerol with 14000 psi, meanwhile the lowest was given untreated WBM with about 4000 psi. This test result indicates that glycerol is a suitable additive to improve WBM lubricity.

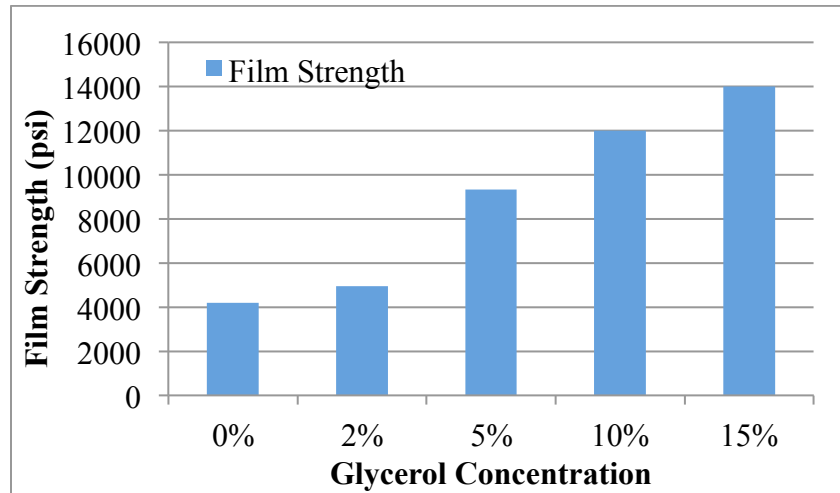


Figure 10. WBM film strength with various glycerol concentrations

### 3.3.2. Rheological Properties

The rheological test shows that plastic viscosity and yield point of WBM tend to decrease as the glycerol concentration increase. On the other hand, gel strength value tend to increase as the glycerol concentration increase. This result indicates that the application of glycerol as additive in WBM gives a good capability in handling cutting suspension. However, viscosifier addition is much recommended to increase the viscosity of glycerol WBM.

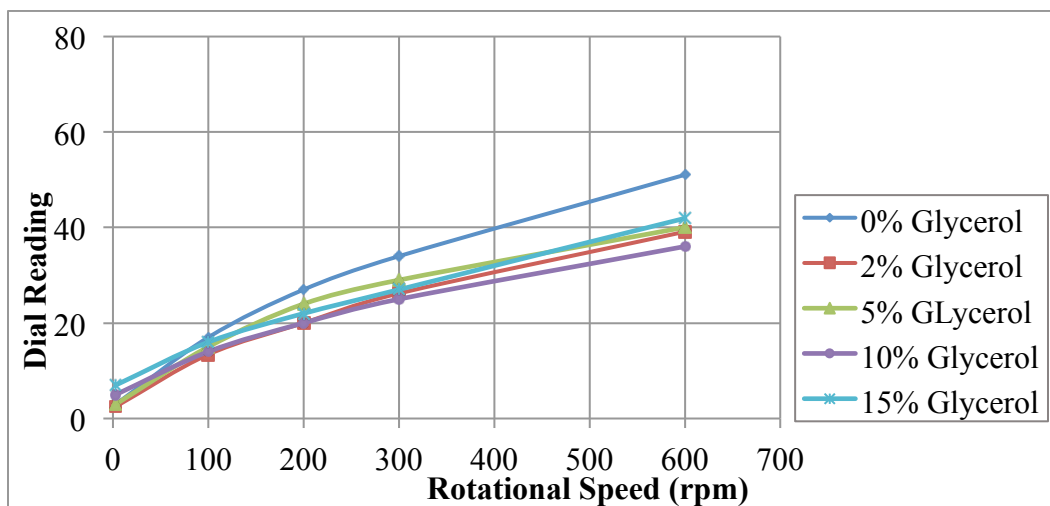


Figure 11. Viscosity characteristics of WBM with various glycerol concentration

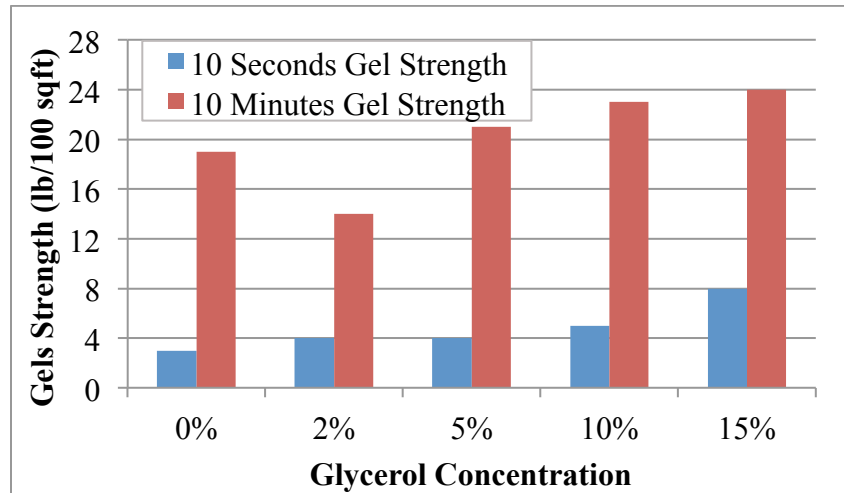


Figure 12. Gel strength of WBM with various glycerol concentrations

### 3.3.3. Filtration Loss

Filtration loss test was conducted by using American Petroleum Institute (API) filter press which measure filtrate volume. Then, API fluid loss was calculated by recorded spurt volume and filtrate volume at 7.5 minutes. The API fluid loss result shows no significant volume difference with glycerol concentration. Thus, glycerol is not an exact additive as fluid loss control.

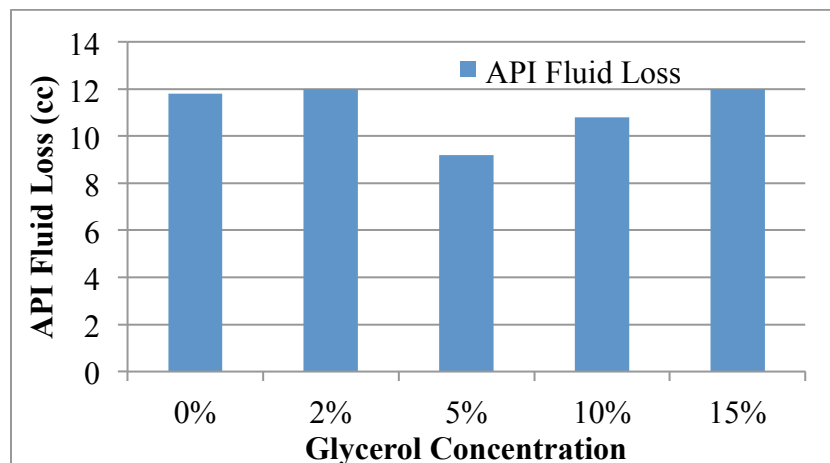


Figure 13. API fluid loss of WBM with various glycerol concentration

The thickness of mud cake which formed during filtration test was also measured. The result which is shown in Figure 14 shows that mudcake is thinner as glycerol concentration increase. This result indicates that glycerol addition in WBM will minimize the risk of differential sticking.

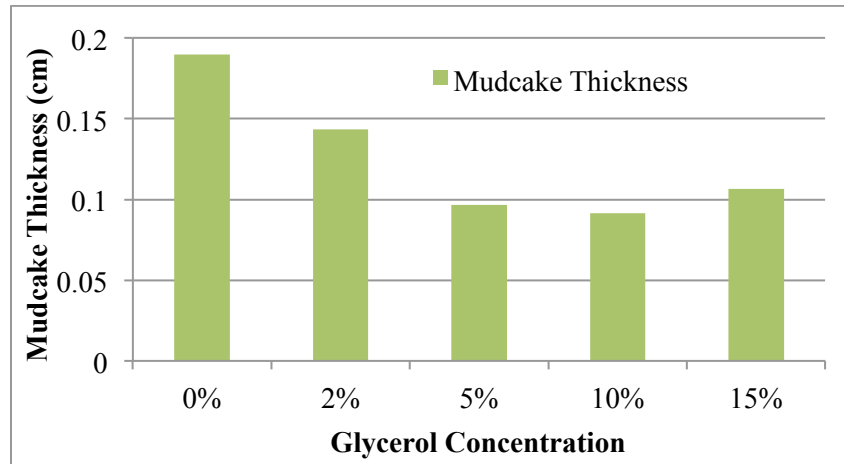


Figure 14. Mudcake thickness of WBM with various glycerol concentration

Afterwards, pH of filtrate was measured and the result is shown in Figure 15. The result shows that pH tend to decrease as glycerol concentration increase. According to the result, glycerol application in WBM shall be accompanied with lime or caustic soda to prevent any damage because of low pH, such as decreasing the solubility of thinner.

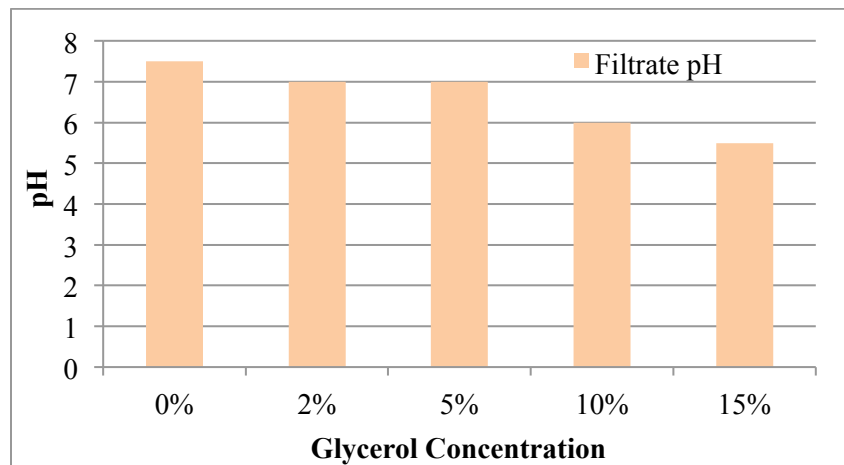


Figure 15. Filtrate pH of WBM with various glycerol concentration

#### 4. Conclusions

1. Glycerol application as base fluid in SBM has been developed. Rheological tests result shows that heated glycerol SBM gives the best capability in handling cutting suspension but shall be accompanied by viscosifier.
2. WBM system using various concentrations of glycerol as lubricant additive has been formulated, with results:
  - a) Glycerol addition is very effective to increase mud lubricity and film strength.

- b) WBM-glycerol system has good capability in handling cutting suspension but shall be accompanied by adding viscosifiers to increase plastic viscosity and yield point.
- c) Glycerol addition gives a thinner mudcake, thus glycerol application is very effective to prevent any differential sticking problem
- d) Glycerol addition reduce mud filtrate pH, thus glycerol application shall be accompanied with base additive, such as lime or caustic soda

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