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Application of Glycerol by-product of Biodiesel Palm Oil as Potential Base Drilling Fluid

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Abstract

Glycerol is by-product of transeterfication process of vegetable oil to produce biodiesel. The production of glycerol increases as the number of biodiesel industries grows. The increment of glycerol is not proportional with its application in industries which cause a drop in crude glycerol price and problem to environment. Overcome this condition, an initial experiment of glycerol characterization as a potential base drilling fluid was performed.

This research covered the formulation of glycerol and quality assessment of glycerol, both crude and purified glycerol, by comparing the characteristic glycerol with former oil base fluids. The characterization of glycerol compound was conducted by Nuclear Magnetic Resonance (NMR) spectrometry, and fluid testing which cover the testing of specific gravity, flash point, pour and cloud point also kinematic viscosity.

The fluid testing result showed that purified glycerol has better physical characterization than the crude glycerol. In addition, purified glycerol characteristic is very supportive to be applicable in drilling fluid system, considering its high flash point value. Instead of physical characteristic, application of glycerol as base drilling fluid gives lower toxic content compared with other base fluid, such as diesel.

Keywords: glycerol, purification, synthetic oil based-mud.

1. Introduction

Oil based mud (OBM) is a drilling mud with biodiesel or mineral biodiesel as the main component. Commonly, oil based mud is used in drilling troublesome shales, High Pressure High Temperature (HPHT) wellbore, sour borehole environments, highly deviated wells which require low torque and drag on drill string – an area where water based mud system cannot give the best result. Oil based mud provides good wellbore stability and remains stable when it contacts with HPHT condition of borehole. However, due to the toxic and high aromatic content, oil based mud cannot be use easily in any geographical locations, especially for environmentally sensitive offshore areas [1].

The disposal of oil contaminated with drill cutting affects the environments pollution. Due to the characteristic of oil based-mud affected environmentally hazard, the government stringently to make a regulation of oil based-mud utilization in drilling system. Therefore, many industries have been replacing the high aromatic oils with lower one (synthetic oil) [2].

One of the alternative synthetic oil which can be used as the basic material of OBM is vegetable oil. The vegetable oil with its characteristics; biodegradable, low toxicity and environmentally friendly, is potential as oil based-mud in drilling system.

Biodiesel is derived from the reaction of transesterification of triglyceride by assisting of base catalyst and glycerol as a side product. Glycerol is a result of the biodiesel production with the quantity approximately 10% [3], and has not been processed widely. Low glycerol usage will give problem to environment later even though glycerol has low toxicity.

This study assessed the characteristic of glycerol to be applicable in drilling fluid system by comparing physio-characteristic of purified glycerol, crude glycerol, and other base fluids. This paper describes the process of purification glycerol, characterization of NMR spectra, and physio-chemical properties of crude glycerol and purified glycerol.

2. Glycerol (Glycerin)

Glycerol is a compound with molecular formula $C_3H_8O_3$ namely 1,2,3-propanetriol with molecular weight 92 [4]. In its pure condition, glycerol is liquid which colorless, high viscosity, odorless, and non-toxic material [5]. The structure of glycerol is shown in Figure 1. The presence of hydroxyl group cause glycerol can soluble in water easily, and also soluble in alcohol, ether, ethyl acetate and other polar compounds. However, glycerol is not soluble in hydrocarbon. The characteristic of glycerol is shown in Table 1.

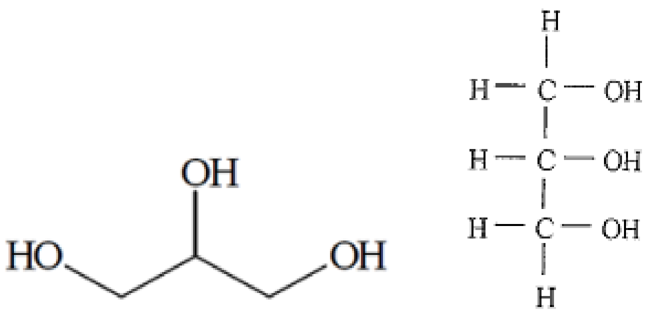

Figure 1. Structure of glycerol

Table 1. Physio-chemical of glycerol [6]

Properties	Remarks
Molecular formula	$C_3H_8O_3$
Molar mass	92
Physical form	Liquid
Melting point	18 ^oC
Boiling point	290 ^oC at 1013hPa
Flash point	160 ^oC
Viscosity	1410 mPa at 20 ^oC
Surface Tension	63.4 mN/m at 20 ^oC

Glycerol could be obtained by three methods; hydrolysis, saponification reaction and transesterification reaction [7]. Transesterfication is a reaction of triglyceride conversion become alkyl ester by adding alcohol and base catalyst, and resulting biodiesel as main product and glycerol as main product. About 10% glycerol is formed through this reaction and still contains many impurities, such as residual of alcohol, and catalyst [3].

In biodiesel transeterification reaction, alcohol works as the source of alkyl, but methanol is more commonly used due to its reasonable although has a good reactivity. Meanwhile, sodium hydroxide (NAOH) or potassium hydroxide (KOH) is commonly used as base catalyst [8].

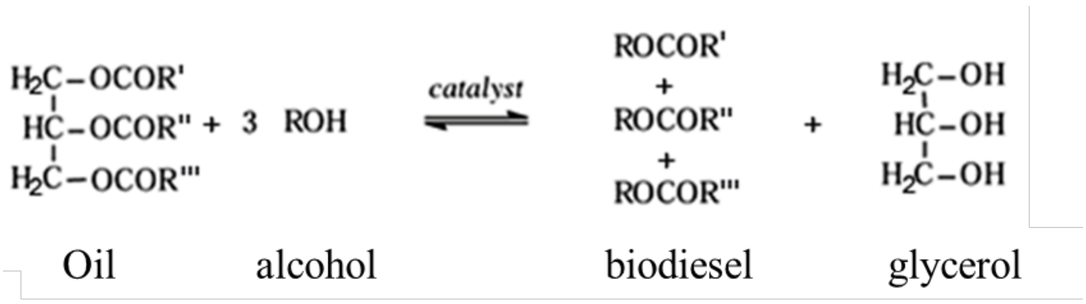

Figure 2. Transestrification process of biodiesel palm oil [3]

3. Experimental

3.1 Purification of Glycerol as By-Product of Biodiesel Palm Oil

In this study, glycerol were derived by transesterification reaction of triglyceride contained in palm oil and methanol with KOH as base catalyst to produce methyl ester (biodiesel) as main product and glycerol as side product. There are several factors may affect the transesterification reaction, such as temperature, ratio of oil and methanol and catalyst concentration [8]. Schematic transesterification reaction is shown in Figure 3. The mechanism of transesterification comprises two processes, where the first is formation of methoxide. Methoxide is formed by methanol reaction and KOH. Second, methoxide attacks carbonyl group of triglyceride.

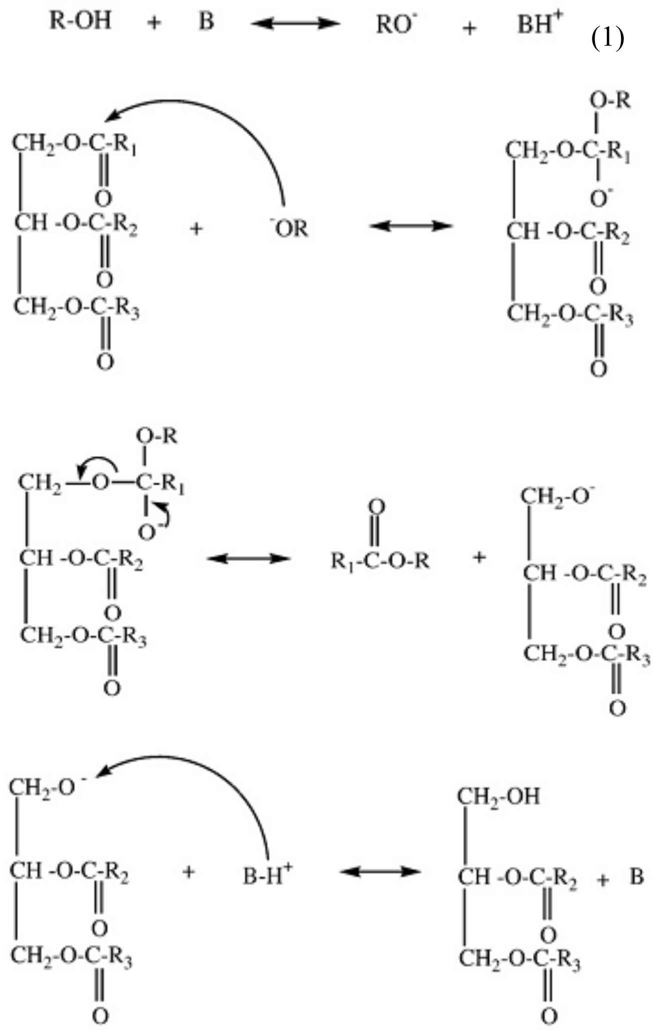

Figure 3. (1) Formation of methoxide and (2) methoxide attack carbonyl group of triglyceride[9]

In this experiment, methanol 15 % (v/v) and KOH 1% (v/v) were used as source of alkyl and base catalyst. KOH and methanol were mixed to produce methoxide, then reacted with triglyceride to produce methyl ester and glycerol. This mixing process was carried out by stirring the methoxide and triglyceride for 1 hour with 100 rpm under 55°C.

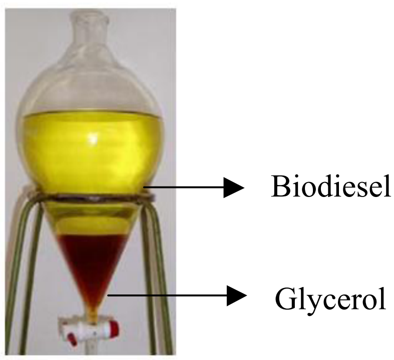

Figure 4. Products of transesterification process [10]

Glycerol, which is obtained from transesterification process, still remains impurities. The impurities commonly contained in crude glycerol are residual of unreacted methanol, soaps and unreacted base catalyst (KOH) [11]. For removing the impurities, crude glycerol was purified.

(A) $KOH + H_3PO_4 \longrightarrow K_3PO_4 + H_2O$

(B)

Figure 5. (A) The reaction of potassium phosphate salt formed (B) The reaction of free fatty acid formed

The purification of glycerol was conducted by adding the phosphoric acid (H_3PO_4) [12], which was performed in laboratory. Crude glycerol was mixed with phosphoric acid solution 5% (v/v) and stirred for 30 minutes then let the fluid settling for 1 hour. The diagram of purification crude glycerol is shown in Figure 6.

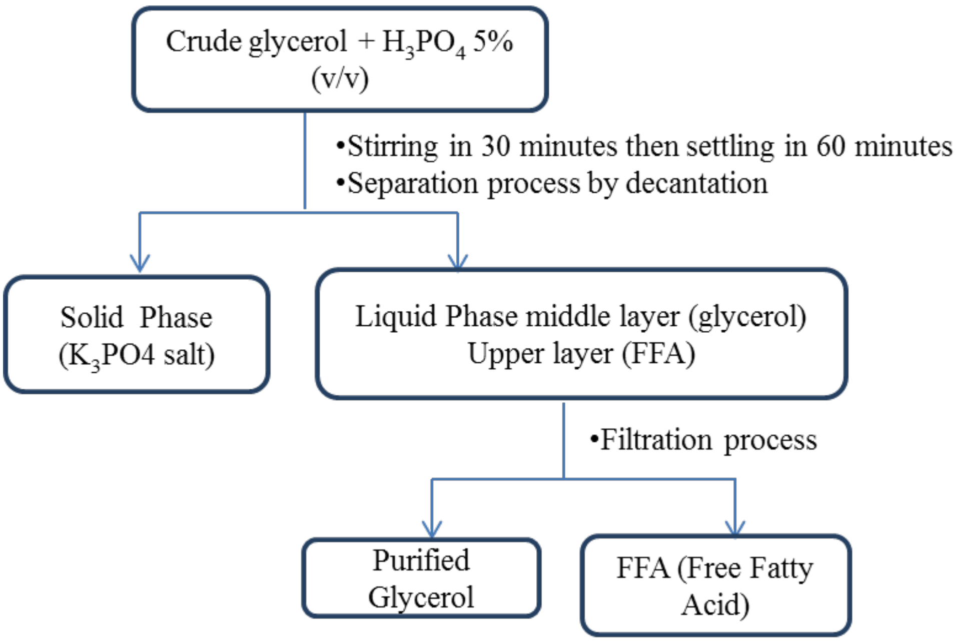

Figure 6. Diagram process of purification glycerol

3.2 Characterization of Glycerol

The glycerol characterization was performed by using NMR to obtain the structure of glycerol and the impurities content inside the glycerol. Furthermore, the characterization was followed by fluid testing to determine glycerol properties as base drilling fluid, accordance with American Society of Testing and Material (ASTM) and American Petroleum Institute

(API). The parameters of test were specific gravity, pour and cloud point, flash point and kinematic viscosity.

Measurement of specific gravity was conducted by using picnometer refers to API 13 B. Meanwhile, pour and cloud point measurements were performed refer to ASTM D97. Cloud point is measured at the lowest temperature which solution start to cloudy and pour point is measured at the lowest temperature which liquid remains pourable. Flash point is measured by using Penky-Martens Closed Cup Tester refers to ASTM D93 and measured at the highest temperature which the solution vapors ignite.

4. Result and Discussion

4.1 Purification of Glycerol as By Product of Biodiesel Palm Oil

From transesterification process, glycerol has dark brown color and still remains impurities (Figure 7). After transesterification process, glycerol was purified by adding the H_3PO_4 and stirred for 30 minutes. After settling the fluid for 60 minutes (Figure 8), the fluid formed 3 layers; free fatty acid (upper layer), glycerol (middle layer), and K_3PO_4 salt (bottom layer). The upper and middle layer are in liquid phase, meanwhile the bottom layer is solid phase. The separation of liquid and solid phase performed by the decantation process and left the sedimentation remained in beaker glass.

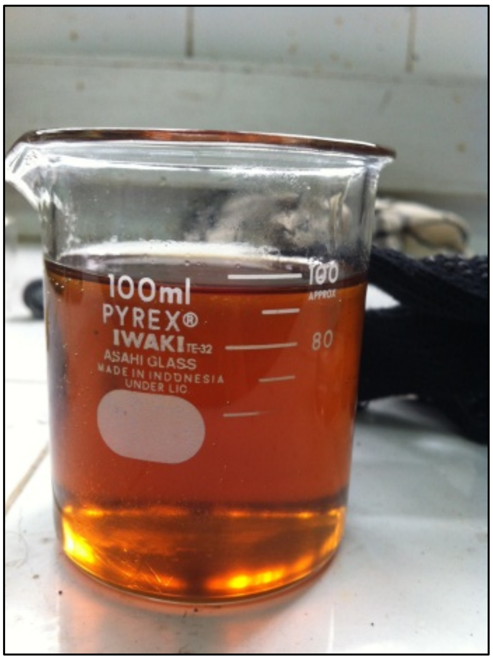

Figure 7. Crude glycerol as side product of palm oil transesterification process

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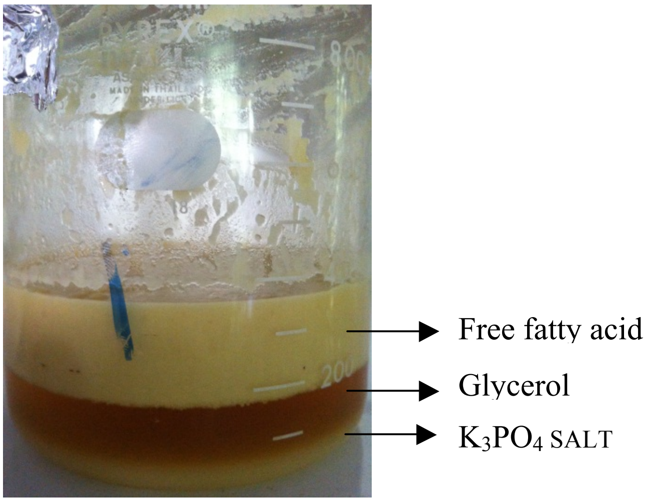

Figure 8. The mixture of H_3PO_4 and crude glycerol after 60 minutes settling

Furthermore, the separation of (glycerol and free fatty acid) were conducted by filtration method with 200 mesh funnel. To remove the salt, filtering process was carried out by filter press apparatus with 30-50 psi. This method is different with the previous one [12] as Farobie used Buchner funnel to separate glycerol and Free Fatty Acid (FFA) from phosphate salts, then followed by the separation of glycerol and FFA using separating funnel. The residual salt could be used as fertilizer after deliver the residual to crystallization process.

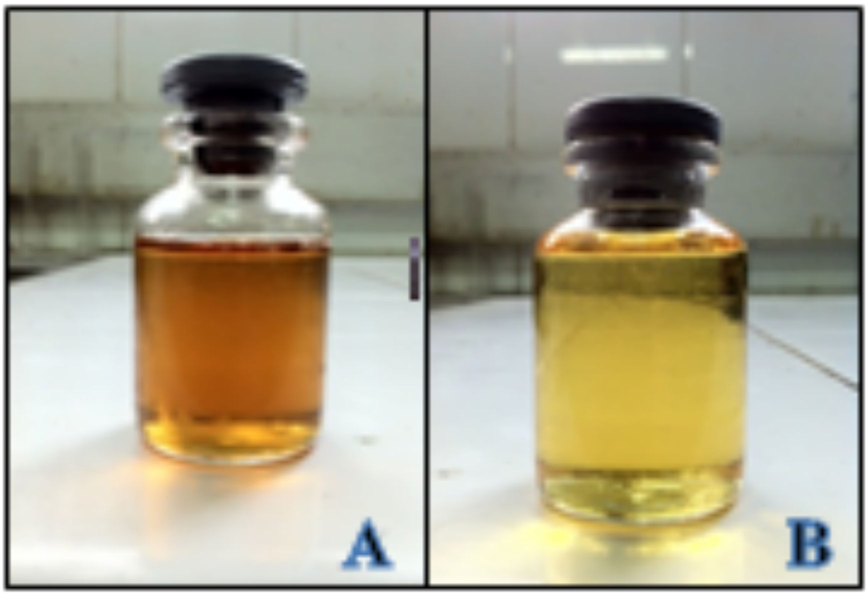

Figure 8. (A) Crude glycerol and (B) purified glycerol

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4.2 Characterization of Crude Glycerol and Purified Glycerol

4.2.1 NMR

In this study, glycerol characterization was conducted by using NMR which was operated at frequency 500 MHz (1H-NMR) and 125 MHz (13C-NMR). The result of NMR spectra of crude glycerol and purified glycerol is shown by Figure 9 and 10. The result show that peak of glycerol compound exist in 3.5 ppm. Crude glycerol has impurities in 2-0.75 ppm and after purification process, in 2 – 0.75 ppm, there were no impurities detected.

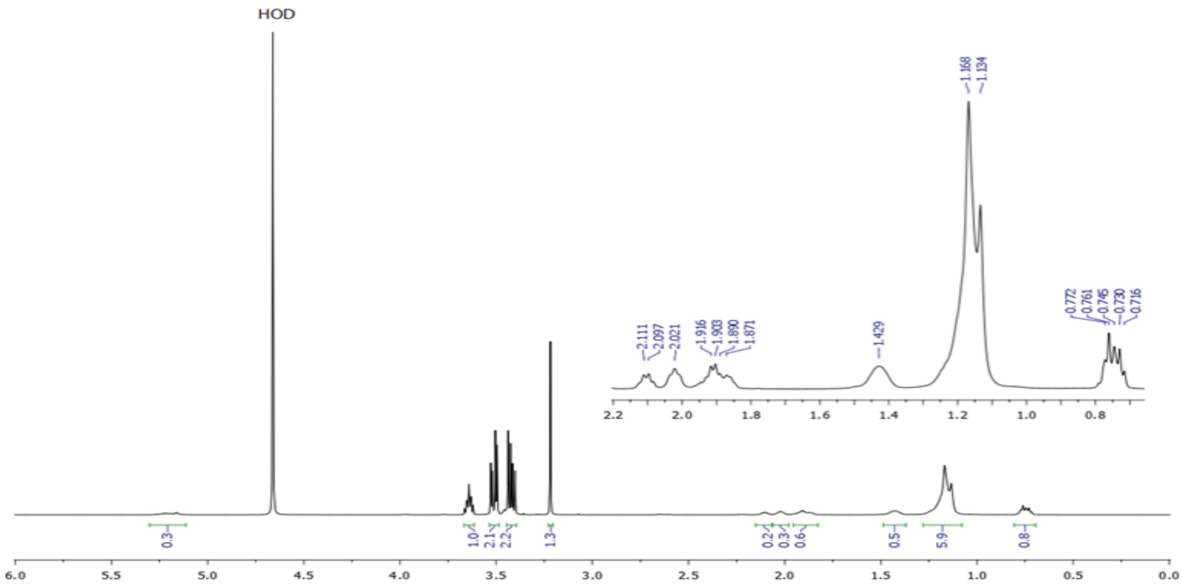

Figure 9. Spectra NNMR of crude glycerol

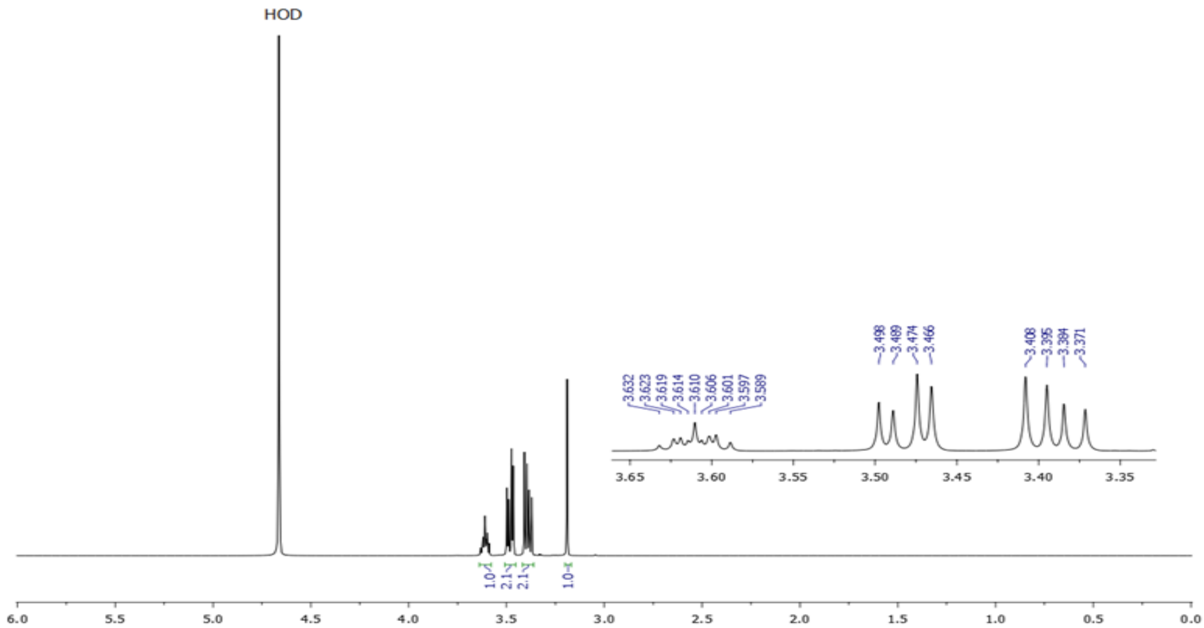

Figure 10. Spectra NNMR of purified glycerol

4.2.2 Physio-Chemical Properties Of Crude Glycerol And Purified Glycerol

The summary of physio-chemical properties of crude glycerol, purified glycerol, and other base fluids is shown in Table 2 and 3. According to the result, purified glycerol has a better quality than crude glycerol because Crude glycerol still contains the impurities and the presence of impurities may interfere the performance of glycerol.

Table 2. Physical properties of base fluid from former studies

Parameter	Biodiesel palm oil (Rubiandini, et al, 2007) [13]	Biodiesel *Jatropha* oil (Priwanza, 2007) [14]	Saraline (Setyawan, et al, 2011) [15]	Sarapar (Setyawan, et al, 2011) [15]	Crude castor oil (Setyawan, et al, 2011) [15]
SG	0.87	0.85	0.78	0.76	0.95
Pour Point (°C)	6.11	11	-16	-11	-21
Boiling Point (°C)	80	120	N/A	N/A	N/A
Flash Point (°C)	112.2	81	81	112.2	271.1
Kinematic viscosity (cSt)	3.7	4.5	3.3	2.5	251.1

Table 3. Physical properties of biodiesel palm oil, crude glycerol, and purified glycerol

Parameter	Biodiesel palm oil	Crude glycerol	Purified glycerol
SG	0.9	1.09	1.24
Pour Point (°C)	5.9	4.4	-12
Boiling Point (°C)	N/A	N/A	N/A
Flash Point (°C)	250	82	99
Kinematic viscosity (cSt)	5	N/A	N/A

The result of specific gravity measurement is shown in Figure 11. According to specific gravity result, purified glycerol has the highest density among all base fluids with 1.24. Meanwhile, crude glycerol has a slight lower density with 1.09.

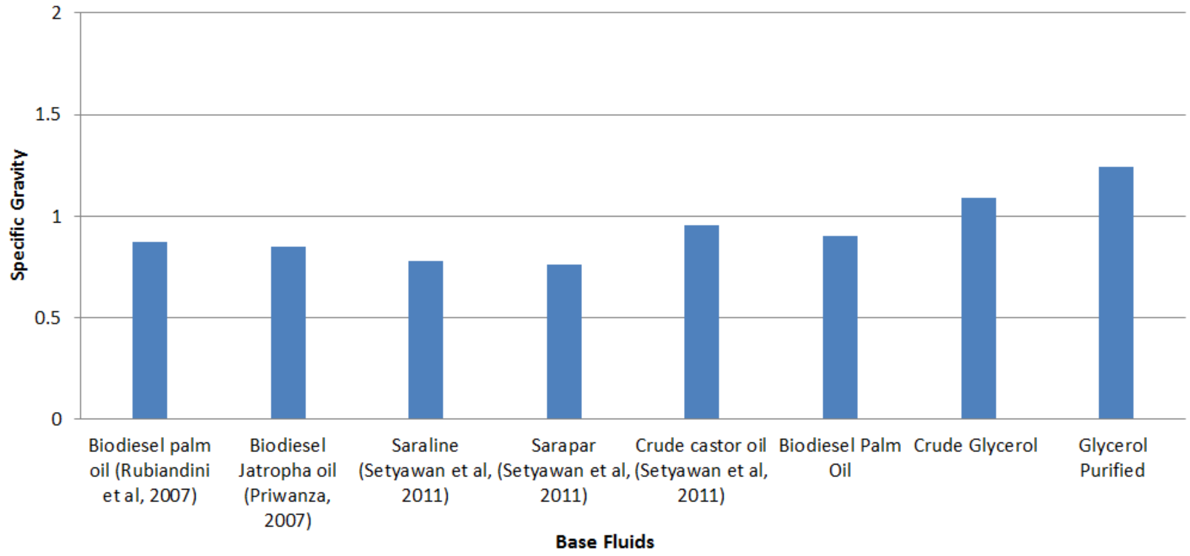

Figure 11. Specific gravity of glycerol compared to other base fluid

The result of pour point measurement is shown in Figure 12. Comparing pour point value, purified glycerol has lower value than crude glycerol. The pour point purified glycerol was -12°C lower than crude glycerol 4.4°C. This result indicates that purified glycerol as base drilling fluid is able to be operated in cold weather and deep water drilling condition.

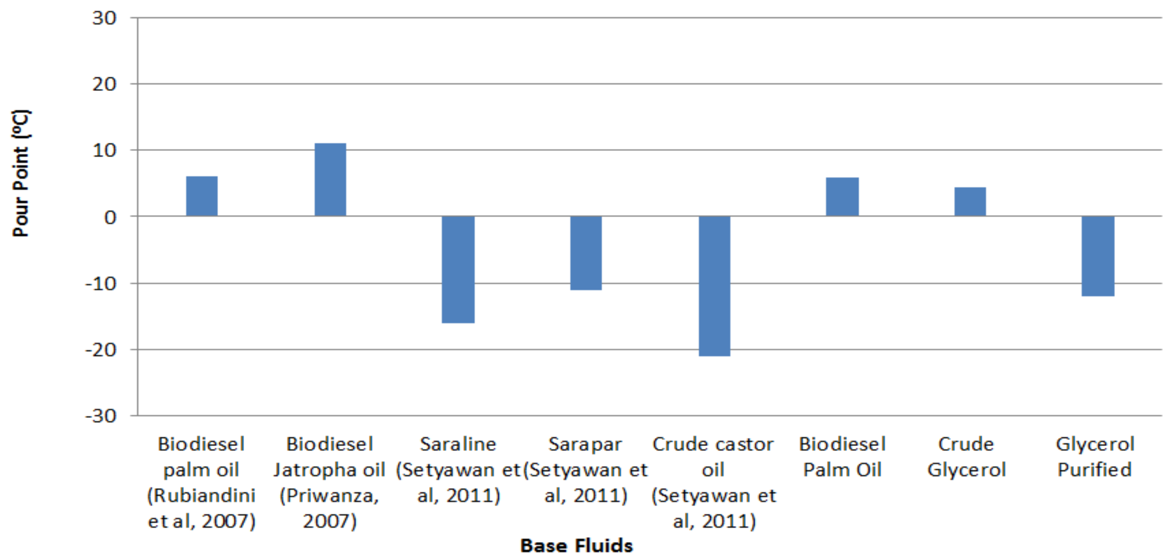

Figure 12. Pour point of glycerol compared to other base fluid

In addition to pour point, Figure 13 shows that purified glycerol (99°C) has higher flash point compared to crude glycerol (82°C) which indicate that purified glycerol is very resistance of fire and also safe to be applicable as base drilling fluid. Higher flash point also ensure better safety in handling, storage and transportation of vegetable oil [1].

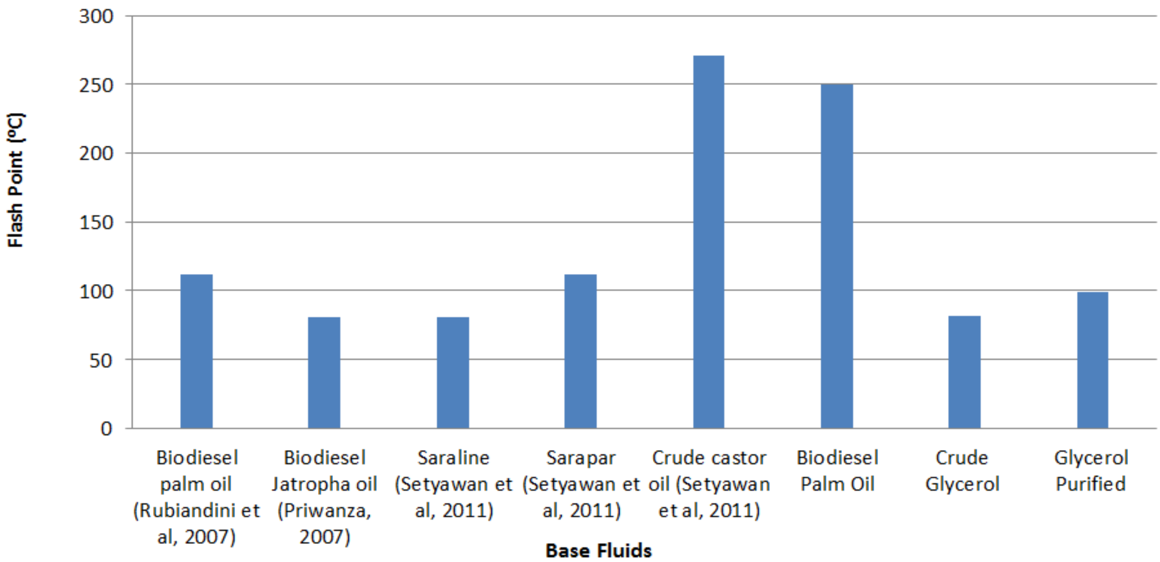

Figure 13. Flash point of glycerol compared to other base fluid

5. Conclusion

1. Purified glycerol has good physical properties compared to crude glycerol because the presence of impurities contain in crude glycerol may affect the performance of crude glycerol.
2. Purified glycerol has higher flash point and lower cloud and pour point than crude glycerol. Higher flash point indicates higher fire resistance capacity of glycerol, also ensures better safety in handling, storage and transportation. Meanwhile, lower pour point indicates good capability during operation in cold weather and deep water drilling. Therefore, the purified glycerol has potential characteristic as synthetic oil based mud.
3. A further development of characterizing glycerol properties and experiment of glycerol application as drilling base fluid is much recommended.

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