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# The effect of antioxidant additives on the growth of deposits on the use of biodiesel fuel (B100) at certain temperatures

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Abstract. Indonesia and several tropical countries produce a lot of energy sources including palm oil, coconut, nyamplung, rubber seeds, kosambi and various other plants. The source can be converted into biodiesel or bioethanol. This is reinforced by Regulation of The Minister of Energy and Mineral Resources, the government issued Indonesia's National Energy Policy under Regulation of The Minister of Energy and Mineral Resources of The R.I. No. 12/2015. This regulation formalized the promotion of biofuels in Indonesia, for both ethanol and biodiesel, and established a 30% biofuel in national energy consumption mandate by 2025. However, consideration of the use of biodiesel fuel is the formation of deposits in the engine or combustion chamber. In this study, the formation of a deposit of biodiesel fuel was carried out by comparison of biodiesel B100-NA without additive with biodiesel variation plus antioxidant additives such as B100 + BHT, and B100 + PG performed by the method of fuel droplet to heat plate to know the characteristics and mechanism of deposit formation On each fuel variation. The research was conducted by the deposition process and evaporation of Diesel fuel which was repeatedly carried out on a hot plate. The plate is heated with temperature variations in the enclosed space so that the conditions are close to the real condition of the engine. This test uses hot room temperature test rig. Use of antioxidant additives to inhibit oxidation in biodiesel is expected to keep the acid number low and increase oxidative stability, which will help prevent excessive deposits in the combustion chamber. This study aims to find the optimal temperature for the growth of the deposit can be controlled.

#### **1. Introduction**

Indonesia and several tropical countries produce a lot of energy sources including palm oil, coconut, nyamplung, rubber seeds, kosambi and various other plants. The source can be converted into biodiesel or bioethanol. This is reinforced by Regulation of The Minister of Energy and Mineral Resources, the government issued Indonesia's National Energy Policy under Regulation of The Minister of Energy and Mineral Resources of The R.I. No. 12/2015. This regulation formalized the promotion of biofuels in Indonesia, for both ethanol and biodiesel, and established a 30% biofuel in national energy consumption mandate by 2025 [1].

Nevertheless, the use of biodiesel with a greater percentage for applications in diesel engines still leaves some problems related to the occurrence of biodiesel degradation and the formation of deposits

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when used as fuel on the engine. Since rolling out the use of biodiesel fuel in engines, there has been an increase in reporting on the formation of deposits in both the combustion chamber and the injectors [2-4]. To date, studies on the mechanism of formation of biodiesel deposits are still small [3, 5, 6]. The ease of biodiesel for degradation is one of the factors that allegedly increases the formation of biodiesel deposits [3]. The addition of antioxidant additives has been shown to increase the stability value of biodiesel tested through accelerated tests in standard 110°C [7, 8], but the effect of antioxidant use on deposit formation has not been widely reported. The formation of deposits on the engine is a fairly complex phenomenon and is highly dependent on combinations of various parameters such as fuel, material surfaces, temperature, pressure, combustion conditions etc. [9].

To address this challenge, further studies and comprehensive research activities with a focus on fuels' characteristics and their deposit formation capability in different engine parts are strongly required. It is worth quoting that research on deposit formation in injector and combustion chamber basically includes measuring the thickness of the deposits in the engine component in response to the application of test and reference fuels [10]. Deposits can contain various materials and residues which gradually grow or accumulate on critical parts of internal combustion engines [6, 11]. Therefore, it is essential to analyze the chemical and physical attributes of deposits in order to figure out the causes. The analysis of micro-deposit structure in this research will be conducted with some analytical tools such as: FT-IR for fingerprint and SEM composition, TEM analysis for micro and nanostructures and EDS to know the physical chemical of the deposit [12].

#### 2. System Description

#### 2.1. Hot Room Temperature Test Rig

To obtain the appropriate deposit sample with the test fuel was tested using hot chamber method and different temperature plate. Each fuel sample is tested under the same conditions.



Figure 1. Hot Room Temperature Test Rig method.

This test rig is designed to test both droplets and spray of injectors. For droplet test, the droplet of fuel is dropped on the heat plate cooled in accordance with the temperature of the engine plate/component, while the room temperature is assumed to be the temperature of the combustion chamber. The temperature of the combustion chamber is varied according to the temperature of the combustion chamber.

Table 1. Caption of Hot Room Temperature Test Rig method.				
Number Caption of Hot Room Temperature Test Rig method				
1	Fuel tank / container			
2	Buffer fuel container			
3	Solenoid Valve Shako PU220AR02-24V			
4	Needle			
5	The droplet entry holes into the furnace			
6	Furnace with heater capacity up to 1200°C			
7	Furnace door			
8	Drip plate / heat plate (AISI 304)			
9	Furnace temperature control			
10	K type thermocouple module (Max6675)			
11	Arduino Uno R3 Microcontroller			
12	Power Supply 24 V DC & Relay Solenoid			
13	Laptop, temperature data display & microcontroller programming			
14	Video camera			
15	K type thermocouple			

Research on the formation of deposits in the use of biodeisel as alternative fuel is planned for 1 year. The formation of Pm/soot and Nox emissions is very important to be used as material for analysis of research results. Research in this time period will present the influence of chemical structure, biodiesel to the deposit formation.

### 2.2. Fuel Testing

2.2.1. Deposition process (Multi Droplet). The deposition process begins with the adjustment of the Hot Room Temperature Test Rig test device, then performs a mass measurement for the drop plate. Set the Hot Room Temperature Test Rig to the temperature per 2000 first drop and then the drop plate is inserted into the combustion chamber and depleted with fuel. After 2000 the first drop, the drop plate is removed and the mass measured again to obtain the mass of the deposit. Testing is done until the droplets reach 6000 and repeated with temperature variations.

2.2.2. Evaporation process (Single droplet). The evaporation process begins with setting the Hot Room Temperature Test, then set the temperature for the first temperature of 250°C. Drop plates are inserted into the furnace and sprayed with fuel once. The evaporation process is recorded using a video camera and the evaporation time is calculated from the video that has been taken. Testing is done up to 350°C and repeated with fuel variations.

#### 2.3. Antioxidant Additives

Additives are the content added to a certain amount of fuel to alter the fuel properties of the fuel. Biodiesel has a low oxidation stability so antioxidant additives are needed. Several studies have proven that the addition of antioxidant additives to biodiesel can inhibit the biodiesel degradation process significantly [8]. Antioxidant additives used in this study are two, namely BHT and PG. Butylated Hydroxytoluene (BHT) has the  $C_{15}H_{24}O$  molecular formula. BHT has a characteristic, which is white crystalline and is widely used because it is relatively cheap, has a molecular weight of 220, has a boiling point of 265°C, a melting point of 69.7°C and slightly smelly [13]. Propyl Gallate (PG) has the molecular formula  $C_{10}H_{12}O_5$ . Propyl errors ( $C_{10}H_{12}O_6$ ) have heat-sensitive characteristics, decompose at its melting point of 148°C, can form a color complex with metal ions, resulting in low antioxidant capability. Three hydroxyl groups make PG a highly reactive antioxidant additive [13].

#### 3. Result and discussion

In this study there are 3 variations of biodiesel sample and given different treatment for each sample. Here is a list of biodiesel samples and treatments.

Table 2. Biodiesel Variation and Treatment.				
Variations of Biodiesel	Additives	Treatment		
B100-NA	No Additives	Heated for 4.5 hours with temperature 80°C		
		and container opened for 12 days)		
B100-BHT	BHT (1000 ppm)	Heated for 4.5 hours with temperature 80°C		
		and container opened for 12 days)		
B100-PG	PG (1000 ppm)	Heated for 4.5 hours with temperature 80°C		
		and container opened for 12 days)		



**Figure 2.** Three variations of biodiesel sample (B100-Na, B100-BHT, and B100-PG)

In the three variations of biodiesel samples, B100-Na, B100-BHT, and B100-PG were performed to find the acid number, peroxide number, and iodine number. This test was conducted by IPB Integrated Chemistry Laboratory, Bogor. This test is conducted to determine the difference in quality of each of the three variations of biodiesel. Where expected differences in the quality of each variation and the influence of additives can inhibit the gradation of quality or oxidation of biodiesel fuel. Below is the test result data of three variations of biodiesel.

Tuble of 1 del properties of the D100 did D100 fuels have been duded duditives							
	Test Dynami	Dynamic	c Kinematic y Viscosity [g/om <sup>3</sup> ]	Acid Numbers	Iodine	Peroxide	
Fuel	Temperature	Viscosity			[mg.KOH/	number	Numbers
	[°C]	[mPa.s]	[ <b>mm</b> <sup>2</sup> /s]	[g/cm]	mg.fat]	[g/100g]	[meq/kg]
B100	40	3.8732	4.5234	0.8563	0.47	46.32	15.17
B100 NA	40	3.7903	4.4263	0.8563	0.50	44.42	11.33
B100 + BHT	40	3.8801	4.5317	0.8562	0.42	47.62	11.34
B100 + BHA	40	3.8801	4.5307	0.8564	0.34	44.45	13.57
B100 + PG	40	3.8309	4.4731	0.8564	0.44	46.26	10.13

Table 3. Fuel properties of the B100 and B100 fuels have been added additives

The above parameters have their respective standards and the following are the available standards to determine whether the biodiesel is still unoxidized or oxidized. The following table is the standard oxidation of biodiesel.

Table 4. Biodiesel Oxidation Standards				
Standard Type	Value	Unit		
Acid number (EN 14214)	Max 0.5	Mg KOH/g fat		
Peroxide number (EN 14214)	Max 10	meq/Kg		
Iodine number (EN 14214)	Max 120	g/100g		

When viewed from existing data, the additive affects the oxidation velocity and is proven to slow the oxidation rate of biodiesel in the sample.

#### 3.1. Test Rig Condition

The arrangement on the test rig is made in such a way as to represent conditions as in the real engine, including the room temperature in the test rig that resembles the temperature of the combustion chamber in the real engine and the temperature of the plate representing the temperature at certain places within the real engine. This can be seen in table 5.

Room Temperature (°C)	Plate Temperature (°C)	Cooler Box Temperatur (°C)	Mass Flow Rate (L/m)
500	250	217	28.2
500	300	271	11.76
500	350	326	6.9

Table 5. Single droplet yield data (evaporation)

#### 3.2. Evaporation Process (Single droplet)

In the test of evaporation time (single droplet), tested at temperatures of 250°C, 300°C, and 350°C. The evaporation process of fuel on the heat plate is observed evaporation character and evaporation time for each fuel tested at each temperature. The evaporation time of the fuel, the temperature of the transition boiling regime and the appearance of fire are obtained from this process.



 Table 6. Single droplet yield data (evaporation)



At a temperature of 250°C, B100-BHT takes the fastest time to evaporate perfectly compared to B100-Na and B100-PG. While at temperatures of 300°C and 350°C, the B100-PG takes a much faster time to evaporate perfectly than the B100-BHT and B100-Na burn perfectly at 300°C and 350°C.

The evaporation time affects the area of the deposit and the mass of the resulting deposit. Depositing deposits occur when the fuel has not fully evaporated but has been re-depleted with a fuel droplet (overlapping condition). The area produced will also become wider or narrow due to plate wetting that is affected by the evaporation time of the fuel. While in the gray zone is the zone where the fuel has undergone a trasition boiling regime. Transition boiling regime does not occur on B100-Na, B100-PG and B100-BHT fuels at temperature variations of 250°C, 300°C, and 350°C.

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**Figure 4.** Time evaporation of one drop B100 Oxidized at each temperature On B100 is xidized.



**Figure 5.** Evaporation time of one drop B100 + PG at each temperature.



**Figure 6.** Evaporation time of one drop B100 + BHT at each temperature.

#### 3.3. Deposition Process (Multi droplet)

The fuel deposition process on the hot plate produces the character and growth of the deposit at each temperature. The observable deposit character is the structure and contour of the deposit surface. Deposit growth can be obtained by measuring the mass of the deposit (the amount of the deposit). The results of the deposition process are as follows.

**Table 7.** The amount of deposit generated from the multidroplet testing of B0 and B100 as much as6,000 drops (per 2,000 drops).

		0,000		/ 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	
Temper	ature 250°C			<b>•</b> '	
	Number of	Deposit Ma	iss [mg]	<i>Total Relative Deposition Mass</i> [10 <sup>-3</sup> ]	
	Droplets	B0	B100	B0	B100
	0	0	0	0	0
	2000	21.6	24.9	1.27	1.74
	4000	78	46.6	4.58	3.79
	6000	82.9	113.4	4.87	5.63
	8000	97.4	172	5.72	10.22
	10000	119.7	190.3	7.03	12.48

#### b. Temperature 300°C

a.

Number of	Deposit Mass [mg]		Total Relative Dep	osition Mass [10 <sup>-3</sup> ]
Droplets	<b>B0</b>	B100	B0	B100
0	0	0	0	0
2000	5.5	4	0.32	0.23
4000	10.1	5.1	0.59	0.3
6000	16.5	41.2	0.97	2.41
8000	22.7	62.1	1.33	3.63
10000	16.4	109.1	0.96	6.37

#### 4. Conclusion

In this paper, forming of deposits from biodiesel with different variation, that are B100-NA, B100+BHT, and B100+PG will be observed with hot surface plate methode to find their characteristics and growth mechanisms of deposits from every biodiesel variation. The main conclusions are summarized as follows:

- (1) Evaporation time B0 is faster than B100 because MEP at B0 occurs earlier or at a temperature lower than B100.
- (2) The evaporation time affects the area of deposit area and the amount of deposit formed. The faster the evaporation time, the smaller the area of deposit produced.
- (3) Temperatures of 250°C will result in the physical wet deposits on B100 and dry physical deposits at B0. A temperature of 300°C will result in a physical deposit that begins to dry on the B100 and a physical deposit that resembles the crust at B0. Temperatures approaching MEP will result in a physical deposit that resembles a crust while temperatures that move away from MEP will result in a wet physical deposit.
- (4) Temperatures of 250°C produce contour-surface contours that have a notably different height between B0 and B100 but the intensity of the hills and valleys on the B100 deposit is less and the rougher areas.
- (5) Temperatures of 300°C produce contour-surface contours that have a contrasting height difference. The elevation of the B100 deposit contour is almost 4 times that of B0, but the spread of the buildup becomes narrower resulting in a mounting deposit.
- (6) The deposit structure B0 is tapered while the B100 deposit structure is spherical. The closer the temperature to the MEP point the more tapered the structure of the deposit B0. The closer the temperature to the MEP point the smaller the sphere of the B100 deposit structure.

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