

## EFFECT OF FUEL SULFUR ON FORMATION OF N<sub>2</sub>O EMISSIONS

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### ABSTRACT

The aim of this work is to investigate the influence of NO/SO<sub>2</sub> on the emissions of N<sub>2</sub>O from diesel engine. A direct-injection diesel engine (model NF-19SK YANMAR) one cylinder was employed to test the emission. This engine works on four-stroke cycle and was operated at 2200 rpm by 25, 50, and 75% engine load. The experiment by three level sulfur content of fuel by adding DBDS into MDO and experiment by emulsion fuel (90% Heavy Liquid Fuel + 10% Water) were conducted in the present work. The result shows that apart from homogeneous interaction between NO, SO<sub>2</sub>, and N<sub>2</sub>O emissions, the temperature of exhaust gas has significant effect on N<sub>2</sub>O formation. Interaction fuel S through reaction  $N + SO \rightarrow NO + S$  and  $NO + O_2 = NO_3$  then  $NO_3 + SO_2 = NO_2 + SO_3$  as would lead to increase in Nitrogen dioxide and Sulfur dioxide concentration. Furthermore in case of emulsion fuel, the correlation between fuel NO and N<sub>2</sub>O exhaust emissions was measured.

**Keywords:** Fuel sulfur, DBDS, Emulsion fuel, Exhaust emissions, N<sub>2</sub>O

### 1. INTRODUCTION

Nitrogen and sulfur are fuel constituents which contribute significantly to atmospheric pollution and to the deterioration of combustion equipment through the formation of NO<sub>x</sub> and SO<sub>x</sub>. In the last thirty years only a small number of investigations have focused on the effect of sulfur on the reaction of nitrogenous species originating from fuel nitrogen.

Reactions of sulfur with N species were proposed to explain the increase of fuel-NO caused by fuel-sulfur:



The latter three being able to remove amine species by NHi-NO reduction reactions, which in turn may lead to higher NO concentration<sup>[1]</sup>.

The decomposition and formation of nitrous oxide (N<sub>2</sub>O) by fuel sulfur has been studied in our research. In the combustion process, oxides of nitrogen are formed mainly from the oxidation of molecular nitrogen present in the combustion air (Thermal NO<sub>x</sub>) and organic nitrogen present in the fuel (Fuel NO<sub>x</sub>). Fuel Combustion involves, as a primary step, devolatilisation, which is where the organically bounded fuel nitrogen is partitioned into volatile-nitrogen and char-nitrogen. In the volatiles stream, nitrogen is known to exist as NH<sub>3</sub>, HCN and tar nitrogen. In the char, nitrogen is bound in aromatic structures. The subsequent step of oxidation results in the conversion of volatile N and char N into NO, N<sub>2</sub>O, and N<sub>2</sub>.

On the combustion of heavy oil, the mass of discharge of air pollutive substance such as nitrogen oxides sulfur oxides, carbon dioxide, dust and smog cannot be avoided, so the research and development of combustion technology preventing the production of such substance has been conducted for a long time. It is indispensable in order to burn heavy oil having high viscosity effectively that heavy oil is heated before the spray at burner and

brought to lower viscosity so that the oil is possible to be sprayed as small particle, and that its evaporation speed and followed mixing with air (oxygen) is accelerated for the diffusion combustion.

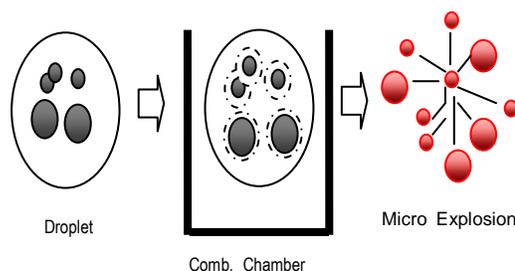
N<sub>2</sub>O has recently become the subject of intense research and debate, because of its increasing concentrations in the atmosphere and its known ability to deplete the ozone layer and also contribute to the greenhouse effect. N<sub>2</sub>O from natural and anthropogenic sources was reported increased in the atmosphere at rate of 0.7 ppb per year. Many researchers were investigating the phenomena of N<sub>2</sub>O from anthropogenic sources. However, only a few data related it from diesel emissions. While the use of emulsified fuel in Diesel Engine has been an active area of research in recent years, some of these studies have only measured exhaust emissions without N<sub>2</sub>O. However, to the best knowledge of author and for the save our atmosphere from greenhouse gas effect, measured of N<sub>2</sub>O is important. The aim of this work is to investigate the correlation between fuel condition and the emissions of N<sub>2</sub>O diesel engine.

## 2. OIL-WATER EMULSION

One technology for solving the problem of fuel cost and high exhaust emission is an oil-water emulsion fuel. The emulsion fuel is to mix heavy fuel oil (HFO) and water that droplet form as water in oil type. This oil-water emulsion fuel has an improved combustion efficiency because particles micro-explode due to the discrepancy of the boiling point between heavy oil and water (heavy oil is 300 °C, water is 100 °C), so that the explosion divides the oil into finer particles and it leads to promotion of diffusion combustion when the emulsion fuel is sprayed into combustion chamber having high temperature<sup>[4]</sup>. The micro-explosion phenomena is caused by the volatility difference between the water and the base fuel. The interior water and/or base fuel become superheated as the emulsion droplet is heated by convective and radiative heat transfer from surrounding combustion gas and flame during combustion.

The participation of water in the evaporation process is expected to lower the droplet temperature. This results in the significant reduction of the intensity of the liquid phase pyrolytic reactions which may lead to the formation of carbonaceous residue. The reduction in the formation of carbonaceous residue is expected to be more remarkable for low volatile fuel. The dilution of water vapor would suppress the chemical reaction in the gas phase due to the reduced rate of heat release in the flame.

Since the high flame temperature is usually a major source of thermal NO production, the suppress of the chemical reaction is expected to lead to the reduced flame temperature and hence the significant reduction of NO production. Figure 1 shows the process of micro explosion in the combustion process. The micro explosion works as water droplets in an oil droplet explosively evaporate inside the combustion chamber in which the temperature is very high, they break the oil droplet into the huge number of tiny droplet.



**Fig. 1 Micro-explosion phenomenon**

Oil-water emulsion fuel according to the present invention is the fuel wherein water particle size is unchangeable and oil-water separation does not occur, which is prepared by adding water (warm water) to heavy oil being a base fuel<sup>[3]</sup>. The mixer from the industrial use is sufficient for the preparation of the present fuel and preferable particle size of water in oil is 20 to 30 μm though depends on the specification of burner equipped on the combustor<sup>[4]</sup>. General industrial water and drinking water are preferable as the water to be mixed and it is preferable that the temperature of water is accordance with one of heavy oil.

### 3. DITERT BUTYL DISULFIDE (DBDS)

Ditert Butyl Disulfide (DBDS) is sulfur containing organic chemical compound with formula  $((\text{CH}_3)_3\text{C}_2)_2\text{S}_2$ . DBDS in concentrated liquid is flammable and insoluble with boiling point 185-215°C. DBDS is used for compare of sulfur contain in the fuel.

**Table 1 Characteristic of DBDS**

Chemical equation	$((\text{CH}_3)_3\text{C}_2)_2\text{S}_2$
Molecular weight (g)	178.4
Boiling point °C	185-215.6
Specific gravity (15/4 °C)	0.92-0.94
S Content (mass%)	35.95
H Content (mass%)	10.17
C Content (mass%)	53.87
C/H Content (mass%)	5.30

### 4. EXPERIMENTAL METHODS

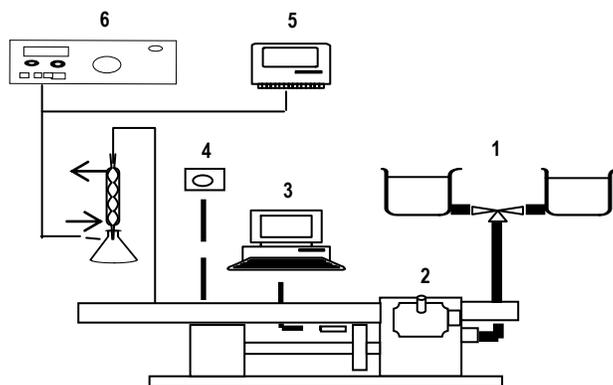
A direct-injection diesel engine (model NF-19SK YANMAR) one cylinder was employed to test the emission. This engine works on four-stroke cycle and was operated at 2,200 rpm by 25, 50, and 75% engine load. The experiment by three level sulfur content of fuel by adding DBDS in MDO and experiment by emulsion fuel (90% Heavy Liquid Fuel + 10% Water) were conducted in the present work.

Detail of experimental fuel can be explained as follow:

1. Marine Heavy Fuel Oil (HFO)  
(S: 2.21 m/m%, N: 0.24 m/m%)
2. Emulsion Fuel (90% HFO + 10% Water)  
(S: 1.46 m/m%, N: 0.07 m/m%)
3. Marine Diesel Oil (MDO)  
(S: 0.08 m/m%, N: 0.02 m/m%)
4. MDO + 2.5% DBDS  
(S: 1.2 m/m%, N: 0.02 m/m%)
5. MDO + 5% DBDS  
(S: 1.836 m/m%, N: 0.02 m/m%)

Figure 2 shows the diagram of experimental setup. The exhaust gas was analyzed by N<sub>2</sub>O, NO, SO<sub>2</sub>, O<sub>2</sub>, CO, CO<sub>2</sub> analyzer. N<sub>2</sub>O emission was measured by Gas Correlation N<sub>2</sub>O Analyzer model 46C and Horiba model PG250 for other emissions. As seen the figure, the engine is started with MDO and changed to other fuel by control the valve.

A hydraulic dynamometer was used with the diesel engine to adjust the engine load. Exhaust gas temperature was measured using a thermocouple located downstream of the exhaust valve. The exhaust gas was introduced through water cooler before entering measuring device without dilution, the cooler using for preventing the device from particulate that include in the exhaust gas, which may lead device's malfunction. Though, it is expected that the water condensation, which take place in cooler may lessen the accuracy of the emissions measurement.



1.Fuel Tank, 2.Diesel Engine, 3.Load Control, 4.Thermocouple, 5.CO/O<sub>2</sub>/NO/SO<sub>2</sub> Analyzer, 6.N<sub>2</sub>O Analyzer

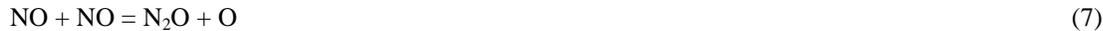
**Fig. 2 Experimental diagram**

## 5. RESULTS AND DISCUSSIONS

### 5.1 Experiment HFO and emulsion fuel

Comparing the two kind of fuel, the burning of oil- water emulsions emitted significantly less NO than the heavy fuel. This is because the water contents of the emulsions causes a phenomenon called heat sink. When heat sink occur it results in water content of the inner phase partially absorbing the calorific heating value of the emulsions, thereby decreasing the burning gas temperature inside the combustion chamber thus restraining the generation of NO.

In case of emulsion fuel, the correlation between fuel NO and N<sub>2</sub>O exhaust emission was measured. Figure 3 shows the result of concentration of NO by emulsion fuel experiment. NO concentration of emulsion fuel is lower than heavy fuel. As consequence the N<sub>2</sub>O decomposed by reaction:



Moreover, the correlation between NO/SO<sub>2</sub>/N<sub>2</sub>O can be explained by reaction below:



And



From this reaction, it can be noted that SO<sub>2</sub> product as determine from fuel sulfur is contribute formatting the N<sub>2</sub>O emissions. The lower product SO<sub>2</sub> by using emulsion fuel than HFO (figure 4) give result at lower N<sub>2</sub>O (figure 5). SO<sub>2</sub> emissions were reacting with H<sub>2</sub>O to form H<sub>2</sub>SO<sub>3</sub>. SO<sub>3</sub> as determine of H<sub>2</sub>SO<sub>3</sub> was reacting with NO inside the exhaust gas. It is result of formation of N<sub>2</sub>O emissions.

At low engine load (25%), the heat loss to the combustion chamber wall is proportionately greater and combustion efficiency is poorer, resulting in higher fuel consumption for the power produced. At high engine load (75%), the friction power is increasing at a rapid rate, resulting in a slower increase in the fuel consumption. As the use of emulsion fuel, the total fuel consumption increases. This is because a larger amount of diesel is showed by an equal amount of water. This means that less diesel fuel is actually contained within each volume of the emulsion.

Tsukahara and Yoshimoto<sup>[6]</sup> have also reported a reduction in fuel consumption in a diesel fuel by emulsion fuel. The reduction fuel consumption with water emulsified diesel may be attributed to formation of a finer spray due to rapid evaporation in the water, longer ignition delay results in more fuel burning in premixed combustion and suppression of thermal dissociation due to lower cylinder average temperature.

**Table 2 Other emissions and fuel consumption data by heavy and emulsion fuel**

	Engine Load					
	Heavy Fuel Oil			Emulsion Fuel		
	25%	50%	75%	25%	50%	75%
CO (ppm)	1657.3	803	781	1766	1013	1366
CO <sub>2</sub> (%)	5.01	7.89	10.4	3.74	5.67	9.65
O <sub>2</sub> (%)	14.2	10.51	7.14	15.93	13.38	7.77
EG Temperature (°C)	345	465	560	385	463	563
Fuel Cons. (L/hr)	1.78	2.56	3.26	2.12	2.7	3.58

**Table 3 Other emissions and fuel consumption data by MDO and MDO+DBDS fuel**

	Engine Load								
	MDO			MDO+2.5%DBDS			MDO+5%DBDS		
	25%	50%	75%	25%	50%	75%	25%	50%	75%
CO (ppm)	845.4	619.8	526.4	811	530	407	799	490	374
CO <sub>2</sub> (%)	3.53	5.15	6.93	4.23	6.28	7.70	4.34	6.47	8.65
O <sub>2</sub> (%)	15.59	12.69	11.4	15.24	12.56	10.46	15.20	12.21	9.42
EG Temp. (°C)	290	390	530	300	398	550	315	450	580
Fuel Cons. (L/hr)	1.54	2.27	3.15	1.66	2.32	2.88	0.15	2.37	3.10

The evaporation and additional mass of water cause the cylinder average temperature to become lower. The variations of the gases exhaust temperature with engine load for the different emulsions also shown in table 2.

Exhaust gas temperature shown increased because of carbon content in the exhaust gas is high.

The latent heat of water will cool the charge due to the evaporation of water, and the cylinder average temperature following injection and before ignition becomes lower as the water percentage increases. This results in lower peak combustion temperature<sup>[5]</sup>. As a result, the CO emissions increased. This was not so obvious in the CO emissions from heavy oil. The formula for calculating CO oxygenating rate  $K_{CO}$  is :  $CO + OH \rightleftharpoons CO_2 + H$  ,  $K_{CO} = 6.76 \times 10^{10} \exp[T/1102] \text{ cm}^3/\text{gmol}$ , according to this formula when the temperature T rises, the CO oxygenation rate rises. As increasing of CO in this experiment, the N<sub>2</sub>O concentration decrease by reaction:  $CO + N_2O \rightarrow CO_2 + N_2$ .

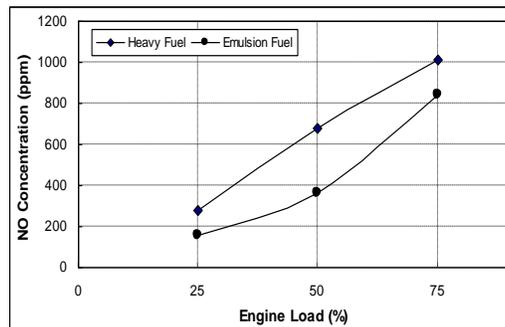


Fig. 3 NO concentration by HFO and emulsion fuel experiment

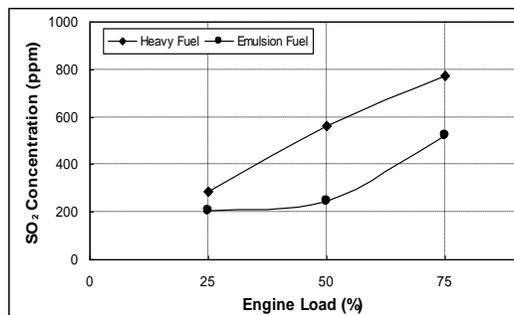


Fig. 4 SO<sub>2</sub> concentration by HFO and emulsion fuel experiment

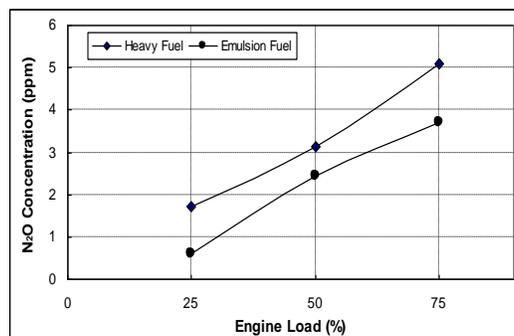


Fig. 5 N<sub>2</sub>O concentration by HFO and emulsion fuel experiment

## 5.2 Experiment MDO and MDO + DBDS

As explained in the experimental section, the effect of increased concentrations of fuel sulfur was assessed by added DBDS into MDO. Figure 6 through to 8 presents the effect of increasing amounts of fuel sulfur on the exhaust emissions. Table 3 shows the data of emissions CO/CO<sub>2</sub>/O<sub>2</sub>, exhaust gas temperature and fuel consumption. CO emission was decreased by added of sulfur into the fuel. However, emission of CO<sub>2</sub> was increased. Data shows, CO<sub>2</sub> increased about 19% and 2% at 25% engine load by adding 2.5% and 5% DBDS into MDO, respectively. It can be noted that increase of fuel sulfur may lead to increased CO<sub>2</sub> diesel emissions. Moreover, exhaust gas temperature was a few increases respectively from 530°C to 550°C and 580°C at 75% engine load by 2.5% and 5% added of

DBDS. Fuel consumption was not change significantly by addition of fuel sulfur.

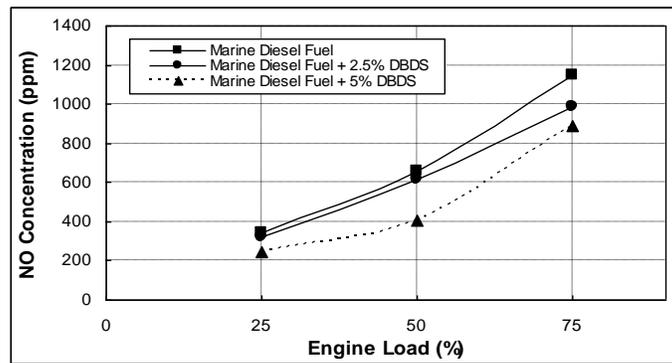


Fig. 6 NO concentration by MDO and MDO+DBDS experiment

A net reduction of NO was observed from all fuels investigated. The largest nominal reduction was obtained from MDO + 5% DBDS with 97 ppm, 251 ppm, and 260 ppm of initial emissions (MDO) at 25, 50, and 75 % engine load, respectively, as seen in figure 6. This results agree with conclusion of addition sulfur caused a drastic increase of NO<sub>2</sub> emissions but reduction of NO<sup>[1]</sup>. As the fuel-air mixture becomes more lean the inter-conversion of NO to NO<sub>2</sub> may play an important role<sup>[2]</sup>. This route leads to the simultaneous decrease of NO and increase of NO<sub>2</sub> concentrations. At low concentrations NO can be oxidized by SO<sub>2</sub> to form NO<sub>2</sub> and SO<sub>3</sub> in the following reactions:  $NO + O_2 = NO_3$  and  $NO_3 + SO_2 = NO_2 + SO_3$ . Figure 7 shows the data of SO<sub>2</sub> emissions by addition of DBDS into MDO. SO<sub>2</sub> emissions gradually increase by increased of fuel sulfur, because main of sulfur dioxide emission is S molecule in the fuel.

Figure 8 shows the result of N<sub>2</sub>O concentration by addition of fuel sulfur (DBDS). The N<sub>2</sub>O concentration increase by increasing of fuel sulfur and exhaust gas temperature. As NO<sub>2</sub> concentration was increased N<sub>2</sub>O increased by reaction:  $NO_2 + N_2 = N_2O + NO$ . N<sub>2</sub>O gradually increase by percentages of DBDS in the fuel. The formation of N<sub>2</sub>O from 1, 1.3 and 1.6 ppm by MDO at 25, 50, and 75% engine load, respectively, to 5, 7, and 8 ppm by MDO+5%DBDS as reported in the experimental results. Experiment data shows that the fuel sulfur can inhibit the formation of nitrogen oxide emissions.

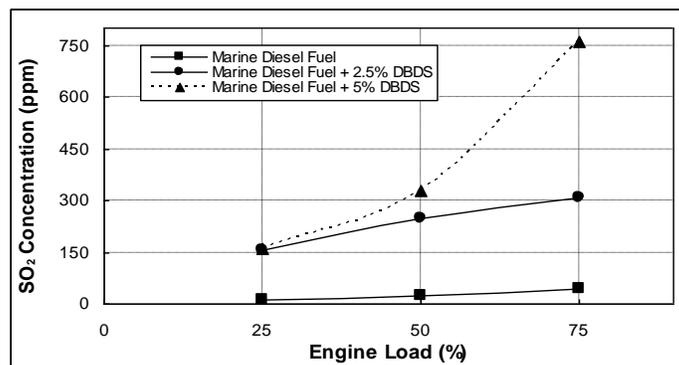


Fig. 7 SO<sub>2</sub> concentration by MDO and MDO+DBDS experiment

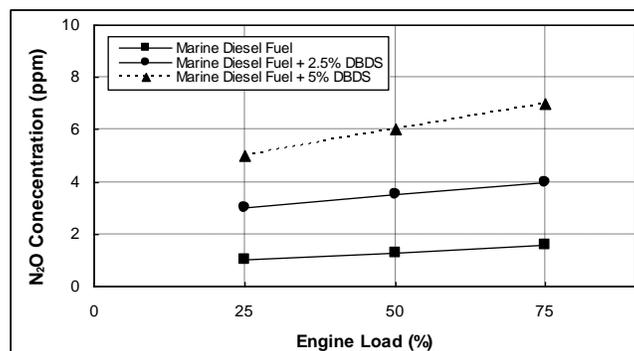


Fig. 8 N<sub>2</sub>O concentration by MDO and MDO+DBDS experiment

## 6. CONCLUSIONS

The present study has shown that emissions of N<sub>2</sub>O can be generated by fuel sulfur. Fuel sulfur by adding DBDS into MDO is contributed significantly formatting the SO<sub>2</sub> emissions. By reaction 8-9, the formation N<sub>2</sub>O was seen in this experiment. It was also found that sulfur dioxide significant inhibition effect on NO emissions. Lower fuel sulfur while using emulsion fuel also reduces the NO emissions and resulting in decrease of N<sub>2</sub>O (NO + NO = N<sub>2</sub>O + O). Moreover the increase of CO by using of emulsion fuel can reduce the N<sub>2</sub>O emissions.

## 7. ACKNOWLEDGEMENT

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## 8. NOMENCLATURE

HFO	Heavy Fuel Oil
MDO	Marine Diesel Oil
DBDS	Ditert Butyl Disulfide
N	Nitrogen
NO	Nitrogen oxide
NO <sub>2</sub>	Nitrogen dioxide
N <sub>2</sub> O	Nitrous oxide
S	Sulfur
SO <sub>2</sub>	Sulfur dioxide
CO	Carbon monoxide
CO <sub>2</sub>	Carbon dioxide
O <sub>2</sub>	Oxygen
EG	Exhaust gas

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