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14 Thermal Analysis of Diesel Engine Cylinder Head Deposits while Operated by Diesel-Water Emulsion Fuel

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ABSTRACT

Four samples of engine carbon deposits derived from diesel fuel in emulsions containing 0; 5; 10 and 15% vol water were subjected to thermogravimetric analysis (TGA/DSC) in air medium. The TGA system was used, allowing rapid exposure of deposit samples to the action of hot gases, thus simulating the actual process occurring inside the combustion chamber. The deposit build up processes were performed on a YANMAR single-cylinder direct-injection diesel engine for period of 25 hours for each set of test fuel. These results were then correlated with elemental analysis as well as infrared spectra for microscopic observations. It has been found that, as the water increases in fuel, less aromatic and less reactive of deposits would be formed.

***Keywords*: Fuel emulsions, Carbon deposit, Diesel engine, Thermal analysis**

1. INTRODUCTION

Diesel engine is the major contributor to NO_X and particulate emission (PM) due to high temperature and pressure combustion. The addition of water in fuel is one of the strategies to control oxides of nitrogen (NO_X), which is detrimental to human health. In addition to potentially damaging human health, NO_X are precursors to ozone (O_3) formation, which could jeopardize to human health and vegetation as well. Finally, NO_X contributes to acid deposition, which has potential damage on vegetation and aquatic system. It has been found by many previous works that the addition of water into diesel engine has a number of possible benefits. The main intention is to reduce peak temperature in the combustion zone. It is believed that the water could lower the gas temperature by means of water evaporation and thus decreasing in the rate of thermal-NO_X formation for Zeldovich mechanism reaction [**1**]. It also may help to improve atomization and mixing, which is attributed to droplet microexplosion [**2**]. This secondary atomization is produced as a series of the disruptive evaporation of the water droplets contained in a fuel drop [**3**]. Water vapour reacts with particulates to produce CO and H_2 in the region deficient in oxygen, consequently lessen the amount of particulate emitted [**4**].

Three principal methods of introducing water into the diesel engines are; water injection into the cylinder using a separate injector, spraying water into the inlet air, and fuel/water emulsions. Among these methods, the use of fuel/water emulsion is the most effective technique for the reduction of NO_X and particulate for direct injection engines. However, emulsified fuel blends tend to lower the combustion temperature randomly [**5**]. Although there are numerous works on the performance of diesel/water emulsion, very limited amount of works are reported in the literature on the deposit characteristics of such fuel and the effect of adding water on the amount and the nature of deposit formed. In fact diesel/water mixtures are expected to form deposits on the cylinder heads of the engine where excess piston deposits can impair engine performance and in severe cases can cause engine breakdown [**6**].

In this paper, thermogravimetic analysis (TG) was used to investigate the effect of water addition in diesel fuel on the oxidative properties of deposits. Furthermore, the chemical complexity of a deposit requires an appropriate characterization to better describe its properties. Several characterization procedures are necessary to distinguish between deposits and would also help to predict the behaviour in a given fuel formulation

particularly specifically on the presence of polymeric additives in the deposit [**7**].

2. COMBUSTION CHAMBER DEPOSITS

Combustion chamber deposits have been studied and characterized in a range of engine system for over forty years. It has been found that deposits form on the combustion chamber wall, the head and the piston top in diesel engines; accumulate to an equilibrium thickness over the few hundred hours of operation [**8**].

Apparently, the formation of combustion chamber deposits would greatly affect the engine performance and drivability. They include decreased volumetric efficiency, increased thermal efficiency due to insulation of the cylinder, the physical interference with valve closing or with piston motion. Some of the important impacts of combustion chamber deposits on engine performance from the standpoint of modern engine design are potential in increasing engine out emissions of pollutants such as unburned hydrocarbons and nitric oxides.

In addition to degrading engine performance, deposit could contribute to the abnormal combustion that affects engine combustion and emission. As deposit is accumulated in the combustion chamber, hydrocarbon emissions (HC) likewise appeared to increase. It is believed that adsorption and desorption of hydrocarbons by these surface deposits is the mechanism that causes this undesirable increase in emissions [**9**]. The one of exhaust gas from fuel combustion which is affects to combustion chamber deposits is the nitric oxides (NO_x). The formation of NO_x during the engine cycle has been shown to have a strong dependence on mean gas temperature in the cylinder, increasing by over 44 percent with an increase in burn gas temperature from 2000 K to 2050 K [**10**]. Thus, the increasing temperatures due to the insulating and heat-storage effects of the deposits can be expected to increase engine-out NO_x emissions. Statistically significant increases in tailpipe NO_x emissions with increasing deposit thickness have been observed experimentally [**11**].

3. EXPERIMENTAL SETUP AND PROCEDURE

The type of engine used in this research work was a single-cylinder direct-injection YANMAR diesel engine. The selected engine specifications are tabulated below in Table 1. The emulsion was prepared instantly prior injection by means of a homogenizer, which is capable of producing fine water droplet up to 200 micron. The investigation was carried out with emulsions containing 0, 5, 10, and 15 percent of water by volume with ordinary diesel fuel (OD) namely OD/100, OD/95, OD/90 and OD/85 respectively. The calorific value and specific gravity of test fuels are listed below in table 2.

The accumulation of deposit was performed without any load for duration of 25 hours at speed 2500 rpm for each set of test fuel. The experimental setups with several ancillary apparatus are shown in Figure 1. Fuel tank temperature was set constantly at 65°C, which is an ideal temperature for emulsion system, and no emulsifying agent was added.

Table 1: Specifications of the Yanmar engine

Model	YANMAR L100AE-DTM
Combustion chamber type	Bowl-in-piston with swirl
Injection type	Direct injection
Number of cylinder	1
Cycle	Four-stroke
Displacement, cc	406
Compression ratio	20:1
Rated power	6.6kW/3600rpm
Type of cooling	Air-cooled

Table 2: Calorific value and Specific Gravity for Diesel/water emulsion fuels

Test Fuel	OD/100	OD/95	OD/90	OD/85
Calorific value (kJ/kg)	45.4	43.5	39.5	35.0
Specific Gravity	0.838	0.843	0.852	0.856

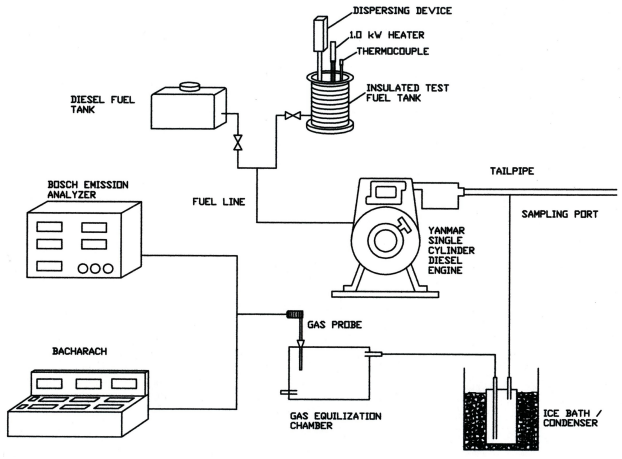


Figure 1 Schematic diagram of deposit accumulation test

The emulsions were continuously homogenized through dispersing device to prevent phase separation during the test. At the end of the test, the engine was

dismantled and the cylinder head deposit was scraped. The deposits were stored in the oven for an overnight prior sample preparation. Dried deposits were grinded in an agate mortar and sieved to the size of 100-μm. In fact, small particle size is preferable in order to avoid problems related to heat and mass transfer when various analyses are performed.

3.1 THERMAL ANALYSIS

Thermal analysis was performed with a NETZSCH STA 409 Simultaneous Thermal Analyzer, which combines simultaneous Thermogravimetry and Differential Scanning Calorimetry (TGA/DSC). In TGA, the weight changes of the sample are continuously recorded as the temperature is increased at a controlled rate. The deposit samples were heated on a thermo balance in flowing air to 110°C and holding it there isothermally for 30 minutes to a constant weight in order to liberate moisture which resides within the interstices of a molecular structure of the deposits. This was to ensure that, the interference of water at high temperature could be minimized and thus reducing errors in the analysis. The sample still in flowing air was then heated at temperature gradient 10ºC to 950°C and once more held there to a constant weight for complete burning. The remaining residual consists only of inorganic salt and oxide, which are identified as ash.

3.2 ELEMENTAL ANALYSIS

Dried deposit samples were analyzed for their elemental composition using PE 2400 Series II CHNS/O Analyzer. This equipment is capable to determine organic materials such as carbon, hydrogen, nitrogen, sulphur and oxygen, which imply its name in the abbreviation form. Deposits were weighed for 2mg and were placed in the soft aluminium crucible before being folded. Care should be taken when folding the aluminium crucible containing deposit since inconsistent preparation might lead to error in analysis.

3.2 FOURIER TRANSFORM INFRARED ANALYSIS

The Perkin Elmer Fourier Transforms-Infra Red spectroscopy (FTIR) was used for this purpose. Dry-grinded deposit samples were mixed with dry and powdered KBr in the ratio of sample to KBr 1:10 and then were pressed to form pellet. KBr is transparent to infrared beam. The obtained spectrums were compared.

4. RESULTS AND DISCUSSIONS

Figure 2 shows the picture was taken to observe the accumulation of deposits after engine running with every fuel samples. The figure shows that deposits will decrease when water increase on fuel emulsions. The variation of typical deposits on this area also showed in this figure. However, the significant differences of deposits formation were illustrated.

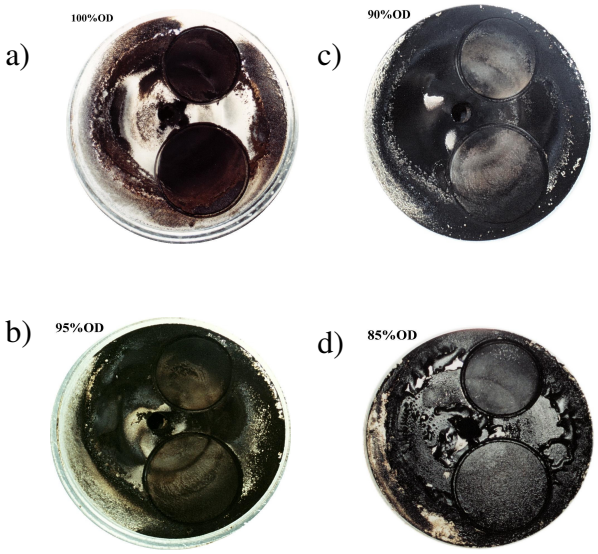


Figure 2.The cylinder head after 25 hours operation: (a) 0% water in OD, (b) 5% water in OD, (c) 10% water in OD, (d) 15% water in OD

4.1 THERMAL ANALYSIS, TG-DSC

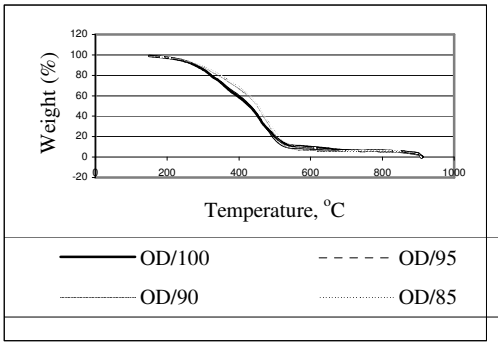


Figure 3 TG Analysis for OD Deposit under Dynamic Conditions and Air Purge

Figure 3 shows the deposits exhibit thermo-oxidative weight loss profile as temperature lifted under air atmosphere. In explaining the above trends, it is better to relate it to DSC profiles in figure 4, which had performed simultaneously with TGA. The transition from one thermal phenomena to another is typically indicated by a change in slope of the weight loss verses temperature curve and peak indicated from DSC plot. The change may not be able to be seen to the eye, but it can be studied by physical means such as in the DSC. DSC was applied for determining heat flows into or out of the sample between the deposit and the atmosphere and is advantageous to detect the degree of endothermicity or exorthermicity of a reaction. The upward peak indicates endothermic process while downward peak is exothermic. The positive peak at particular temperature means heat flows to the deposit for

volatilization of molecular weight compounds whereas at higher temperature heat was absorbed by deposit for thermal degradation by breaking of chemical bonds of large organic thermally unstable organic compound. For negative peak, it reflects oxidation or burning away of particular material at corresponding temperature by releasing heat out from the sample.

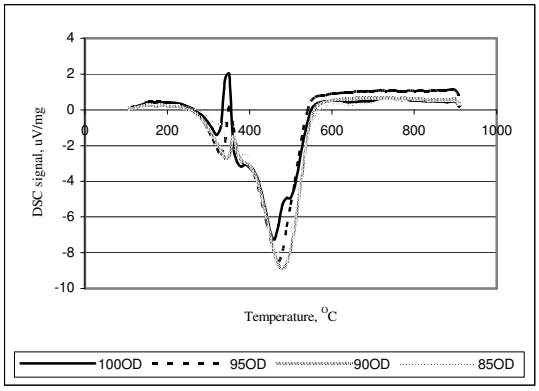


Figure 4 DSC Profiles of Diesel Carbon Deposit Derived from Diesel-water Emulsion with Varying Amount of Water

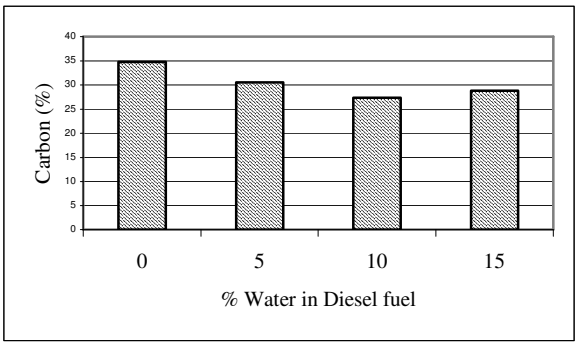
Figure 4 represents DSC curve due to the thermal-oxidative decomposition under air atmosphere. It indicates two main peaks, which resolved clearly on the plot. The first peak, which is the endotherm peak, designated thermal decomposition or pyrolysis, which occurred at maximum heat released at temperature range of 325-358ºC. Most of volatiles were liberated under this temperature region. This liberation of volatiles ends at the temperature range 377-385 ºC. The heating proceeded until the second peak appeared which is known as exotherm peak, which is due to thermal-oxidative decomposition that occurred at temperature range 459-476ºC. It was clear that, although devolatilization and deposit burning are not uniquely separated, devolatilization is essentially complete before the main burning peak temperature is reached. Hence, deposit oxidation is not a single event but it is a summation of concurrent consecutive reactions.In elucidating the succession peaks, it is better to look into a microscopic point of view. The initial weight loss from ambient to 200ºC can be attributed to the volatilization of moisture and largely unoxidized low and medium boiling hydrocarbons. As what can be seen in figure 3, further heating produces the broad endothermic DSC peak at 200ºC, which probably due to the volatilization of the high boiling oil fraction as well as partially oxidized fuel and oil components. Further heating resulted a distinct overshoot peak in the 300-400ºC regions and finally became weak as the amount of water increased. This is in agreement with weight loss profiles, which show slight deflection of curve and became diminished as the proportion of water increased. This was due to the thermal degradation process of polymeric components as well as the vaporization of highly oxidized hydrocarbons. Therefore, this conclusively demonstrated that most of the volatile came from the high-density hydrocarbon components since it exhibits large endothermic peaks.

The exortherm peaks were due to combustion of end volatile products known as fixed carbon. It is the measure of a solid combustible material in deposit after the expulsion of volatile matter [**12**]. The higher the fixed carbon content the higher the exortherm peak will be which indicates the amount of carbon being burnt. As above-mentioned, the complete devolatilization occurred at temperature between 377 to 385ºC. After this stage, the deposit has undergone ignition stage until it produced maximum temperature ranging at 459-476ºC. By focusing the exortherm peak, it can be said that the ignition of deposit has been described in just a few hundredths of a second with the onset of burning in less than half a second. Therefore, it can be concluded that, the degree of endothermicity of deposits reduced when water is added. There is a strong relationship between the degree of endothermicity and volatile content. For high volatile deposit, more heat is absorbed by deposit to liberate volatile fraction and thus would give high peak intensity while less volatile would give off low intensity peak

4. 2 TG AND ELEMENTAL ANALYSIS

Elemental analyses were obtained on four set deposits for C and H. The investigation has chosen to study on one aspect, which was C/H ratio, on deposits with varying amount of water. As illustrated in Figure 5, the elemental analysis of the deposits indicates carbon, and some amount of hydrogen mainly composes the deposits. This was in agreement with many statements claimed that engine deposits were primarily carbonaceous in appearance. The quantity of hydrogen content could reflect the weight loss exhibits by TG analysis in which the higher hydrogen contents would give larger weight loss would be [**7**]. The trend shows a decreasing order as the proportion of water in fuel increased. This conclusively demonstrated by TG result on thermo-oxidative decomposition where OD/100 decomposed much faster than other followed by OD/95, OD/90, and OD/85, which exhibit a trend.

Figure 6 represents the range of C/H ratio that is known as aromaticity. The aromaticity values are derived from density information and have not been experimentally verified. In fact, they are somewhat different than the true values. Nevertheless, the trends would be the same. The above trend shows the degree of aromaticity of deposits, which become less as the amount of water in fuel increased. OD/100, it indicates the highest C/H ratio followed by OD/95 and OD/90 but increased back for OD/85.



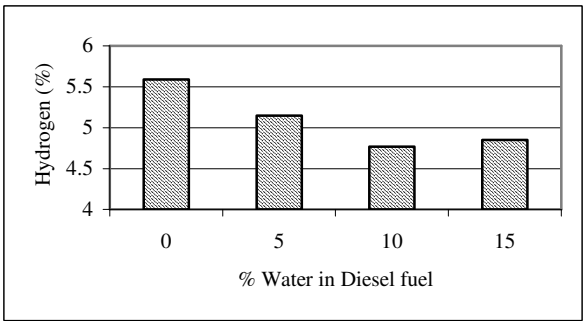


Figure 5 Percentage Carbon and Hydrogen in Diesel Carbon Deposits Derived from Diesel- water Fuel Containing Varying Proportion of Water.

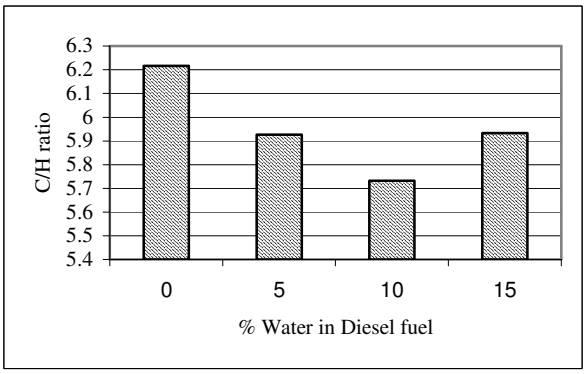


Figure 6 Degree of Aromaticity (C/H ratio) of Diesel Carbon Deposits

Since the aromaticity value reflects the density of deposit, there is also a correlation between aromaticity and deposit reactivity. In fact, aromaticity is a property of hydrocarbon having alternating single and double bonds between adjacent carbon atoms in a benzene-ring (C_6H_6) configuration. The unsaturated hydrocarbon identified by one or more benzene rings or by chemical behaviour is similar to benzene. Because of the multiple bonds, aromatics are usually more reactive and have higher solvency than paraffin's and naphthenes. This is in agreement with TG analysis, which OD/100 tends to decompose quickly, compared to fuel/water deposits. It was believed that more aromatic structures underwent decompositions by breaking off chemical bonding for high-density deposit and finally gives larger weight loss. This phenomenon reflects the stability of deposit to decompose. Therefore, it can be concluded that as the amount of water increases, less reactive deposits would be formed due to lower aromaticity. The water content in diesel reduced the aromaticity of fuel. As more aromatic occur in fuel, more aromatics are found in the deposit as evidence by elemental analysis.

4.3 FTIR ANALYSIS

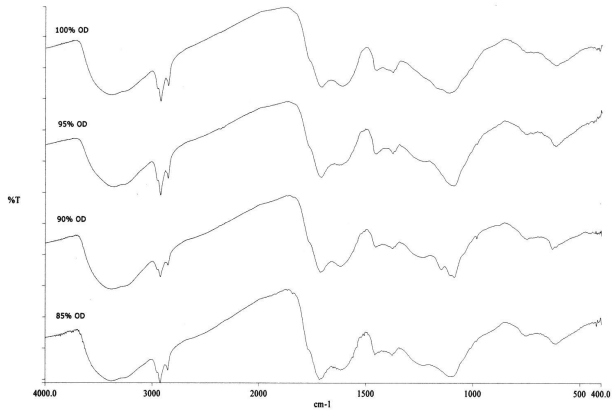


Figure 7 Infrared Spectra of Carbon deposit derived with various proportion of water

The infrared spectra of deposits display much detail, and suggest a variety of chemical functionality to be presented. Figure 7 demonstrate deposit samples that derived from four set of test fuel have shown similarity in terms of characteristics and chemical functionality. The most prominent band in the spectrum of every deposit is due to the carbonyl group. Infrared spectroscopy shows that the oxygen functionality includes ketones (possibly as anhydrides) and aryl and alkyl ethers. In terms of oxygen functionality, we may identify –OH (stretch at 3383 cm^{-1}), aromatic anhydride carbonyl (stretch at 1775cm^{-1}), other carbonyl C=O (stretch at 1715 cm^{-1}), and C-O (stretch at 1000-1250 cm^{-1}). Carbon-oxygen bonds are also believed to play a major role in establishing the intermolecular bonding forming the "polymeric" materials, which significantly contributed to the density of deposit [**13**]. In addition, the level of oxygen in the residue was expected for the inorganic ash (metal salts and oxides).The presence of –OH was probably due to the presence of sorbed water or primary amine (N-H bond) stretching (3497-3077cm^{-1}), which shared same absorbencies. The fact that the existence of amine functional group seems to be possible since the nitrogen atom may probably originate from the air that interfered in the combustion and finally made-up part of deposit. Other than oxygen functionality, the

spectrum also indicates stretching band peak at 2854 and 2924 cm^{-1}, which attribute to methylene and methyl groups. Next, the spectrums indicate ketones, aldehydes, carboxylic acids, lactones, acid halides, anhydride, amides, and lactams show a strong C=O stretching absorption band in the region of 1870-1540 cm^{-1}. In fact, useful characteristics group frequency bands often involve couple vibrations. This couple interaction, which attributed to ketonic carbonyl groups, resolved clearly at frequencies of 1715-1617cm^{-1}. It results from appreciable coupling is prevented by the intervening carbon atoms. Its relatively constant position, high intensity, and relatively freedom from interfering bands make this one of the easiest bands to recognize in IR spectra. These highly suggest that oxygen is one of the bundle elements, which composed the entire bulk of deposits. Obviously, when focusing at the absorbency range of 1160 to 1378 cm^{-1} for OD in figure 7, there is an increasing peak within such region as the amount of water increase in fuel. This might be attributed to some chemical transformation has occurred in the deposit. However, the problem with the IR spectra is the fingerprint region that is so cluttered for organic material to be able to make sense or identify the structure of compounds.

5. CONCLUSION

Combustion chamber deposits are complex materials, which are difficult to characterize. In spite of these difficulties, the investigation has expanded the description of the deposit. The appropriate combination of conventional techniques used for deposit characterization, like thermal analysis (TG-DSC) and thermal analysis with elemental analysis provide suitable results to establish differences between deposit materials. The TGA analysis shows that each deposit sample derived from test fuel with varying amount of water has unique thermal-oxidative characteristics, by virtue of the specific proportions of the fractions present in it. From the investigation, it is agreeable that the presence of water in diesel in the form of emulsion would increase the amount of deposit formation. This would definitely violate the intention of adding water to diesel fuel in order to reduce NOx since the increase of deposit thickness would act as blanket that could increase in-cylinder temperature. TGA can be used as a consistent method for relative degradation rating of engine carbon deposit, offering many advantages over the 'deposit rating method'.

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