Oxidation Behaviors of Gasohol Deposit

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Abstract

Nowadays, the costs of the fossil fuel have continuously increased. To survive from this problem, we need to find the new alternative energy sources to replace the fossil fuel. Ethanol fuel is focused. The side effect when using gasoline or blended ethanol fuel is the adhesion of carbonaceous deposits on the intake port wall will directly result to performance engine because they restrict air flow. Intake deposits have also been shown to affect exhaust emissions, particularly volatile organic compounds (VOCs) and oxide of nitrogen (NO_x). In order to investigate the chemical composition of deposit, scanning electron microscope with energy dispersive spectrometry (SEM-EDS) is used to study. The carbonaceous species of deposit may be in the form of C_xH_y for gasoline fuel, whereas the carbonaceous species may be C_xH_yO for blended ethanol fuel. The oxidation kinetics of deposit formed gasoline and blended ethanol fuel are studied by thermo-gravimetric analysis (TGA) and it can be also determined the activation energy for the reaction between deposit and oxygen. The apparent activation energy of deposit formed gasoline and E20 (gasoline 80% + ethanol 20%) fuel are 156 and 149 kJ/mol, respectively. As a result, the lower apparent activation energy of E20 deposit may be expected that there is oxygen molecular inside the deposit.

Keywords: Deposit, Thermo-gravimetric analysis, Activation energy.

1. Introduction

As gasoline price increases and the emissions of pollutant from the passenger cars or motorcycles into atmosphere are becoming more and more concern. Now, the alternative fuel plays an important role for lessening pollutant emissions from these cars and motorcycles.

Among alternative fuels, ethanol is one of fuels employed most widely. The reasons are in the followings. First, it is derived from the direct fermentation of sugars, fermentation of starches and cellulose after chemical or enzymatic pretreatment that can call bio-ethanol.

Secondly, ethanol (C_2H_5OH) is made up of a group of chemical compounds whose molecules contain a hydroxyl group (-OH) bonded to carbon atom; so, the oxygen content of this fuel favors the further combustion of gasoline [1-4].

Many researchers attempted to use ethanol and its blends with commercial gasoline fuel in an automotive gasoline engine. They found that the engine performances with ethanol and its blends with normal gasoline fuel were comparable to those of pure gasoline.

A lot of studies are needed to conduct in order to understand the properties and behavior of ethanol and its blended in the combustion chamber. One of the important studies is a basic research on deposition remains of fuel in engine. Carbon deposits mainly build up on many parts of engine such as injectors, intake valves and ports, and the combustion chamber. Intake valves and ports are subject to more deposit build up than fuel injectors because they operate at high temperature. Heavy valve and port deposits reduce maximum engine power because the restrict air flow [5].

In term of emissions, Intake valve deposits have also shown negative contribution emission of hydrocarbon (HC). It is believed that adsorption and desorption of hydrocarbons by the deposit is a mechanism that causes this undesirable increase in emission [5-6]. These effects are still not well known. Furthermore, different types of gasoline fuel have different properties and show different combustion behaviors. Thus, those fuel characteristics increase the possibility of increase deposit formation in engine.

In this study, deposit formed E0 E20 and E85 were selected for physical and chemical analysis which were used to be the basic information and compared with deposit from real engine in the next step. The basic physical and chemical characteristics have also been analyzed by scanning electron microscope with EDS attachment. The functional groups of the component in fuel deposits were analyzed by using Fourier transforms infrared (FTIR) spectroscopy which allows us to determine the impact of different types of fuel on carbon deposit formation. Furthermore, the oxidation behaviors of each deposit are investigated by using thermo-gravimetric analysis (TGA) technique.

2. Experimental

2.1 Hot surface deposition test

Deposit formation in the intake system of an engine is a complex phenomenon that cause various engine problem such as reduced engine performance, increased some kind of emissions and caused engine damage. To observe the deposit formation when using gasoline and ethanol blended fuel by using a simplified method which is referred to as the hot surface deposition test (HSDT). This HSDT is used to simulate and investigate deposit formation for gasoline and ethanol blended fuel instead of using the engine test.

The parameters for this test are five surface temperatures (150, 163, 175, 188 and $200^{o}C$) and percentage of ethanol (0, 20, 85 and

E0	E20	E85	E100

Fig. 1 Photograph of fuel deposits at surface temperature 200 ^{o}C for 10 hours test time

100%). The test time is 10 hours for all tests. Then after each tests, the surfaces are covered by fuel deposit, as exemplified Fig.1 shows the deposit formed by using gasoline, gasohol and pure ethanol on the surface when the surface temperature is 200 ^{o}C. Hence, the deposits generated on the surface during the tests have been to observe by microscopy to characterize the deposits morphology. Also thermal behavior and chemical analysis have been carried out.

2.2 Physical and chemical analysis

A range of analytical techniques are used to characterize and analyze the deposits generated on the hot surface deposition test.

## 2.2.1 Scanning electron microscope with x-ray dispersive energy analysis

The scanning electron microscope use to examine the morphology of the deposits is a JEOL JSM-6400 instrument couple with x-ray dispersive energy system for the chemical elements analysis.

2.2.2 Thermo-gravimetric analysis

The thermal and oxidation behavior of the deposit formed gasoline and gasohol fuel has been studied by thermo-gravimetric analysis (TGA).

For the thermal and oxidation analysis, the operating conditions are as follow: about 6 mg of samples are placed in an alumina pan, temperature increases at a rate of 10 ^{o}C/min from 50 ^{o}C to 800 ^{o}C under oxygen atmosphere. The thermal behavior of gasoline deposits is compared to the gasohol deposit (E20, E85). The measurement of the weight loss indicated the percentage in weight of volatile organic matters at 800 ^{o}C.

The chemical kinetics of each sample is assumed to be the chemical reaction between deposit and oxygen, as shown in Eq. (1). Amount of each deposit ash is can be observed by this method.

$$Deposit_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad (1)$$
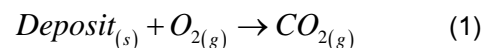
The calculation of kinetic data from TGA curve is based on the formal kinetic equation:

$$-\frac{d[M]}{dt} = k[M]^{n}[O_{2}]^{m} \qquad (2)$$

where:

[M]: the summation of number of remaining moles of carbon at each time step undergoing reaction

t: time

k: reaction coefficient

n: reaction order

The reaction coefficient k can be expressed by the Arrhenius equation:

$$k = Ae^{-\frac{E}{RT}} \qquad (3)$$

where:

A: frequency factor

E: activation energy

R: gas constant

T: absolute temperature

By substitution of Eq. (3) into Eq. (2) the following form of kinetic equation is obtained:

$$-\frac{d[M]}{dt} = Ae^{-\frac{E}{RT}}[M]^n[O_2]^m \qquad (4)$$

If the time step is set small enough we can assume that TGA curve is composed of very small linear segments of *dt* length at which the reaction rate is constant. The logarithmic form of the above equation gives:

$$\ln\left[-\frac{1}{[M]^n}\frac{d[M]}{dt}\right] = -\frac{E}{RT} + \left(\ln A + m\ln[O_2]\right) \quad (5)$$

E can calculate from the slope of a parametric plot of $\ln\left[-\frac{1}{[M]^n}\frac{d[M]}{dt}\right]$ vs. $\frac{1}{T}$. The last term on the right-hand side of Eq. (5) is a function of the overall frequency factor and it is assumed to be a constant. In order to be easy for calculation, the reaction order is assumed to be 1 [9-14].

2.2.3 FT-IR spectroscopy

The gasoline, E20 and E85 deposits were investigated with a Perkin Elmer FT-IR spectrum GX, within the range 400-4000 cm^{-1}.

Each FT-IR spectrum was the result of 10 co-added scans at a nominal resolution of 4.0 cm^{-1}. A mixture of solid samples and KBr pellets were pressed into wafers and they were used for the recording data.

3. Result and discussion

3.1 Chemical elements

The chemical elements in the deposits and identified by EDX may be divided into three groups: (I) the first group includes the main elements detected (carbon and oxygen); (II) the second group contains the fuel additive elements detected (sodium, silicon, aluminum, iron, calcium and zinc) and (III) the third group includes contamination elements (chlorine), which is considered ethanol solves the component of fuel tank. The chemical elements of each fuel deposits show in Table 1.

3.2 Reaction characteristics

The thermo-gravimetric analysis (TGA) curves of the deposits obtain under oxygen atmosphere are shown in Fig. 2. In this figure, the TGA curves may be divided into three regions.

In the first region, from 50 $^{\circ}$C to 100 $^{\circ}$C, it can be considered the evaporation of water molecules. In this region, the weight of deposit is decreased 1.5%. In the second region, from 100 $^{\circ}$C to 440 $^{\circ}$C, that is assumed to be hydrocarbon oxidation. In this region, the weight of deposit is decreased 46-89%. In the third region, from 440 $^{\circ}$C to 550 $^{\circ}$C, that is assumed to be carbon oxidation. In this region, the weight of deposit is decreased 1-46%. Above 550 $^{\circ}$C, thermo-

gravimetric curves attain another equilibrium

Table 1 Chemical element of each fuel deposits.

level, where residual are metallic salt, fuel level,

Fuel	Element (%)									
deposit	C	O	S	Na	Al	Si	Cl	Ca	Fe	Zn
E0	71.76	27.99	-	0.15	0.05	0.04	-	-	-	-
E20	62.97	36.33	0.05	0.56	0.05	0.03	-	-	-	-
E85	62.67	32.72	0.28	0.74	0.05	2.87	0.10	0.10	0.11	0.36

where residual are metallic salt, fuel additive and ashes.

Fig. 3 shows the derivative curves of each fuel deposits. It is clearly observed the reaction rate of deposit can be divided into 3 regions. In the first region (50-100 $^{\circ}$C), there are not significant different among 3 fuel deposits because of evaporation of water molecules. In the second region (100-400 $^{\circ}$C), E85 deposit can rapidly oxidized due to high percentage of oxygen in this fuel, in the other hand; there is no oxygen in E0 deposit in this region. Thus, the reaction rate of E85 deposit is higher than E0 and E20 deposits. In the third region (440-550 $^{\circ}$C), correspond to the oxidation of carbon component. Due to E85 deposit has low carbon component when comparison to E0 deposit, thus, it can observer the low reaction rate of E85 deposit in this region but reaction rate of E0 and E20 deposits can clearly observe.

Fig. 4 shows the calculation of activation energy of E0 deposit by using the chemical reaction, reaction rate and Arrhenius as shown in Eq. (1) to Eq. (5), respectively. This result shows the oxidation reaction can be divided into three regions.

In the first region, as shows in the blue line (250 to 341.7 $^{\circ}$C), the activation energy is 56 kJ/mol, which is the beginning of the reaction.

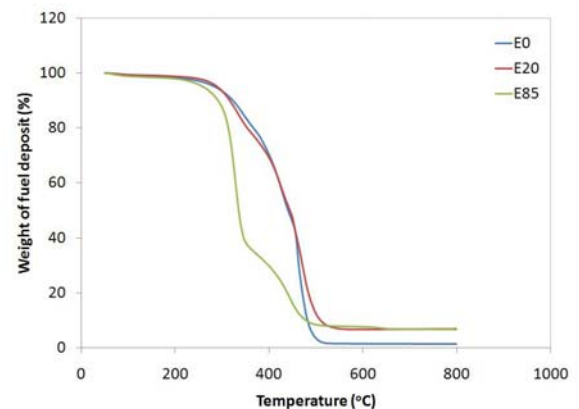It can attribute to the low molecular weight product in E0 deposit.

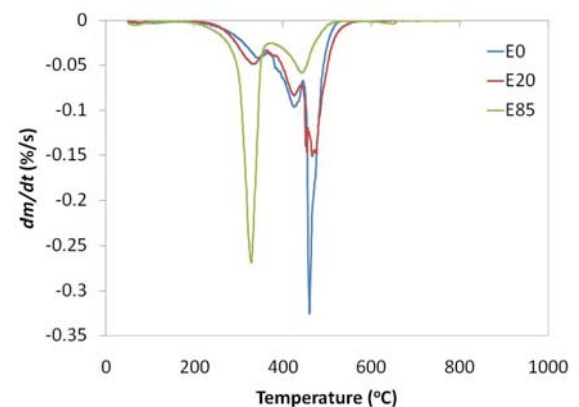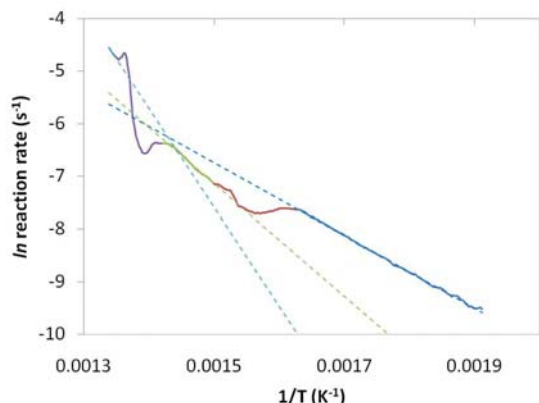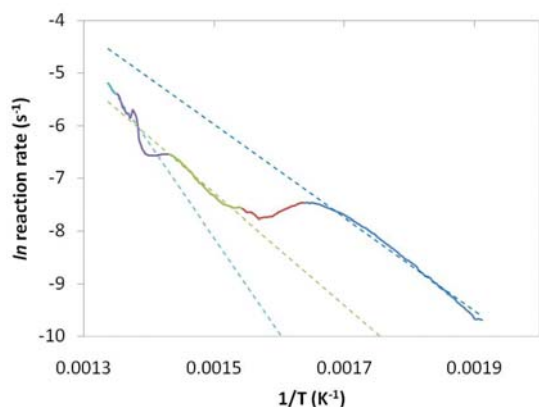Fig. 2 TGA curves of the fuel deposits under oxygen atmosphere

Fig.3 Derivative curves of fuel deposits under oxygen atmosphere

In the second region, shows as the green line (395 to 430.8 $^{\circ}$C), the activation energy is 89 kJ/mol. In the third region, shows
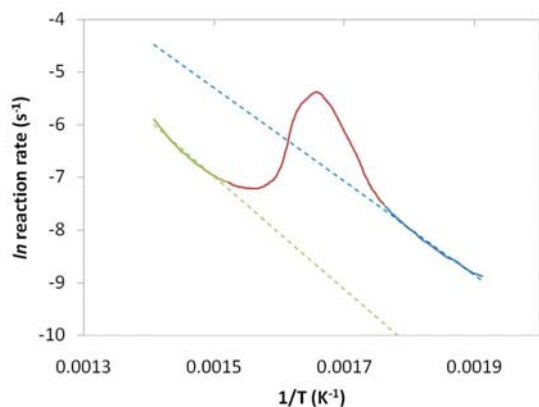
as the cyan line (471.7 to 474.2 $^{\circ}$C), the activation energy is 156 kJ/mol. It can attribute

(a)

(b)

(c)

Fig. 4 Arrhenius plot for calculation of activation energy of reaction between deposit and oxygen by using TGA technique (a) E0 deposit, (b) E20 deposit and (c) E85 deposit

In case of the calculation of activation energy of E20 and E85 deposits are similar to

to the reaction between carbon and oxygen.

that of E0 deposit. The result of these energy shows in table 2.

For oxidation of E0 deposit uses the highest activation energy when compare to E20 and E85 deposits. Because of oxygen molecular inside E20 and E85 deposits, thus, deposits form E20 and E85 fuel are easier to oxidize compare to that with gasoline fuel.

Table 2 Activation energy of each fuel deposits

Fuel deposit	E_a (kJ/mol)		
	250-341 $^{\circ}$C	395-430 $^{\circ}$C	471-474 $^{\circ}$C
E0	57.4	88.8	156.3
E20	73.3	88.5	149.9
E85	73.9	88.8	-

3.3 Chemical characterization of the deposits

Infrared spectra of the deposits (Fig. 5) show similar absorption band, but with varying intensities depend on the sample and severity of the test.

For these three samples, the bands are found at similar position. The band at 3440 cm^{-1} region for E85 deposit sample shows strong intensity indicates the presence of a large amount of O-H group [7-8]. In case of E20 deposit, this band is weaker intensity than E85 deposit. That means the amount of O-H group in E20 sample is lower than E85 sample. For gasoline deposit, the band of O-H group does not show. Deposits obtain from each fuel present intense IR bands between 2920 cm^{-1}-2950 cm^{-1} and 1365 cm^{-1}–1467 cm^{-1}. These bands are attributed to characteristic of the

vibration of C-H group [7-8]. The bands at 1700 cm^{-1} region are attributed to C=O carbonyl vibrations of oxidation products. The bands at 1103 cm^{-1}-1116 cm^{-1} are attributed to stretching vibration of C-O. Moreover, the bands at 1103 cm^{-1}-1116 cm^{-1} indicate the oxidation of fuel deposit [8].
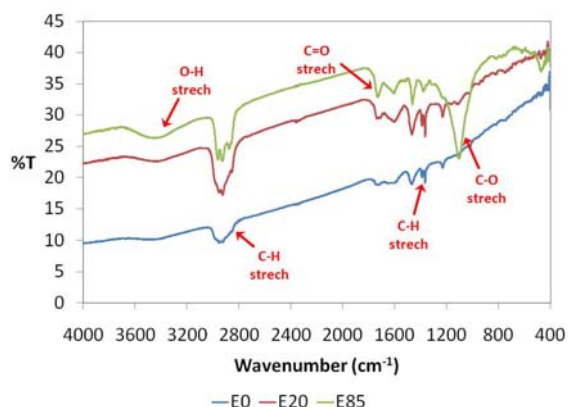

Fig. 5 Infrared spectra of gasoline, E20 and E85 deposits

4. Conclusion

The analytical techniques are used to characterize and analyze in deep detail for the physical and chemical characteristics of fuel deposits for better understanding.

1) SEM/EDX analysis shows chemical elements containing in the fuel deposits. The main elements are carbon and oxygen. The carbonaceous species of deposit may be in the form of C_xH_y for gasoline fuel, whereas the carbonaceous species may be C_xH_yO for blended ethanol fuel.

2) The thermal and oxidation behavior of deposits are analyzed by thermo-gravimetric analysis. They can be divided into 2 major groups, hydrocarbon and carbon. E85 deposit is easier to oxidize than E0 and E20 deposits.

Moreover, the total activation energy of deposit formed E0 is higher than that of E20 and E85. Because of the oxygen molecular inside the E20 and E85 deposits, even though gasohol ash larger than that of gasoline.

3) FTIR analysis can confirm the presence of alkyl groups, aromatic rings and the oxygen molecular inside carbon deposit.

5. Acknowledgement

6. References

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