

Effects of High Boiling Point Fuel Additives on Deposits in a Direct Injection Gasoline Engine

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ABSTRACT

The effects of high boiling point fuel additives on deposits were investigated in a commercial turbocharged direct injection gasoline engine. It is known that high boiling point substances have a negative effect on deposits. The distillation end points of blended fuels containing these additives may be approximately 15°C higher than the base fuel (end point: 175°C). Three additives with boiling points between 190 and 196°C were examined: 4-tert-Butyltoluene (TBT), N-Methyl Aniline (NMA), and 2-Methyl-1,5-pentanediamine (MPD). Aromatics and anilines, which may be added to gasoline to increase its octane number, might have a negative effect on deposits. TBT has a benzene ring. NMA has a benzene ring and an amino group. MPD, which has no benzene ring and two amino groups, was selected for comparison with the former two additives. The base gasoline was a Toyota in-house premium grade test gasoline with properties in the range defined by the Japanese Industrial Standards (JIS) (RON: approximately 100) with no detergent content. Test gasolines were prepared by blending the base gasoline with 10% of each additive by volume. The concentration of the additives was set to 10% to accelerate deposit formation. The engine operating conditions for examining deposit formation were an engine speed of 1,600 rpm and medium load. Deposit formation was examined over a period of 30 hours, after which the fuel consumption was approximately 200 L. It was found that amino group additives caused large increases in deposits. Compared to the base gasoline, the piston top deposits were about twice as thick with the TBT blend and about four times as thick with the NMA blend. The MPD blend caused compression leakage after fuel consumption of 10 L because the piston rings stuck to the grooves. Chemical analysis of the deposit formation mechanism suggests that deposits were formed by high boiling point polar substances that penetrated into the quenching zone near the combustion chamber surfaces, and then oxidized, polymerized, or carbonized, and adhered to the surfaces.

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INTRODUCTION

Deposits in an internal combustion engine decrease engine performance and worsen emissions. This paper describes the effects of high boiling point additives on engine deposits, particularly in the combustion chamber of turbocharged direct injection (DI) gasoline engines that are steadily becoming more prevalent in the market.

Kalghatgi [1] and Shu et al. [2] reviewed that combustion chamber deposits (CCD) decrease engine performance and worsen emissions even in modern engines with relatively low oil consumption. However, the formation mechanism of these deposits could not be fully explained. Watanabe et al. [3] found that changes in emissions due to CCD was affected by the distillation characteristics of the fuel, and that fuels containing high boiling point components resulted in greater deposit formation. Noma et al. [4-5] performed tests using a DI gasoline engine and found that CCD increased when both the concentration of aromatics in the fuel and the T90 distillation temperature was high. Cheng [6] fabricated a deposit sample probe to examine in-cylinder deposits in more detail. This study reported that

porous body deposits were formed from high-viscosity liquids created by the temperature curve between metallic surfaces and hot combustion gases. In a separate report [7], the same author concluded that the coolant temperature, air-fuel (A/F) ratio, and boiling point of the fuel had major effects on deposit formation. Uehara et al. [8] and Esaki et al. [9-10] developed an analysis method to identify the CCD formation mechanism. This method found that deposits were caused by aromatics in fuel, but that aromatics were necessary to increase the octane number. It was reported that aromatics could be reduced by increasing the alkylate content of the fuel. The CCD deposit formation mechanism in a gasoline engine was identified as follows: substituent groups of aromatic components in gasoline are oxidized at high temperatures and pressures in the quenching zone outside the flame region, and then polymerized via these polar groups. This process was reported as making a large contribution to CCD formation. Owrang et al. [12] stated that fuel might have only a minor effect on deposit formation in some cases. This research found that engine oil is the predominant cause of deposit formation and that fuel does not have the closest correlation to deposits. Marie et al. [13]

confirmed from the results of lubricating oil sludge tests that sludge formation increased when N-methyl-aniline (NMA) was present. Martin et al. [14] investigated the effects of polar components in gasoline containing NMA on deposits in the intake system. After studying the effects of these fraction components at 190°C or more, this research concluded that the lack of polar components had no effect on deposit formation. However, in this case, the NMA content in the fuel was low (between 0.1 and 0.2%) and the study was limited to deposits in the intake system.

In summary, the reports described above found that high boiling point aromatics have an adverse effect on deposit formation, but that the effects of polar substances are not clear. For this reason, the research describes in this paper below aims to identify the effects of aromatics and polar substances on deposits. Test fuels were prepared by blending a base fuel (a Toyota in-house premium grade test gasoline with properties in the range defined by the Japanese Industrial Standards (JIS)) with no detergent content, a maximum sulfur content of 10 ppm, and a distillation end point of approximately 175°C) with one of three high boiling point (190 to 196°C) additives to a volume of 10%. The effect of these test fuels on deposit formation was then examined. The high additive concentration (10%) was set to accelerate deposit formation. Two of the selected additives are an aromatic and an aniline that may be added to gasoline to increase its octane number and might have a negative effect on deposits. The third additive, which is not an aromatic and has more amino groups, was selected for comparison with the former two additives. The three additives were as follows: a C11 aromatic hydrocarbon called 4-tert-butyltoluene (TBT), NMA (a polar substance with a benzene ring and amino group), and 2-Methyl-1,5-pentanediamine (also referred to as 2-methylpentamethylenediamine or C6 diamine, and abbreviated as MPD), which has no benzene ring and two polar amino groups. Deposit formation from the intake manifold to the inside of the combustion chamber was investigated using the analysis method described by Esaki et al. [9, 10, 11]. Deposits in the combustion chamber, which are greatly affected by the fuel content, were studied by analyzing the functional group distribution within the deposit cross-section, focusing on the deposits at the piston top.

This paper discusses the deposit formation mechanism based on these results. The results found that the deposits accumulated in layers. This study used low-calcium (Ca) engine oil for turbocharged gasoline engines [15], which was found to adhere in large quantities to deposit surfaces when the engine is started or stopped. The analysis suggests that deposits were formed by high boiling point polar substances that penetrated into the quenching zone near the combustion chamber surfaces, and then oxidized, polymerized, or carbonized, and adhered to the surfaces.

DETAILS OF TESTS

Test Engine

Table 1 shows the specifications of the commercial 2-liter turbocharged engine used for the tests. A combustion pressure sensor was attached to cylinder No. 4 to monitor the pressure inside the cylinder.

Table 1. Engine specifications.

Combustion Type	Direct Injection Spark Ignition
Type	Inline 4-Cylinder
Displacement (cm ³)	1998
Bore (mm)	86
Stroke (mm)	86
Compression ratio	10:1
Valve Timing	Variable
Intake System	Turbocharged

Deposit Formation Operating Conditions

Table 2 shows the operating conditions adopted to facilitate deposit formation. The valve timing used the Atkinson cycle to create conditions under which large amounts of combustion gas are blown back into the intake manifold. Stoichiometric A/F ratios were adopted and the ignition timing was set to the minimum advanced spark timing for the best torque (MBT) for the base fuel (fixed at 25.5 degrees before top dead center (BTDC)). Fuel injection was restricted to DI only using a fan-shaped fuel spray from the side. The port injector was not used for fuel injection and was attached just to observe the deposits formed by the blowback gas to the intake manifold. The tests were performed under wide open throttle (WOT) and closed wastegate conditions. Engine torque output was approximately 110 Nm (brake mean effective pressure of approximately 0.7 MPa). The engine was warmed up from room temperature and then switched to the deposit formation operating conditions. Each test was performed for 2.5 hours and the emissions (total hydrocarbons (THC), carbon monoxide (CO), nitrogen oxides (NOx), and smoke) were measured at 15-minute intervals. The engine was then cooled down and stopped. This cycle was repeated twelve times, resulting in a total deposit formation operating time of 30 hours. An automated driving function of the open real-time intelligent optimization network (ORION) was used to ensure constant operating conditions from engine start to stop.

After the 30-hour operating period, the engine was disassembled, photographs were taken, and deposit samples obtained. Subsequently, combustion-related parts positioned above the connecting rods except the cylinder head and cylinder block were replaced with new parts. The parts that were replaced included the pistons, piston rings, direct injectors, port injectors, intake valves, exhaust valves, valve stem seals, and valve springs. The cylinder head and cylinder block were repeatedly cleaned to remove the deposits. After completing this maintenance, the engine was re-assembled and the oil replaced with fresh oil. After breaking in with a Toyota in-house premium grade test gasoline with properties in the range defined by JIS, containing detergent (this fuel is different from the base fuel), engine data related to spark timing sensitivity was measured close to the deposit formation operating conditions to verify that the engine operation

was normal and unchanged from the base performance. The oil was then changed again. These breaking in and oil replacement steps were also carried out before the start of the first test.

Table 2. Engine operating conditions.

Engine Oil	SAE 0W-20 for Turbocharged Gasoline Engine
Air-Fuel Ratio	Stoichiometric
Intake Valve Open (° BTDC)	-26
Intake Valve Close (° ABDC)	90
Exhaust Valve Open (° BBDC)	22
Exhaust Valve Close (° ATDC)	48
Intake Temperature (° C)	38
Engine Speed (rpm)	1600
Direct Fuel Injection Pressure (MPa)	20
Injection Start Timing (° BTDC)	315
Spark Timing (° BTDC)	25.5
Throttle & Wastegate	WOT & Closed Wastegate
Coolant Temperature (° C)	88
Oil Temperature (° C)	95

Engine Oil

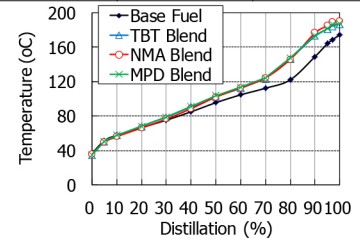
The tests used low-Ca specification engine oil for turbocharged gasoline engines (SAE grade: 0W-20). As described above, the engine oil was replaced twice each time the fuel was changed.

Test Fuel Preparation

Table 3 shows the properties of the four test fuels used in this study. The first fuel is a Toyota in-house premium grade test gasoline with properties in the range defined by JIS with no detergent content. The test fuels were prepared by blending this base fuel with one of three high boiling point (190 to 196°C) additives to a volume of 10%. The first additive was TBT, a C11 aromatic hydrocarbon. The second additive was NMA, which is a polar substance with a benzene ring and amino group. The fuel blended with NMA had an extremely high research octane number (RON) of 106, which demonstrates the significant octane number improvement effect of this additive. The third additive was MPD, which has two polar amino groups and no benzene ring. These three blended fuels are abbreviated as TBT, NMA, and MPD blends in this paper. The high volumetric concentration (10%) of the blends was selected to accelerate deposit formation, and was adopted to help shorten the time in which the fuel additives affect deposit formation. As shown in Table 3, the distillation end point of the blended fuels containing these high boiling point additives, was approximately 15°C higher than the base fuel. The four fuels were tested in the following sequence: NMA blend, base fuel, TBT blend, and MPD blend.

Table 3. Test fuel properties.

Fuel	Base	4-tert-Butyltoluene (TBT) 10 Vol. %	N-Methyl Aniline (NMA) 10 Vol. %	2-Methyl-1,5-pentanediamine (MPD) 10 Vol. %
Density (g/cm ³)	0.7521	0.7625	0.7742	0.7613
RVP (kPa)	51.1	50	53.1	52.5
IBP (°C)	36.6	34.7	35.8	34.9
T10 (°C)	51.4	57.8	49.9	57.8
T50 (°C)	95.6	102.6	102.3	103.8
T90 (°C)	149.1	173.5	176.1	173.7
EP (°C)	174.4	186.8	190.0	187.4
H/C	1.766	1.732	1.710	1.844
Nitrogen (m/m)	-	-	0.0167	0.0274
RON/MON	99.4 to 99.3/87.1 to 86.9	100.8/88.1	106/90	-
LHV (MJ/kg)	42.44	42.68	41.83	41.13
Sulfur (ppm)	6			
Aromatic (Vol. %)	35.7 to 36.1			
Olefin (Vol. %)	16.5 to 18.2			
Oxygen (Mass %)	0.1 (-)			
Existent Gum (mg/100mL)	0			



Analysis Methods for Deposits

Bulk deposits were sampled from metallic surfaces and analyzed chemically by transmission micro Fourier transform-infrared spectroscopy (FT-IR) as well as thermogravimetrically by thermogravimetric-differential thermal analysis (TG-DTA). The thermal decomposition properties were analyzed using pyrolysis gas chromatography-mass spectroscopy (PGC-MS). The analysis used the method described by Esaki et al. [9, 10, 11]. The thickness of the deposits on the piston top surface was measured at twelve positions using a calibrated eddy current gap sensor. Scanning electron microscopy (SEM) and imaging infrared (IR) (Attenuated Total Reflectance (ATR) imaging) were used to observe and analyze cross-sections of the deposits from the piston top.

RESULTS

Changes in Engine Conditions Due to Deposit Formation Operating Conditions

The test engine was operated under deposit formation conditions after changing from the fuel used to break in the engine to the test fuel. In most cases, the deposit formation operation phase started automatically, and ran without any concerns for a total of 30 hours (twelve 2.5-hour cycles). The total fuel consumption in this 30-hour period was approximately 200 L.

However, an issue occurred after the test fuel was changed to the MPD blend. Immediately after changing to the MPD blend, starting the deposit formation operating conditions, and obtaining stable torque output of approximately 110 Nm, the pressure in the crankcase began to rise. Normally, this pressure is negative. However, in the case of the MPD blend, the crankcase pressure became positive and torque fell when the pressure exceeded several kPa. This was diagnosed as an engine abnormality and the test was stopped. After confirming the engine condition and restarting the test, the pressure inside the

crankcase rose again. The test was stopped once more when the pressure exceeded 5 kPa. Subsequently, the fuel was changed back to the fuel used for breaking in to examine the effects of the fuel. In this case, only the fuel was changed, not the oil. With the fuel used for breaking in, the engine gradually returned to its condition before the MPD blend was used. With the replacement fuel under the deposit formation operating conditions, the pressure inside the crankcase fell to around 0 kPa, and torque did not decrease. This result confirmed that the issue was caused by the fuel. When the fuel was changed back to the MPD blend, injection abnormalities inside the direct injectors resulted in large torque fluctuations. These torque fluctuations were resolved by increasing the injection pressure to 20 MPa. Subsequently, the pressure increase inside the crankcase and the reduction in torque with the MPD blend were observed. Figure 1 shows the time history of the engine data under these final operating conditions.

These graphs show the results of engine operation when the torque demand was changed from 70 Nm to 90 Nm at the engine speed of 1600 rpm. Although engine operation was stable at 70 Nm, changes occurred when the torque was increased to 90 Nm. The spark timing was changed by the engine control (torque demand operation). At a constant A/F ratio, no major changes were observed in THC emissions other than a gradual drop as the engine parts warmed up due to the increase in load. The exhaust pressure and temperature also did not change greatly. This supports the premise that no major changes in combustion or significant inflow of oil into the combustion chamber occurred. Over time, the pressure inside the crankcase increased and engine operation became unstable. Torque fell once the crankcase pressure exceeded 4 kPa. Then, the engine performed an emergency stop since the crankcase pressure exceeded the safety standard of 10 kPa. At this point, a total of around 10 L of the MPD blend had been consumed. After stopping, the engine was disassembled and the deposits sampled. This engine test found that MPD may cause significant issues in engines at a concentration of 10%.

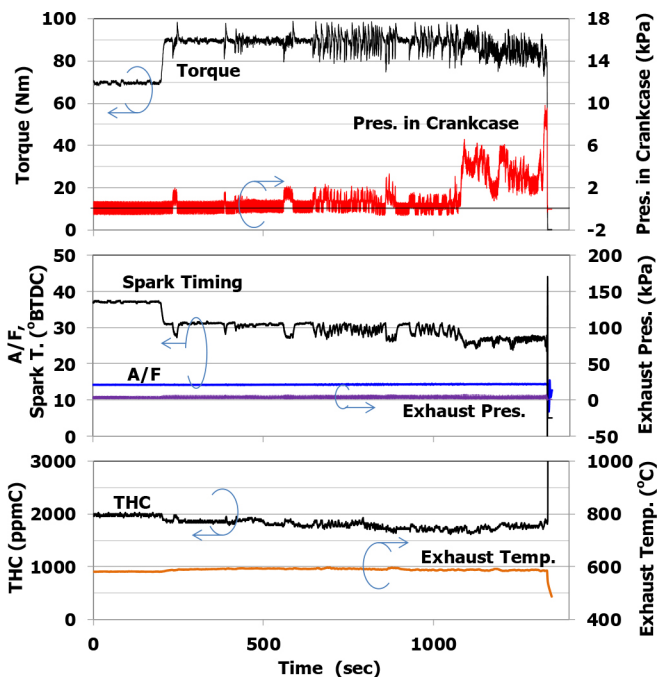


Figure 1. Time history of engine data with MPD blend.

Engine Exhaust Emissions

Figure 2 compares the emissions characteristics and maximum combustion pressures (Pmax) with each fuel under the deposit formation operating conditions. NOx increased due to the generation of fuel NOx in the fuels containing nitrogen. No major changes in CO occurred between the fuels. Compared to the base fuel, the THC level increased slightly with the blended fuels in the following order: TBT, NMA, and MPD blends. Over time, the changes in NOx and THC became larger, which is thought to be due to the effects of the increase in deposits. Although smoke was also measured, it rarely exceeded a filter smoke number (FSN) of 0.1, and generally remained between FSN 0 and 0.05. As described above, engine operation could not be continued under deposit formation conditions with the MPD blend. However, increases in smoke were not observed up to when the compression leakage occurred.

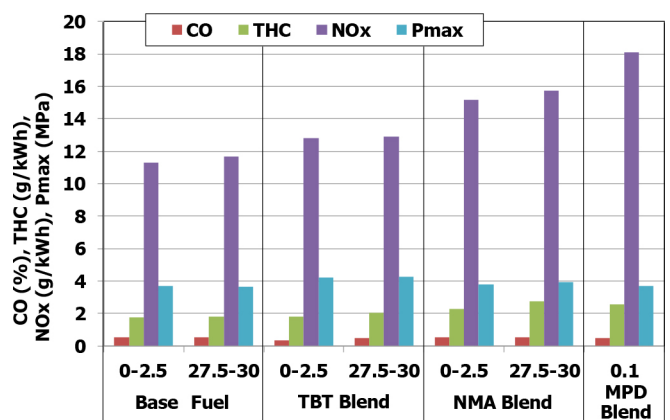


Figure 2. Comparison of emissions and cylinder pressures for each fuel (horizontal: deposit formation operating time (hours) and fuels)

Deposit Observation Results after Deposit Formation Operation

Figure 3 shows photographs of the areas around the direct injectors and piston after the test engine was operated under the deposit formation conditions. These photographs show the results after 30 hours of operation (fuel consumption: approximately 200 L) with the base fuel, TBT blend, and NMA blend, but only after an extremely short operating time (fuel consumption: approximately 10 L) with the MPD blend. Deposits with the TBT blend were slightly higher than with the base fuel. With the NMA blend, deposits increased further to the extent that the outline of the direct injector can no longer be seen clearly. In contrast, use of the MPD blend resulted in large amounts of deposits around both the direct injector and piston. The piston rings are pushed into the ring grooves and do not protrude to the outside. This sticking of the piston rings caused the compression leakage, which led to the increase in pressure inside the crankcase and the decrease in torque.

The following analysis focuses on the base fuel, and the TBT and NMA blends after 30 hours of operation.

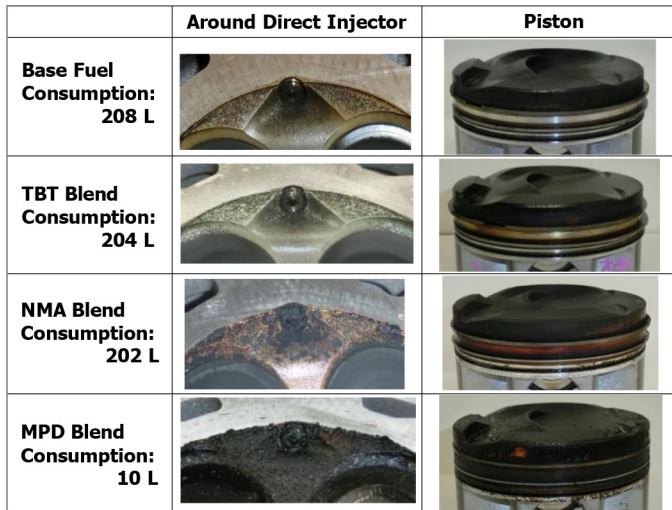


Figure 3. Comparison of deposits around direct injector and piston for each fuel.

Thickness of Piston Top Deposits

Figure 4 compares the thickness of the deposits at the piston top with each of these three fuels. The deposit thickness at the piston top was measured at twelve positions, starting from position (1) at the exhaust valve side and extending to position (12) at the intake valve side. Position (12) is the closest to the direct injector. Excluding the deposits at position (1), which is thought to be due to the effects of oil moving upward, the deposits were thicker closer to the direct injector. The increase in thickness in deposits close to the side injection direct injector agrees with the results identified by Watanabe et al. [5], despite the different injection pressure and piston cavity shape. The broken red lines show the average thickness of the twelve measurement positions. The average deposit thickness with the TBT and NMA blends was twice and four times that with the base fuel, respectively. Therefore, it can be concluded that high boiling point aromatic hydrocarbons increase deposits, and that NMA, an aromatic with a high boiling point and amino group causes a substantial increase in deposit thickness.

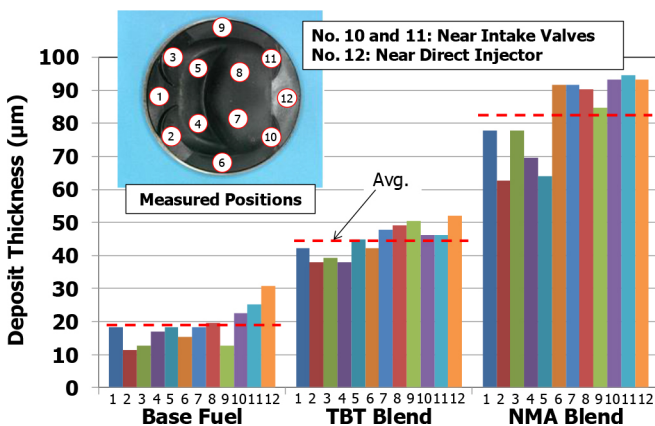


Figure 4. Thickness of piston top deposits.

TG-DTA on Deposit Bulk

The deposits were heated under atmospheric conditions and the reduction in mass and thermal changes were observed. Figure 5 shows the TG results.

At the piston top, deposit formation with the base fuel was affected roughly equally by oil (oil additives + oxidized organic products + residual components = 50%) and fuel (volatile components + soot = 50%). With the TBT and NMA blends, fuel was judged to have a larger effect than oil due to the high soot content of the deposits (70%) and the lower level of residual components after heating. These results suggest that the deposits are thick and thermally insulating, and that the deposit surfaces have a higher temperature. The upper portion of the intake valve head was analyzed. Here, the soot content was relatively low and the amount of base oil additives was high. The high oil level is probably due to the effects of oil dropping down from the valve. On the cylinder wall close to the direct injector, the soot content also decreased and the amount of oil additives increased slightly. The results around the spark plug were similar to the results near the intake valve.

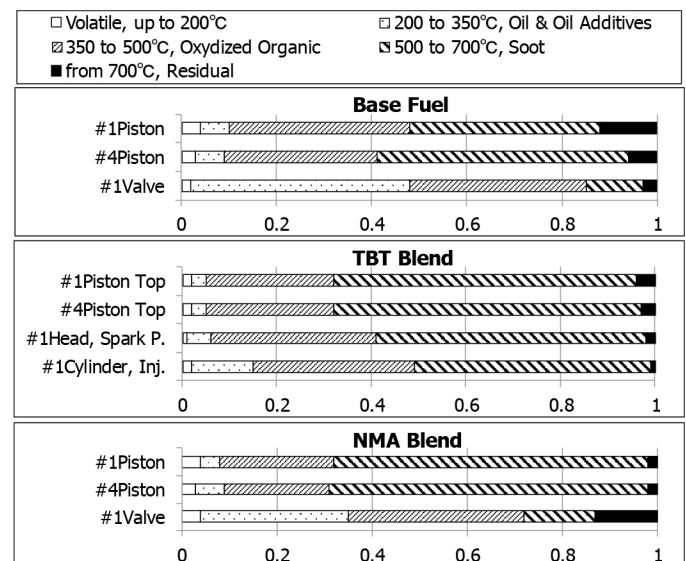


Figure 5. Results of TG on deposits.

Therefore, it is concluded that piston top analysis is an effective means of examining the effects of fuel on deposit formation, which is the main objective of this research.

Transmission Micro FT-IR on Deposit Bulk

Figure 6 shows the results of FT-IR analysis performed on the deposits sampled from each position. The absorbance ratio is on the vertical axis. The reference wavenumber is $1,600\text{ cm}^{-1}$ since this shows the polymerization of benzene rings. The “hill” portions of the piston top refer to positions (3) and (4) from Fig. 4, and the “cavity” portions refer to positions (7) and (8).