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A Study on the Reduction of Cold Start Hydrocarbon from Gasoline Engines Using Hydrocarbon Adsorbers

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Experiments were carried out to investigate the characteristics of the hydrocarbon (HC) emissions and to reduce cold start hydrocarbons in gasoline engines. An HC adsorber was, used and it coated was by Pd/Rh catalyst with zeolite on a honeycomb monolith. The HCs were efficiently trapped at temperatures below 100℃ by physical adsorption. After adsorption, they were reduced gradually by the catalytic oxidation of Pd/Rh catalysts as the adsorber temperature increased above 100℃. Increasing amounts of methane, ethylene and n-butane were emitted as the fuel-air mixture became richer and the engine speed decreased. As the temperature of adsorber increased, high-number carbons into low-number carbons. Thus, the C4 concentration decreased significantly during the first 30 seconds, and the C2 concentration increased continuously.

Key Words : Gasoline Engine, Emission, Catalyst, Warming Up, Hydrocarbon, Adsorber, LEV(Low Emission Vehicle)

1. Introduction

The worldwide trend toward stricter emission regulations will continue in the coming years because ozone formation by photochemical reactions in the atmospheric air is directly related to NOx and reactive organic gases contained in the vehicle exhaust hydrocarbons. Strong emphasis on further reduction of the HC emissions, or NMOG (Non-Methane Organic Gas), in the LEV (Low Emission Vehicle)-Ⅱ emission standards has been recently introduced by the California Air Resources Board (CARB, 1998).

Significant portions of the total pollutants are emitted during the first stage after the start-up of an engine. During this time both the engine and the exhaust system are cold, therefore, the catalytic converter does not efficiently operate until its temperature reaches a minimum value of alrent 300℃ (Engler et al., 1993). In addition, the engine is operated with a fuel-rich mixture to maintain vehicle drivability. Hydrocarbons emitted during the first two minutes of the FTP-75 test amount to 80% of the total hydrocarbons emitted during the entire test duration of over 30 minutes (Choi et al., 1998; Shin, 1997).

Close-Coupled Catalyst(CCC) (Choi et al., 1998), Electrically Heated Catalyst(EHC) (Mizuno et al., 1994) and In-line Hydrocarbon Adsorber) (ILA) (Buhrmaster et al., 1997) have been developed to reduce cold start emissions. However, thermal deactivation due to the exposure to the high temperature exhaust gas may take place in CCC. Also the EHC system consumes additional electric power, and its supplementary cost is high. The use of an adsorbent bed such as a hydrocarbon trap (Engler et al., 1993; Buhrmaster et al., 1997) has been investigated in previous studies. Nevertheless, studies have not been done on the reduction characteristics of individual

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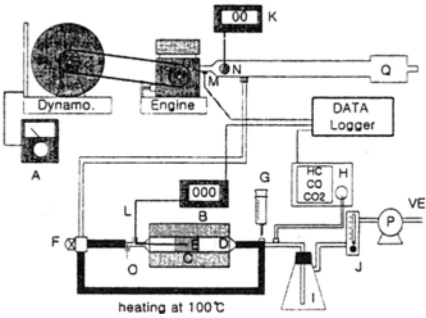
hydrocarbons. Therefore, in this study, experiments were carried out to investigate the reduction characteristics of total hydrocarbon (THC) and of light individual hydrocarbons (LIHCs) on the HC adsorber.

2. Experiment and Procedures

2.1 Experimental setup

The experimental setup is composed of a gasoline engine coupled to an engine dynamometer, a preconditioning apparatus for sampled HC, and an analyzing device as shown in Fig. 1. The dynamometer is an air-cooled eddy current type, and has a maximum absorption capacity of 10 PS. The engine is an 197cc single cylinder engine with a carburetor type fuel system. The preconditioning apparatus is an electric furnace that maintains a constant sampled gas temperature. HC adsorber catalyst is fitted in a quartz tube within the furnace. The vacuum pump controls the exhaust gas flow rate through a needle valve. All temperatures and the exhaust gas analyzer signals (Horiba, MEXA-554JK) were recorded in real-time on a data logger (Advantest, R7326B). The exhaust gas sampling line length is 2 meters, and we ignored the lag in the exhaust gas analyzer. LIHCs were analyzed by gas-chromatograph (GC) with a Flame Ionization Detector (FID) (HP-6890).



A : Dynamometer controller, B, K : Temperature indicator
C : Furnace, D : Quartz tube, E : Catalyst, F : 3-way valve
G : Syringe, H : Gas analyzer, I : Water impinger,
J : Flow meter, L, M, N : Thermocouple, O : Muffler,
P : Vacuum pump

Fig. 1 Schematic diagram of experimental setup

2.2 Experimental procedures

The HC adsorber used for HC after-treatment was a Pd/Rh catalyst-loaded zeolite monolith type (62 cell/cm^2). It was set in a 19ϕ×40mm quartz tabe. Its temperature was measured by a 0.5ϕ K-type sheathed thermocouple inserted in the center. The adsorber temperature was set at 50, 100, 200 and 300℃ to investigate the characteristics of THC adsorption on adsorber. The space velocity (SV) value was controlled as 20,000 1/hr. The sampling line was heated to 100℃ by a ribbon heater to prevent moisture from condensing in the gas stream and adsorption of HC components on the inner tube. A moisture trap was placed before the GC to remove water in the exhaust gas. THC, CO and O_2 concentrations were measured continuously for 30 seconds at the adsorber inlet and for 330 seconds at the adsorber outlet.

A 50 cc glass syringe was used as the sampling bag for adsorption experiments during transient states. LIHCs were sampled at the adsober outlet at 30, 90, 150 and 270 seconds after the beginning of adsorption, respectively. The syringes were stored in an oven maintained at 100℃ and were analyzed immediately.

The GC instrument parameters are as follows. A capillary column (HP-PLOT/Al_2O_3, 30m×0.53mm×15μm) was used. The column temperature was maintained at 100℃ for 5 minutes, raised to 180℃ at a rate of 10℃/min. and kept at that temperature. 21-species standard gas of hydrocarbons (Supelco) was used for quantitative calibration of LIHCs. Since the adsorption efficiency of HC adsorber is higher at lower temperatures, the LIHCs adsorption experiments were done at 50 and 100℃.

3. Results and discussions

Physical and chemical types of adsorption exist. The physical adsorption of gases by solids increases with decreasing temperature, whereas the chemical adsorption locally occurs on certain surfaces or surface sites with heats of adsorption up to 800 kJ/mole (Webb and Orr, 1997).

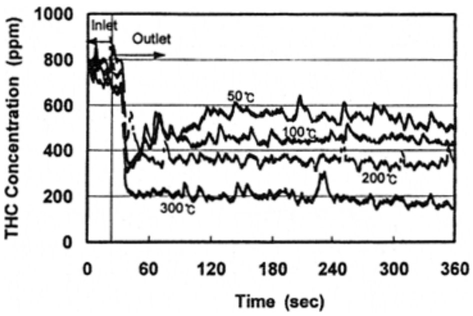


Fig. 2 THC concentration vs. time for various adsorber temperatures.

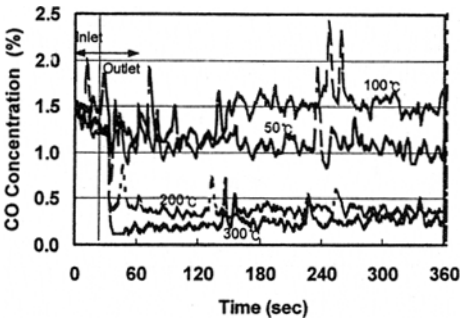


Fig. 3 CO concentration vs. time for various adsorber temperatures

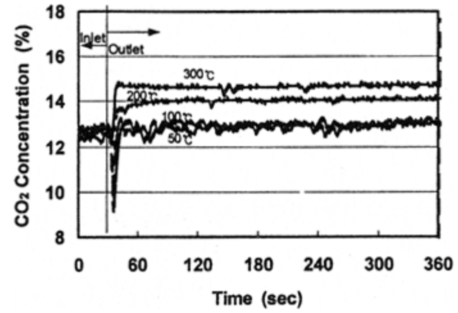


Fig. 4 CO_2 concentration vs. time for various adsorber temperatures

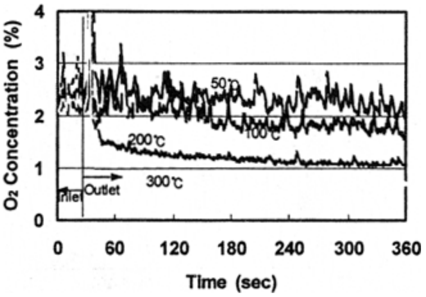


Fig. 5 O_2 concentration vs. time for various adsorber temperatures

3.1 THC adsorption

Figure 2 shows the THC adsorption characteristics at various temperatures. Engine speed and excess air ratio were 1,000 rpm and 1.1 during the measurements. Concentrations for the first 30 seconds were measured at the adsorber inlet adsorber, and then it was measured at the outlet. Engine-out THC inlet gas ranged between 700 and 800 ppm. At the adsorber temperature of 50℃, the THC concentration after the adsorber dropped 300 ppm at the beginning of adsorption, and then gradually increased up to 600 ppm. As the adsorber temperature increased, the THC emission at outlet of the adsorber gradually decreased. It can be inferred that physical adsorption reduces THC in the low temperature range (<50℃), but chemical adsorption takes over the role as the temperature of adsorber increases.

Figure 3 shows the characteristics of CO adsorption at different temperatures. For the adsorber temperature of 50℃, the CO concentration decreased with time due to physical adsorption. For the adsorber temperature of 100℃, the CO concentration decreased during first 60 seconds, and then it increased to the inlet concentration of 1.5%. Thus, physical adsorption of CO is break at temperatures above 100℃. As the adsorber temperature increased up to 200℃, CO emission decreased due to the catalytic oxidation on the activated Pd/Rh catalyst.

Figure 4 shows the CO_2 concentration measured simultaneously with THC. For the adsorber temperatures of 50 and 100℃, the CO_2 concentration was almost constant at 12.5%. But at 200 and 300℃, the CO_2 concentration abruptly increased.

Figure 5 shows the O_2 concentration measured simultaneously with THC. The O_2 concentration was almost constant at the adsorber temperature of 50℃. But at 100℃, the O_2 concentration decreased. Decreasing O_2 and increasing CO_2 concentrations at elevated temperature mean that there is oxidation reaction on the Pd/Rh catalyst coated on the adsorber.

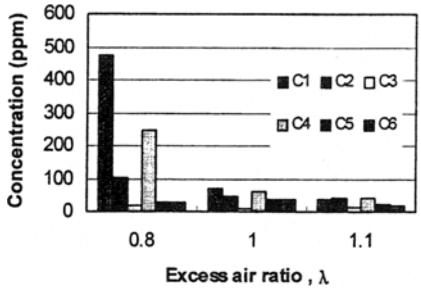


Fig. 6 LIHC emissions for $\lambda=0.8$, 1.0 and 1.1 at 1000 rpm

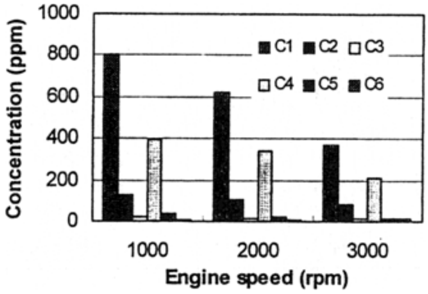


Fig. 7 LIHC emissions for engine speeds of 1000, 2000 and 3000 rpm at $\lambda=0.75$

3.2 Emission characteristics and adsorption of LIHCs

Figure 6 shows the distribution of LIHCs (light individual hydrocarbons) emitted from the engine running at 1000 rpm at various values of excess air ratio λ. The reference point is $\lambda=0.8$. As the mixture becomes leaner, the amount of HC decreases. In the cases of $\lambda=1.0$ and 1.1, the total concentrations decreased by 70.6 % and 80.5 %, respectively, relative to the case of $\lambda=0.8$. For $\lambda=1.0$, C1, C2, C3 and C4 decreased by 85.3, 53.1, 36.3 and 75.5%, but C5 and C6 increased by 31.6% and 28.4%. Especially for $\lambda=1.1$, C1, C2, C3, C4, C5 and C6 decreased 92.5, 57.4, 30.2, 83.3, 17.4 and 27.7%, respectively.

Figure 7 shows the LIHC emission characteristics according to the engine speed at a rich condition ($\lambda=0.75$). As the engine speed increased, individual hydrocarbon concentrations decreased at 2000 rpm and 3000 rpm, the total hydrocarbon concentrations are only 19.8% and 48% of that at 1000rpm. Comparing the values at 3000 rpm to those at 1000 rpm, C1, C2, C3, C4 and C5 decreased by 53.6%, 35.5%, 24.4%, 46% and 48.3%, respectively, and C6 increased by 135.4%. Thus, hydrocarbon concentration increases as the fuel/air mixture becomes rich and the engine speed decrecses. Especially, C1, C2 and C4 components exist at higher rates in light individual hydrocarbons.

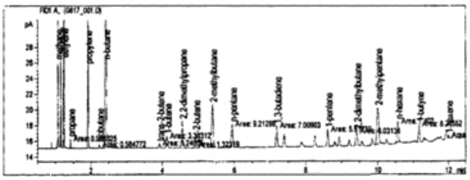


Fig. 8 GC chromatogram of the adsorber outlet at 30 seconds after the engine start up (Adsorber temperature=100℃)

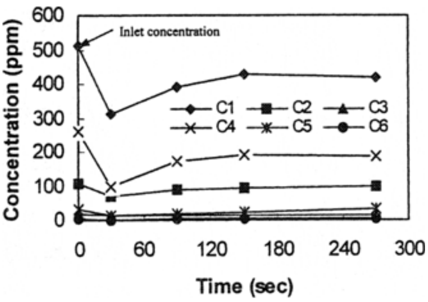


Fig. 9 LIHC asdsorption vs. time at the adsorber temperature of 50℃

Figure 8 shows the outlet emission chromatogram at 30 seconds after the engine start up. The adsorber temperature, excess air ratio, and engine speed were 100℃, 0.8, and 1000 rpm, respectively. Engine out emissions showed that methane, ethylene and n-butane in LIHCs are the major constituents at 59.8%, 10.5% and 29.2%, respectively. The total hydrocarbon emissions decreased by 12.9% compared with the engine out emissions. C1, C2, C4, C5 and C6 decreased by 10.7%, 4.6%, 47.2%, 51.1% and 59.7%, respectively, and C3 increased by 3.4% compared to the engine out emissions.

Figures 9 and 10 represent the adsorption characteristics vs. time at the adsorber temperatures of 50 and 100℃, respectively. Engine operating conditions were 1000 rpm and $\lambda=0.8$. At 50℃ (Fig. 9), C1 and C4 concentrations sharply decreased during first 30 seconds after the engine start-up, and then they gradually increased

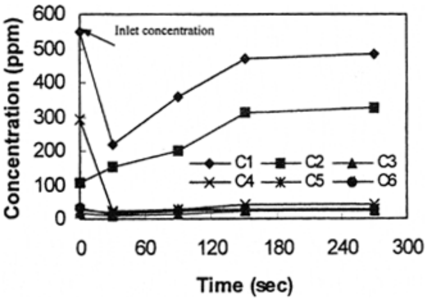


Fig. 10 LIHC adsorption vs. time at the adsorber temperature of 100℃

between 30 and 150 seconds. The concentrations of the other components did not change.

At 100℃, the results are similer to those of Fig 9, except for the C2 concentration (Fig. 10). It is interesting that the C2 concentration increased from the engine start-up to 150 seconds. It may be due to the breakdown of high number carbons into low number carbons in the adsorber material.

4. Conclusions

The reduction characteristics of hydrocarbons on the HC adsorber loaded with Pd/Rh catalyst were investigated with model gas and engine bench tests. The results obtained are as follows.

(1) As the adsorber temperature increased, the amount of adsorbed THC decreased. Above 100℃, the THC concentration after the HC adsorber significantly decreased because of the catalytic activation by the Pd/Rh catalyst.

(2) As the A/F became rich and the engine speed became low, methane, ethylene and n-butane were emitted as the major constituents of LIHCs.

(3) As the adsorber temperature increased, high number class of carbons broke down into low number class of carbons. Therefore, C4 decreased significantly during the first 30 seconds and C2 increased continuously.

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