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Original Research Article

Investigation of Effect of Propane and Methane Gases on Commercial Catalytic Converter Activity

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Abstract

The hydrocarbon in the gas mixture is extremely influential both on the CO and HC oxidation efficiency, and on NO reduction efficiency. There are complex chemical differences between the gasoline fuel and NG and LPG fuels in the reaction mechanisms of the three-way catalytic converters. For this reason, the gas mixture that simulates the stoichiometric burning exhaust gases was prepared by choosing propane to represent the LPG fuel, and the methane to represent the NG fuel as hydrocarbon.

The HC, CO and NO conversion efficiencies of the catalytic converter were tested by changing the hydrocarbon type used in the gas mixture in 10000/h space velocity and between the temperatures of 150 °C and 500 °C with 25 °C intervals. The propane was oxidized at much lower temperatures than methane, which is consistent with the C-H connection energy. In addition, the propane is a more active reducing agent in reducing the NO, and it is possible to reach the NO conversion efficiency at lower temperatures with propane. Methane or propane existing in the gas mixture as hydrocarbon is not influential on the CO conversion efficiency at a significant level and the T90 temperature of CO is reached at around 200 °C in the existence of both gases.

Key Words: Exhaust emissions, catalytic converter, activity; propane, methane, TWC

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1. Introduction

The vast majority of the contaminants in vehicles consist of the exhaust gases that are produced due to the combustion in the engine. With the complete combustion of the gasoline, which contains paraffin and aromatic hydro-carbons, theoretically only carbon dioxide (CO₂) is released outside as emission. In case of incomplete combustion, and in high combustion temperatures, exhaust gas composition contains nitrogen oxides (NO_x), carbon monoxide (CO) and unburned hydrocarbons (HC).

With the air pollution reaching dangerous dimensions, the limits on the exhaust emissions increased in a fast pace. These limit values in spark-ignited engines may be obtained via three-way catalytic converters (TWC), which removes the HC, NO_x and CO emissions simultaneously.

The main components in TWCs are substrate (ceramic or metal base material), carrier (wash-coat) and very thin active metal layer [1]

Cordierite (2MgO. 5SiO. 2Al₂O₃) is one of the ideal materials for high exhaust temperatures due to its thermal expansion coefficient being much lower, its melting point being over 1300 °C, and its showing high thermal and chemical durability. For these reasons, cordierite is used widely today in catalytic converter applications of motor vehicles [2].

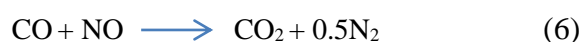
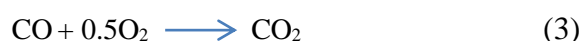
The materials that are active as catalytic may be distributed over porous carriers with metal oxide structures such as alumina (Al₂O₃), silica (SiO₂), titania (TiO₂), ceria (CeO₂), zirconia (ZrO₂), and lanthana (La₂O₃) [3]. The most widely used material among these carrier systems for environmental applications is γ -Al₂O₃ [4,5]. Although metal oxides are more active at higher exhaust temperatures, they become sintered and therefore lose their activation. For this reason, only noble metals are used in commercial applications because they have high activity levels and high resistance against thermal degradation. Noble metals are expensive, but they are used as 1.8 g/L, in other words, about 1-2 g typically in

automobile catalytic converters. The molar ratio of the platinum (Pt) and palladium (Pd), which are used for oxidation, is usually chosen as 2:1. Pd is more active in the oxidation of carbon monoxide, olefins and methane when compared with Pt. While both noble metals show similar activities in the oxidation of the aromatics, platinum is more active in the oxidation of paraffin hydrocarbons. Pd tends to be sintered less than Pt over 980 °C. Rhodium (Rh), on the other hand, is used generally in the reduction of NO_x. In a TWC, the rate of Pt+Pd to Rh is about 5:1 and 10:1. The active metal amount in the automobile catalytic converter is about 0.1-0.15% of the monolith weight [6,7].

There are more than two hundred hydrocarbons like alkanes, alkenes, alkynes, aromatics and alcohols in the exhaust gas of a typical gasoline engine. The types of the hydrocarbons also influence the removal of CO and NO_x in TWC. Especially methane (CH₄) is known for its difficult oxidation in TWC because of its extremely stable C-H bond. Nearly 8-10% of a typical exhaust gas HC compound consists of methane [8]. Generally butene (C₄H₈) [9], ethylene (C₂H₄) [9], propene (C₃H₆) [9-12], toluene (C₇H₈) [10, 12], xylene (C₈H₁₀) [10], octane (C₈H₁₈) [10], propane (C₃H₈) [10-12], CH₄ [9-11,13] have been used generally in TWC activity studies. The oxidation activity in the catalytic converter has been determined as C₃H₆> C₇H₈> C₈H₁₀> C₈H₁₈> C₃H₈> CH₄, respectively, depending on the C-H bonding energy of the different hydrocarbons [10].

There are complex chemical differences between the natural gas (NG) and gasoline engines in terms of the reaction mechanisms of the TWCs. For this reason, the removal of CH₄ oxidation alone from other reactions will make the examination of exhaust gases of NG engines easier [13-16]. Although there are various gases, the main contents of the liquid petroleum gas (LPG) are C₃H₈ and butane (C₄H₁₀) [17]. For this reason, C₃H₈ is the hydrocarbon chosen for the examination of the exhaust gases of the LPG engines, and CH₄ is the hydrocarbon chosen for the NG engines. The effects of the CH₄ or C₃H₈,

which exist in the gas mixture that simulates exhaust gas, on the HC, CO and nitrogen oxide (NO) conversion efficiency of TWC have been examined in stoichiometric conditions and at various temperatures. It is expected to take place the following oxidation (1-3) and reduction reactions (4-6) on the TWC between the simulated exhaust gases:



2. Materials and Methods

The commercial TWC with monolith structure on which Pd/Rh were loaded at a rate of 5/1 as active metal on the cordierite with 400 cpsi (cell/inch²) cell density coated with alumina was obtained from Matay Exhaust Company. The total active metal content of the catalytic converter is 1.765 g/L (1.471 g/L Pd and 0.294 g/L Rh).

The catalytic converter activity test system is given in Figure 1. The catalytic converter sample was prepared by cutting in 2.5 cm diameter and 2.5 cm length, placed in quartz tube. Protherm brand horizontal tube furnace was used for desired gas temperature.

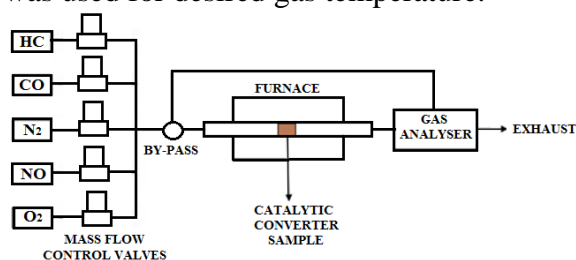


Fig. 1: Schematic figure of the catalytic converter test system

In order to obtain the proper gas mixture, nitrogen (N₂) at a purity of 99%; oxygen (O₂) at a purity of 99.9%; NO at a purity of 99.9%; and CO, CH₄ and C₃H₈ gases at a purity of 99.5% were sent to the tube furnace after they were adjusted in a proper flow with Alicat MC brand mass flow control valves that can

make measurements at an accuracy of 0.2%. The effects of the methane and propane to the conversion efficiency of TWC were examined in stoichiometric gas mixture rate. The following formulas have been used to calculate the lambda (λ) of the gas mixture [1].

$$\lambda = \frac{2 * \text{O}_2 + \text{NO}}{4 * \text{CH}_4 + \text{CO}} \quad (\text{for methane})$$

$$\lambda = \frac{2 * \text{O}_2 + \text{NO}}{10 * \text{C}_3\text{H}_8 + \text{CO}} \quad (\text{for propane})$$

For the purpose of observing the effect of CH₄ and C₃H₈ on the catalytic converter activity, the tests were repeated under the same conditions. For the stoichiometric gas mixture, 1% CO, 0.05% NO, 0.975% O₂, 0.25% CH₄ or 0.1% C₃H₈ that were balanced with N₂ were sent. All of the tests were performed at 10000/h space velocity. The space velocity of the gas flow is found by dividing the gas flow (L/h) to the volume of the catalytic converter (L).

The desired temperature in the furnace was set with thermocouples. The activity tests were performed between 150 °C and 500 °C with 25 °C intervals to observe the effect of the temperature on the catalytic converter conversion efficiency. In order to detect the gas concentrations before and after the catalytic converter with 1 ppm, 0.01% and 1 ppm accuracy for HC, CO and NO respectively, a Horiba Mexa-584L brand exhaust emission analysis device was used. The conversion efficiency values were obtained by dividing the gas concentration after the catalytic converter by the gas concentration before the catalytic converter and then by multiplying it by a hundred.

3. Results and Discussion

The activity tests of the commercial TWC were performed by changing the types of the hydrocarbons in the gas mixture. The graphics showing the effects of the methane and propane in the gas mixture on the catalytic converter hydrocarbon conversion efficiency according to the temperature are given in Figure 2. As it is obvious in the figure, the TWC starts to convert propane at a lower temperature when compared with

methane, and reaches T50 temperature (the temperature at which 50% conversion occurs) at about 275 °C. It reaches the T90 temperature (the temperature at which 90% conversion occurs) at about 350°C. In methane gas, on the other hand, it reaches the T50 temperature at nearly 325 °C, and to T90 temperature at about 435 °C. These values confirm the data in the literature suggesting that methane oxidizes later than propane.

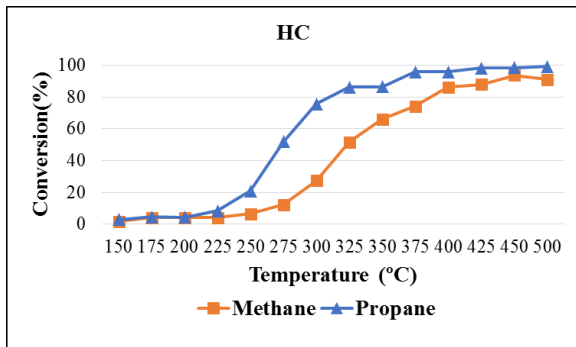


Fig. 2: Effects of CH₄ and C₃H₈ in the gas mixture on the catalytic converter HC conversion efficiency

Figure 3 shows the effect of methane and propane in the gas mixture on the catalytic converter CO conversion efficiency according to temperature. It is observed that the existence of methane or propane in the gas mixture does not affect the CO conversion efficiency much. However, in case methane is used at lower temperatures as 200 °C, the CO conversion efficiency occurs at a rate which is 5% more when compared with propane. In the existence of both gases, the T90 temperature is reached at about 200 °C. In addition, since propane oxidizes at higher temperatures and consumes all of the oxygen in the gas mixture, a very low decrease is observed in the oxidation of CO.

Figure 4 shows the effect of methane and propane in the gas mixture on the catalytic converter NO conversion efficiency according to temperature. When there is methane in the gas mixture, it has 5% more NO conversion efficiency than propane at lower temperatures (150-250 °C). The T50 temperature was reached at 275 °C, and the T90 temperature was reached at 315 °C for propane. The T50 temperature was reached at 325 °C, and the T90 temperature was reached

at 435 °C for methane. After 450°C, the NO conversion decreased a little in the gas mixture that contained methane.

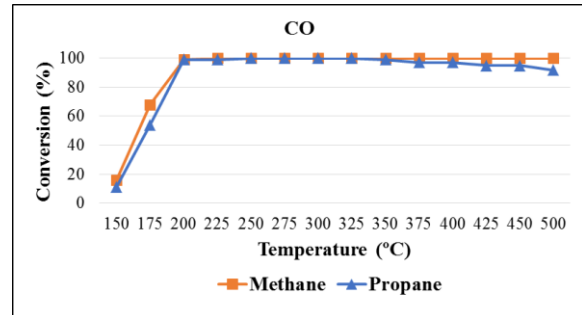


Fig. 3: Effects of CH₄ and C₃H₈ in the gas mixture on the catalytic converter CO conversion efficiency

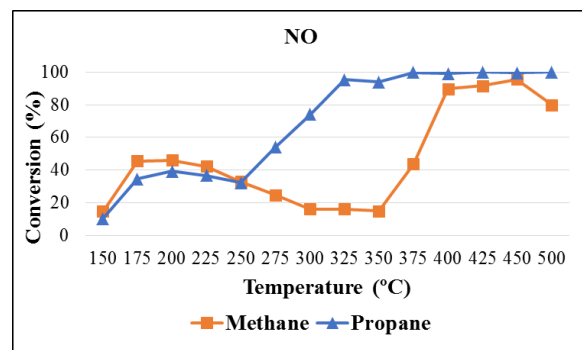


Fig. 4: Effects of CH₄ and C₃H₈ in the gas mixture on the catalytic converter NO conversion efficiency

In Figure 5 and 6, the CO, HC and NO conversion efficiencies of the TWC when there are methane and propane in the gas mixture, depending on the temperature, are given respectively on the same figure. Since the reduction of NO is realized via CO and HC, which exist in the gas mixture, it is directly related with the CO and HC conversion curves of the catalytic converter.

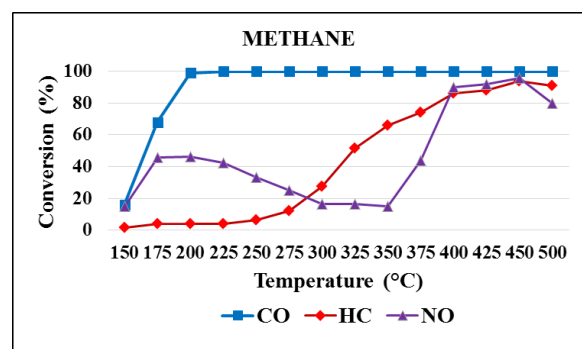


Fig.5: The CO, HC and NO conversion efficiencies of the TWC for methane in the gas mixture

As it may be observed in Figure 5 and Figure 6, since there is still CO in the gas mixture until about 200 °C, the NO conversion efficiency increases. Over 200 °C, there is no

CO left in both gas mixtures, and therefore, NO reduction is only occurred via hydrocarbons. The conversion efficiency drops a little at low temperatures, because the reaction of NO with methane and propane is low between 200-350 °C for methane and between 200-250 °C for propane in the gas mixture. Since the reaction speed of the NO and hydrocarbons increase over 250°C for propane and over 350 °C for methane, the NO conversion efficiency increases at a great pace.

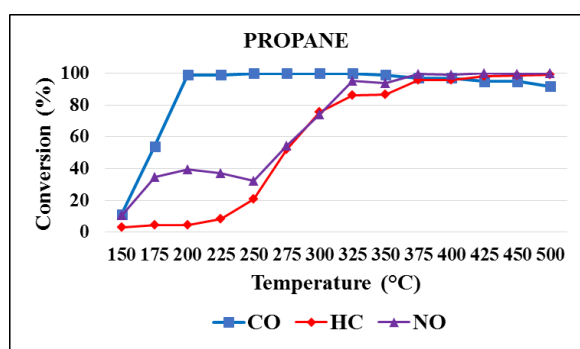


Fig.6: The CO, HC and NO conversion efficiencies of the TWC for propane in the gas mixture

4. Conclusions

The reaction mechanism of TWC are extremely complex. The interactions between HC, CO and NO change constantly at low and high temperatures. It is observed that the type of the hydrocarbon in the gas mixture is highly influential both on CO and HC oxidation efficiency and on the NO reduction efficiency.

When the HC, CO and NO conversion efficiency of the TWC is tested in case there are methane or propane in the gas mixture, in stoichiometric condition depending on the temperature, it has been observed that propane oxidized at lower temperatures than methane, which is consistent with the C-H bonding energy. For this reason, the exhaust gas of an engine using LPG is more easily converted in the catalytic converter when compared with the exhaust gas of an engine using NG, since it has hydrocarbon with short carbon chain. In addition, it has also been observed that propane is a more active reducing agent in NO reduction, and higher NO conversion efficiencies were obtained with propane at lower temperatures. It is

observed that methane or propane existing in the gas mixture as hydrocarbons does not have significant changes in CO conversion efficiency.

Acknowledgments

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