Catalytic Converter Reducing Dual Fuel (Natural Gas/Diesel) Engine Emissions

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Using natural gas combined with diesel fuel in diesel engines provides a considerable contribution to modern industrial societies in order to control air pollution and, also, generalize and facilitate the use of public vehicles. In spite of the attractive features of this idea, including reduction of NO\textsubscript{X} and particulates, there is an important burden imposed upon the system at low to intermediate torques, namely high concentration of CO and unburned total hydrocarbons (THC), mostly composed of methane. In this work, based upon the oxidation of CO and unburned HCs and through experimental results, application of a monolithic oxidizing bifunctional catalytic converter as a novel complementary for the dual fuel (natural gas/diesel) engine is introduced. This novel method called switching is used to keep high temperatures across the converter and has the advantage of converting the hydrocarbons.

INTRODUCTION

The diesel-engined vehicle is a critical part of the transportation system supporting modern industrial societies. Desired economical and technical aspects, reliability, simplicity, long term durability and derivability are some of the advantages of these engines. They are also a major consumer of petroleum fuels and a major contributor to urban air pollution. The search for alternative fuels has been encouraged by both the limited supply of petroleum and the severe local pollution problems in some countries. The ideal replacement for diesel fuel would be one retaining the advantages of such engines, while reducing emissions. The dual fuel approach reduces diesel consumption by replacing most of the injected diesel with natural gas (up to 90\%) which is premixed with the intake air. Lower C/H ratio of natural gas, combined with

the cycle efficiency, results in about 15\% lower carbon dioxide emissions and, thereby, less greenhouse effect. On the other hand, cleaner combustion of the dual fuel system yields in less lube oil contamination, hence, longer overhaul intervals [1].

In this type of engine, a small amount of diesel fuel is injected to ignite the natural gas which resists autoignition even at diesel compression ratios. Natural gas is one of the most abundant, economic and widely distributed alternative fuels, thus having the potential of significantly reducing diesel consumption. Dual fuel engines using a smart controller can optimize the ratio of natural gas and diesel fuels to simultaneously provide normal engine output, low fuel consumption and low emissions [2]. Dual fuel engines minimize the soot and nitric oxides emissions associated with diesel engines at high power levels [3,4]. The idle emissions are very low, similar to the base diesel engine. However, at part load, combustion of lean natural gas mixtures can lead to significant emissions of carbon monoxide and unburned hydrocarbons (i.e., mostly methane). To optimize natural gas utilization while minimizing pollution, an oxidizing catalytic converter is used. However, at high compression ratios, the lean burn nature of the diesel engine provides a very low exhaust temperature, considerably lower than that of similar Otto engines, although resulting in lower NO\textsubscript{X} formation and longer lubricant life which, in turn, causes extended overhaul periods for the engine. These latter phenomena make it difficult to obtain a good catalytic conversion.

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Application of an intelligent control system, injecting single diesel fuel at idling and low loads has solved the problem of high CO and THC formation at low power levels; however, the catalytic converter must be able to reduce CO and THC emissions associated with low to intermediate loads. In this paper, results of the application of an oxidizing monolith catalytic converter in the exhaust of a dual fueled engine are described. It is to be reiterated that complete removal of CO is an impressive success, although the complete conversion of THCs is not possible. Furthermore, the rate of THC conversion with temperature shows a dramatic drop with time. The main reason for this THC conversion degradation is the usage of switching method which is based upon the creation of an unsteady state condition in the reactors for increasing the conversion. For the first time in this field, this method has been used in catalytic converters for vehicles, although there are a few experiments conducted on dual fuel catalytic converters.

EXPERIMENTS

Based upon the equipmental set-up available in the Mechanical Engineering Department at the University of Alberta, previously used by Checkel et al. [5], a 4-cylinder Japanese 4BE1 Isuzu direct injection 3.6 liter engine was converted to a dual fuel (diesel/natural gas) system. Table 1 summarizes the main instruments employed in this set-up. The choice of the engine is based on its wide application all over the world. Injection package and other requirements were built and supplied by the Alternative Fuel Systems, a Canadian company. Figure 1 illustrates the basic scheme of the injection system. All important variables necessary for controlling the natural gas to diesel fuel and air to fuel ratios and the desired power output are transferred to the injection system.

All three different converters used in this research were tailor made by several well-known producers of catalytic converters, designated in this research by a, b and c. Important parameters like temperature at several points in the converter, concentration of species like CO, CO₂, NOₓ, O₂ and THC, pressure drop across the converter, air, natural gas and diesel fuel mass flow rates were measured and raw data was transferred to a computer and processed, utilizing CATREAD software [6].

RESULTS AND DISCUSSION

Amongst tested converters, the performance of just one was relatively confirmed. The main problem encountered with the two other converters was the rapid aging and quick drop of the THC conversion. Due to the lack of pertinent information from the converter manufacturers, the reason behind this function could not be explained or elaborated. This phenomenon is considerably intensified when the switching method is applied. Through this latter phenomenon, the flow direction switches between the two ends of the converter alternatively and regularly, using the fittings

<table>
<thead>
<tr>
<th>Measured Quantity</th>
<th>Instrument Model and Serial</th>
<th>Range</th>
<th>Resolution/Repeatability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exhaust O₂</td>
<td>Taylor Servomex OA.137</td>
<td>0-25%</td>
<td>~ 0.1%</td>
</tr>
<tr>
<td>Exhaust CO₂</td>
<td>Beckman 864 NDIR</td>
<td>0-20%</td>
<td>~ 0.05%</td>
</tr>
<tr>
<td>Exhaust CO</td>
<td>Beckman 864 NDIR</td>
<td>0-1%</td>
<td>~ 0.01%</td>
</tr>
<tr>
<td>Exhaust THC</td>
<td>Beckman GC 72.5 FID</td>
<td>0-1.2%</td>
<td>5 ppm</td>
</tr>
<tr>
<td>Exhaust NOₓ</td>
<td>Beckman 955 Chemiluminescent</td>
<td>0-0.2%</td>
<td>1 ppm</td>
</tr>
<tr>
<td>Dynamometer</td>
<td>Mid-West MD1014W Eddy Current</td>
<td>0-6000 rpm</td>
<td>1 rpm 0.1 kW</td>
</tr>
<tr>
<td>Fuel Consumption</td>
<td>GSE Scale GSE 550</td>
<td>0-60 kg</td>
<td>5 g</td>
</tr>
<tr>
<td>Air Flow</td>
<td>ASME Nozzle per SAE J244</td>
<td>0-200 l/s</td>
<td>1 l/s</td>
</tr>
</tbody>
</table>
and valves installed on the converter. Test results demonstrate that if the switching is started at high loads and exhaust temperatures corresponding to low unburned THC emissions, it would be possible to retain and even increase the temperature across the converter when shifting toward low loads and exhaust temperatures corresponding to high THC emissions, thus, taking advantage of higher conversions due to higher temperatures.

The following depicted results are related to the single flow of exhaust in the converter with no switching conditions; however, a couple of tests on switching were performed during these experiments. Figure 2 shows that the performance of converter b deteriorated drastically after a short period of operation. Thus, the performance of these converters was not satisfactory and detailed information on their performance will not be further presented.

Figures 3 and 4 present the THC conversions vs temperature for the converter a, the one with the best observed performance, at constant engine speed of 1500 and 2600 rpm, while Figure 5 provides the CO conversion vs temperature at constant 1500 rpm speed for the same converter. Here, study is focused on THC and CO conversions, because the NOx emission may be easily reduced using the Exhaust Gas Recycle (EGR)
The engine is set to produce the least possible NO\textsubscript{X} at the expense of higher THC and CO formation which are oxidized over the catalyst [8,9]. In this way, new environmental standards might be reached for diesel engines. Based on the experience gained in this research, smoke formation will be negligible for O\textsubscript{2} concentration greater than 6% at the exhaust. This is a definite advantage of the dual fuel system over the pure diesel system. In Figures 3 and 4, the presented curves are the best fits with first order reaction of the THC and CO catalytic oxidation. In this general form, temperature and residence time are the main variables.

\begin{equation}
\ln k = -\frac{A}{T} + B, \tag{1}
\end{equation}

where:

\begin{equation}
A = \frac{E}{R} \quad \text{and} \quad B = \ln k_0 . \tag{2}
\end{equation}

Consequently, different \( A \) and \( B \) constants are determined for each conversion vs temperature curve.
The variable parameter for these sets of curves is time, in other words, the catalyst age, hence, the conversion variations with time as a function of temperature are investigated. The S-shaped curves are well fitted with the first order reaction form. The acceptable stability of the engine at constant speeds of 1500 and 2600 rpm is the reason why these speeds are chosen. In other words, at some intermediate speeds, intense vibration is a severe problem impinged upon testing. Each experimental point on the curves of Figures 3 to 5 (i.e., of the best fitted curves) is an operational point of the engine at a constant speed during shifting from idling to the maximum possible torque. At higher speeds, this maximum torque is increased resulting in higher exhaust temperatures.

In Figures 3 and 4, the gradual reduction of maximum conversion at a certain constant speed and gradual movement of the S-shaped curves are evident. On the other hand, in Figure 5, maximum CO conversion is not limited with time since behaviors displayed in Figures 3 and 4 are not observed here. Results concerning reduction of emissions for the same Isuzu engine (i.e., 4BE1) have been reported by Checkel et al. [5], under the same dual fuel conditions described above, where comparison is made with the condition of diesel fuel only.

The variation of constants $A$ and $B$ with the age of the converter, based upon calculation from the Equation 1 for each set of tests and best THC fitted curves, is presented in Table 2. When looking for a correlation among these constants and the age of the converter, it is possible to reach an analytical function which may summarize the experimental results during the tests and determine the maximum possible THC conversion consequently. A logarithmic function can well fit these behaviors at constant 1500 and 2600 rpm engine speeds separately. At 1500 rpm, there is an excellent agreement between the data and the fitted

**Table 2.** THC fitted $A$ and $B$ constants through Equation 1 at different engine speeds.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>Date (1997)</th>
<th>Speed (rpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-11148.21</td>
<td>16.3499</td>
<td>April 23</td>
<td>1500</td>
<td></td>
</tr>
<tr>
<td>-10158.6</td>
<td>15.0231</td>
<td>April 24</td>
<td>1500</td>
<td></td>
</tr>
<tr>
<td>-15021.4</td>
<td>20.7094</td>
<td>April 24</td>
<td>2600</td>
<td></td>
</tr>
<tr>
<td>-8818.9</td>
<td>13.0822</td>
<td>April 25</td>
<td>1500</td>
<td></td>
</tr>
<tr>
<td>-13537.1</td>
<td>18.6497</td>
<td>April 25</td>
<td>2600</td>
<td></td>
</tr>
<tr>
<td>-9212.0</td>
<td>13.4777</td>
<td>April 28</td>
<td>2600</td>
<td></td>
</tr>
<tr>
<td>-4933.2</td>
<td>7.8471</td>
<td>April 30</td>
<td>1500</td>
<td></td>
</tr>
<tr>
<td>-5309.45</td>
<td>7.4067</td>
<td>June 9</td>
<td>1500</td>
<td></td>
</tr>
<tr>
<td>-7422.56</td>
<td>11.1357</td>
<td>June 9</td>
<td>2600</td>
<td></td>
</tr>
</tbody>
</table>

Function. It is evident from Figure 6 that the THC conversions during the tested period of the converter age follow the real experimental results very well; however, at 2600 rpm, where the adaptation of the logarithmic function with available results is not ideal, the calculated THC conversions shown in Figure 7 deviate from the experimental data. Nonetheless, the logarithmic function produces the best possible fit. Although it is not possible to predict the THC conversions after the tested period of the converter age, this description may well demonstrate the behavior of the system, if the converter age and engine speed are known. For the CO species, where the conversion results oscillate around a clear area and aging is not

![Figure 6. THC conversion as a function of temperature based on the empirical model at constant 1500 rpm.](image1)

![Figure 7. THC conversion as a function of temperature based on the empirical model at constant 2600 rpm.](image2)
a destructive effect, there is no need to look for an empirical fitting. The aforementioned $A$ and $B$ are, then, the apparent kinetic constants including the transport phenomena in the converter as well. A general theoretical model, including simultaneous effects of reaction kinetics and transport phenomena, is currently being studied by this research group which may hopefully predict the THC conversions after the tested period of the converter age.

As shown in Figures 3 and 4, the maximum real exhaust temperatures are about 550°C for a constant speed of 1500 rpm and 650°C for 2600 rpm, corresponding to the maximum possible torques for these speeds. The reason for showing the graphs after about 350°C only is because the dual fuel system becomes operable roughly at this temperature which corresponds to about 50% of the maximum load on the engine at constant speed of 2600 rpm. As natural gas is the dominant fuel at medium to high torques, the curves indicate catalytic oxidation of the unburned methane in the exhaust gases.

Despite the similarity in the characteristics of the curves in Figures 3 and 4 and the reduction of maximum THC conversion with time and gradual shifting of the curves towards the higher temperature side, it is clear that the rising part of these S-shaped curves in Figure 4, for the speed of 2600 rpm, appears at higher temperatures than that in Figure 3 for a constant speed of 1500 rpm. This can be attributed to the effect of residence time in the reactor. In other words, at higher engine speeds, exhaust mass flow rates are higher and since the converter volume is constant, residence time for the exhaust gases is shorter. It should be remembered that the increase in the engine speed can exert higher loads on the engine, resulting in higher exhaust temperatures. This, in spite of shorter residence time in the converter, increases the THC conversions.

It can also be seen from Figure 4 that deactivation of catalyst is reduced at higher engine speed which can probably be attributed to the partial regeneration of the catalyst at higher exhaust temperatures and presence of catalytically active species like Pt and Pd in the converter.

Figure 5 represents the CO conversion vs temperature. A similar S-shaped behavior for the oxidation of CO is also observed. At 270°C, CO conversion is nearly 100%. This is in agreement with the results reported by Lynch and Wanke [10], describing the oscillating nature of CO oxidation over the Pt and Pd catalysts when all the reaction governing variables are kept constant. Therefore, the movement in the position of one of the points in the rising section of the S-shaped CO oxidation curve creates an insignificant shift of the best fitted curves to right or left. Consequently, there is a defined region for the CO oxidation without any observed aging effect in this limit. Finally, the results illustrate a near complete removal of CO from the exhaust gases by the converter. The magnitudes of constants $A$ and $B$ in Equation 2 for the THC emissions have the highest decreasing rate with respect to time for fresh catalyst in the converter, but as aging develops, the values stabilize.

As can be concluded so far, exhaust gas temperature has a profound effect on conversion capability of THC emissions. In this study, a novel method called “switching” is devised and utilized for assessment of catalytic converter performances. The “switching method” is the alternative entrance of the engine exhaust gases to the converter in direct and reverse flow conditions. Analysis of the experimental results of the switching method illustrates that, despite the high temperature creation in the converter, this concept cannot be easily modeled. In Figure 8, the effect of switching at constant engine torque and speed (2600 rpm) is demonstrated with an exhaust temperature of about 648°C. As can be seen with different after-switching times, variation of temperature across the converter length is different where the maximum temperature, which occurs 260 seconds after switching time at a length of 30 cm of the converter, is 685°C. The minimum temperature appears at the converter length of 10 cm with a value of 660°C which is 12°C more than the engine exhaust gas temperature. Figure 9 represents the results of switching when reducing the load values, causing lower exhaust temperatures and higher THC exhaust emissions. The engine exhaust temperature varies from 591 to 601°C, while the minimum temperature in the converter at switching condition is about 665°C with a maximum of 730°C. It should be remembered that the maximum temperature,
due to switching, moves between the two ends of the converter. This switching technique, although not thoroughly perfect, has certainly decreased the THC emissions of the tested engine equipped with the converters under study. For thorough modeling of this method, more work is required [11].

CONCLUSION

1. In this research, application of dual (natural gas/diesel) fuel as an effective means of controlling urban air pollution caused by diesel engines is introduced.

2. The use of monolithic oxidizing catalytic converters in selected dual fuel diesel engines for producing minimum possible NOX and controlling other emissions, in order to achieve new environmental standards associated with different engine power outputs, is studied.

3. In this study, type a of the tested catalytic converters has proved to reduce CO emission close to 100% while conversion of total hydrocarbon emissions, especially at the lower end of the engine load is not satisfactory.

4. Use of a new and novel technique, called “switching method”, which increases the temperature across the converter, has proved to increase the efficiency of the converter for THC emissions.

ACKNOWLEDGMENT

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NOMENCLATURE

A and B  
\[ \text{time-dependent constants} \]

\[ T \]  
\[ \text{absolute temperature (K)} \]

\[ E \]  
\[ \text{activation energy (J/gmole)} \]

\[ R \]  
\[ \text{universal gas constant (8.314 J/gmole. K)} \]

\[ k \]  
\[ \text{apparent rate constant} \]

\[ k_0 \]  
\[ \text{pre-exponential factor} \]

REFERENCES


