“Passive SCR for lean gasoline NO_x control: engine-based strategies to minimize fuel penalty associated with catalytic NH₃ generation”

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Graphical abstract

Abstract

Lean gasoline engines offer greater fuel economy than common stoichiometric gasoline engines. However, excess oxygen prevents the use of the current three-way catalyst (TWC) to control nitrogen oxide (NO_x) emissions in lean exhaust. A passive SCR concept, introduced by General Motors Global R&D, makes use of a TWC that is already onboard to generate NH_3 under slightly rich conditions, which is stored on the downstream SCR. The stored NH_3 is then used to reduce NO_x emissions when the engine switches to lean operation. In this work, the effect of engine parameters, such as air-fuel equivalence ratio and spark timing, on NH_3 generation over a commercial Pd-only TWC with no dedicated oxygen storage component was evaluated on a 2.0-liter BMW lean burn gasoline direct injection engine. NO_x reduction, NH_3 formation, and reductant utilization processes were evaluated, and fuel efficiency was assessed and compared to the stoichiometric engine operation case. Air-fuel equivalence ratio was found to be one of the most important parameters in controlling the NH_3 production; however, the rich operation necessary for NH_3 production results in a fuel consumption penalty. The fuel penalty can be minimized by adjusting spark timing to increase rich-phase engine out NO_x emissions and, thereby, NH_3 levels. Additionally, higher engine out NO_x during engine load increase to simulate acceleration resulted in additional fuel savings. A 10% fuel consumption benefit was achieved with the passive SCR approach by optimizing rich air-fuel equivalence ratio and spark timing while also utilizing acceleration load conditions.

Keywords: passive SCR; TWC; lean NO_x reduction; NH_3 formation

1. Introduction

Concerns about greenhouse gas emissions and dependence on petroleum have motivated governments around the world to develop regulations that require significant improvements in vehicle fuel economy. In the U.S., the fuel economy regulations for light-duty vehicles will require the corporate average fuel economy (CAFE) to increase to 54.5 miles per gallon by 2025, which is more than 50% higher than the current regulations. These regulations have motivated vehicle manufacturers to pursue a range of technologies that reduce petroleum consumption. To ensure their adoption in the marketplace, these technologies must comply with increasingly stringent exhaust emissions regulations for pollutants such as nitrogen oxides (NO_x), carbon monoxide (CO), hydrocarbons (HCs), and particulate matter (PM). The recently approved U. S. Environmental Protection Agency Tier 3 emissions regulations require more than 80% reduction in NO_x and non-methane HCs from the current Tier 2 Bin 5 emission standard. Meeting both the 2025 CAFE standards for fuel economy and the Tier 3 emissions regulations will require significant advancements in engines, powertrains, and emissions control.

In the U.S., the light duty vehicle fleet is dominated by gasoline engines operating at stoichiometric air-to-fuel ratios (AFR) [1]. Stoichiometric exhaust conditions are suitable for a three-way catalyst (TWC) to effectively control NO_x , CO, and HC emissions to regulated levels. Lean operation can increase fuel economy of a gasoline engine by as much as 10-20% over stoichiometric [2], [3]. While TWCs can effectively oxidize CO and HCs under lean conditions, they are unable to reduce NO_x in the presence of excess oxygen; thus, a different emissions control technology is required for the abatement of NO_x emissions from lean-burn gasoline engines. While urea-based selective catalyst reduction (SCR) has proven effective in controlling NO_x emission from diesel vehicles, the urea storage and delivery components can be large and add significant cost. As such, onboard NH_3 production via a passive SCR approach is of interest [4], [5]. In a passive SCR system, NH_3 is generated over a close-coupled TWC

during periodic slightly rich operation and subsequently stored on an underfloor SCR catalyst. Upon switching to lean, NO_x passes through the TWC and is reduced by the stored NH_3 on the SCR catalyst. This approach is particularly attractive for lean gasoline engines because it makes use of a TWC that is already onboard and eliminates or greatly reduces the need for the urea system.

The effectiveness of a passive SCR system depends on efficient and selective NH_3 generation and utilization over the TWC+SCR catalysts. Since the rich operation necessary for NH_3 generation incurs a fuel consumption penalty, minimizing the duration and magnitude of the rich excursions is critical and will require a combination of engine management and emissions control optimization. During rich/lean cycling, the NH_3 produced while rich and the NO_x produced while lean ultimately control cycle timing and fuel consumption [6]. Overall, increasing the ratio of lean to rich operation will increase fuel efficiency. Primary approaches to increase lean operation time while maintaining the proper cycle averaged NH_3 to NO_x ratio include: (1) increasing engine out NO_x emissions and selectivity of NO_x to NH_3 conversion over the TWC during rich operation and (2) decreasing engine out NO_x emissions during lean operation.

The most important engine parameters that affect NO_x emissions are the air-fuel equivalence ratio, spark timing, and exhaust-gas recirculation (EGR) rate [7], [8]. This study aims to understand how these parameters affect NH_3 production, with a particular goal of minimizing the fuel consumption associated with catalytic NH_3 generation. Our initial flow reactor screening of TWCs with different formulations showed that a commercial Pd-only TWC containing no dedicated oxygen storage component (OSC) achieved the highest NH_3 selectivity and the best estimated fuel consumption [9]. Other researchers have also showed that Pd-based TWCs are more selective to NH_3 production compared to other precious metal based catalysts [10]–[15]. As such, the same Pd-only TWC used in the previous flow reactor evaluations was chosen for this study.

2. Material and methods

2.1 Engine Platform

All experiments were conducted on a lean gasoline engine coupled to a motoring direct current dynamometer that controls the engine speed and load. The engine was removed from a European Model Year (MY) 2008 BMW 1-series 120i (E87) vehicle. It is a 4-cylinder 2.0-liter naturally aspirated direct-injection gasoline engine that has a rated power of 125 kW at 6700 revolutions per minute (rpm) and a torque of 210 Nm at 4250 rpm. Table 1 summarizes the engine specifications. The engine was operated on a EEE-Lube Certification Gasoline (Haltermann Solutions) containing no ethanol. Table 2 shows key gasoline fuel properties provided by the vendor.

The engine uses a spray-guided combustion system design. In this design, a piezoelectric injector is located at the top center of the combustion chamber, with a spark plug in close proximity to the injector. This geometry allows ignition of the fuel as it is injected, which results in shorter mixture formation time compared to wall-directed and air-directed combustion systems [16]. With shorter mixture formation time, lean engine operation can be extended to higher speeds and loads, resulting in additional fuel savings. The overall air-fuel equivalence ratio, or λ (ratio of actual AFR to stoichiometric AFR), during lean operation ranges between 1.3 and 2.2. Up to 20% reduction in fuel consumption can be achieved with lean operation relative to stoichiometric. The engine, however, only operates lean over a portion of the engine's speed and load range (up to 4500 rpm and 75% load). Outside the lean operating range, at higher engine speeds (>4500 rpm) and loads (>75%), the engine operates in the stoichiometric combustion mode. The engine can also operate in the stoichiometric mode over its entire operating range. For this study, modifications to the stoichiometric mode were made in order to operate the engine rich ($\lambda < 1$) for NH_3 generation. Details on an additional rich combustion strategy available on this engine can be found in our previous publication [6].

The factory engine control unit was replaced with a custom full-pass control system developed by National Instruments - Powertrain Controls Group. The controller mimics the original equipment manufacturer (OEM) combustion strategies and, furthermore, enables full control of all engine parameters, including fuel injection quantity and timing, spark timing, λ , and EGR rate which allows full control of the different modes of combustion. Additional information on the engine setup, performance and emissions can be found in [2], [3], [6].

2.2 Three-way catalyst

The Pd-only TWC evaluated in this study was the front portion of a commercial dual zone catalyst formulation from a 2009 PZEV (Partial Zero-Emissions Vehicle) Chevrolet Malibu. The Chevrolet Malibu TWC is a single 1.3-liter monolith with a dual zone catalyst formulation. The front 0.6-liter portion of the catalyst contains 4.4 g of Pd and no dedicated OSC, while the rear portion has a lower total precious metal loading (1.0 g, with 4:1 Pd:Rh) plus an OSC. The catalyst properties of the dual zone Malibu TWC are summarized in Table 3. For this study, the front portions of three Chevrolet Malibu TWCs were cut out, mounted in series in a stainless steel can and installed in the engine exhaust in a close-coupled configuration. The combined volume of the Pd-only Malibu TWC was 1.3 liters. The catalyst was degreened on the engine for twenty hours at temperatures ranging between 650 and 750°C prior to evaluation.

2.3 Emission Sampling

Raw exhaust was sampled at the TWC inlet (TWC_{IN}) and outlet (TWC_{OUT}) locations. The sample was routed through a heated filter prior to analysis. A California Analytical Instruments (CAI) heated flame ionization detector (FID) was used to measure total unburned hydrocarbons. An MKS Instruments MultiGas Model 2030 HS FTIR Spectrometer with a heated 5.11 m multi-pass gas cell was utilized to measure multiple gases, including CO, CO₂, nitrogen monoxide (NO), nitrogen dioxide (NO₂), nitrous

oxide (N_2O), and ammonia (NH_3). A magnetic sector mass spectrometer with a capillary sampling system (SpaciMS) was used to measure H_2 and O_2 . Details on the SpaciMS technique can be found in the publication by Partridge et al. [17].

2.4 Experiment protocols

2.4.1 Steady-state experiments

A series of steady state experiments were carried out to evaluate the influence of engine operating parameters on the formation of NH_3 over the TWC during slightly rich operation. Air-fuel equivalence ratio and spark timing were varied over a number of engine operating conditions shown in Table 4. These operating points were chosen to produce a range of exhaust gas compositions, temperatures, and space velocities. For the air-fuel equivalence ratio experiments, λ was varied from 0.90 to 1.01 at each of the operating points. For the spark timing experiments, spark timing was adjusted to the most advanced timing while achieving MBT (Maximum Brake Torque). External EGR was disabled during these experiments to maximize engine out NO_x emissions. These experiments assessed the trade-off between NH_3 yield and fuel penalty as a result of increased fuel consumption from running rich.

2.4.2 Lean/rich cycling experiments

To assess NO_x reduction, NH_3 formation, reductant utilization, and fuel efficiency improvements under realistic operating conditions, a series of rich/lean cycling experiments were performed where the engine alternated between rich ($\lambda=0.96 - 0.99$) and lean ($\lambda \approx 2.0$) operation. These experiments were designed to be representative of the conditions a passive SCR system would encounter under realistic driving conditions. Load step and fixed load cycling experiments were carried out to simulate acceleration and “cruise” driving events, respectively. During load step experiments, the engine alternated between rich operation at 8 bar brake mean effective pressure (BMEP, a measure of engine

load) and lean operation at 2 bar BMEP while maintaining 2000 rpm engine speed. The load was fixed at 2 bar BMEP for both lean and rich portions of the cycle during the fixed load experiments. A feedback control strategy based on cumulative NH_3 produced by the TWC during rich operation and NO_x emissions during lean operation was implemented on the engine to control lean/rich cycle timing. The mode switch was triggered when the TWC outlet NO_x or NH_3 ($\text{NO}_x:\text{NH}_3=1$) reached 0.027 mol per liter of catalyst, which represents approximately 25% of the NH_3 storage capacity of a small pore Cu-zeolite SCR catalyst at 300°C based on prior flow reactor measurement, which showed that at higher NH_3 loadings (>50%), NH_3 slip can occur due to NH_3 release during the switch from rich to lean conditions.

3. Results and discussion

3.1. Steady-state experiments

Initial experiments focused on quantifying how the key engine operating parameters (λ and spark timing) impact exhaust composition and fuel consumption under steady state engine operating conditions. The maps generated during these steady state parameter sweeps were subsequently used in selecting optimal operating parameters for use in the load step and fixed load cycling experiments, designed to more closely mimic operation of the engine and emissions control system on a vehicle.

3.1.1 Increasing NH_3 production through λ control

An engine operating point can be classified into one of three modes of operation based on the air-fuel equivalence ratio: stoichiometric ($\lambda=1$), rich ($\lambda<1$) and lean ($\lambda>1$). Figure 1a shows the variation of three regulated pollutants (CO, HC and NO_x) as a function of λ at a 2000 rpm 8 bar BMEP operating point; NH_3 is also included since it is of primary interest in this study. For $\lambda<1$, where the mixture of fuel and air in the combustion chamber contains excess fuel, richer mixtures result in a decrease in fuel efficiency and

an increase in unburned hydrocarbons and partial oxidation products (CO and H₂). As shown in the figure, this results in increased HC, CO and H₂ emissions at lower λ s.

The exhaust gas composition changes substantially as it passes through the catalyst, and the magnitude of this change depends on λ . Figure 1b shows exhaust gas composition as a function of λ at the outlet of the Pd-only TWC. The approximate inlet catalyst temperature at this condition is 700°C. As seen in the figure, the TWC is very effective in converting CO, HC and NO_x emissions to CO₂, H₂O and N₂ at stoichiometric conditions. Slight deviations from stoichiometric, however, lead to significant changes in TWC outlet gas composition. At these temperatures, lean operation results in complete oxidation of CO and HC emissions, but the presence of excess oxygen prevents NO_x reduction. Under rich conditions, limited oxygen availability results in CO and HC slip, but the NO_x reduction activity is very high, with NO_x concentrations always less than 20 ppm. The TWC converts the incoming NO_x to a mixture of N₂ and NH₃, with selectivity to NH₃ strongly depending on λ . To further illustrate this point, the concentration of NO_x and NH₃ at the TWC inlet and outlet locations, respectively, are plotted in Figure 2a along with the NO_x conversion efficiency and NH₃ yield in Figure 2b. The NO_x conversion is defined as $(NO_{x\text{ in}} - NO_{x\text{ out}}) / NO_{x\text{ in}} * 100\%$, where NO_x includes both NO and NO₂. The NH₃ yield is defined as $NH_{3\text{ out}} / (NO_{x\text{ in}} + NH_{3\text{ in}} + 2 * N_2O_{\text{in}}) * 100\%$. As shown in Figure 2a, the effluent concentration of NH₃ sharply increases as λ decreases until it reaches a maximum at $\lambda=0.96$, and then slowly decreases with lower λ values as the feedgas NO_x level decreases. The inlet NO_x and outlet NH₃ concentrations are identical for $\lambda \leq 0.96$, indicating that all of the NO_x is converted to NH₃, which can also be seen from the equal NO_x conversion and NH₃ yield in Figure 2b. These results indicate that, in this region, NH₃ formation is limited by the NO_x availability at the catalyst inlet. For λ between 0.97 and 1.00, on the other hand, the NH₃ yield is limited by the reductant availability, as illustrated by the decreasing concentrations of HC, CO and H₂ in Figure 1a, and as λ increases the reduction of NO_x becomes more selective to N₂.

The likely pathway for NH₃ formation is through the reaction between NO and H₂, as shown in Equation 1:

In an SI engine, H₂ is always present with CO in the engine exhaust as a result of incomplete combustion. They are formed at the flame front by incomplete oxidation of HC compounds [7], [18], and, as seen in Figure 1a, are very sensitive to λ . In addition to in-cylinder H₂ generation, H₂ can also be formed in a catalyst through water gas shift (WGS) (Equation 2) and steam reforming reactions (Equation 3) as shown in Figure 1b.

Adams et al. showed that a considerable amount of NH₃ can be formed from NO+H₂O+CO gas mixtures [10]. The ratio of H₂ to CO in the engine exhaust was 0.75 at $\lambda=1.00$, while the equilibrium ratio at 700°C is about 1.3. Additional H₂ generation inside the TWC is, therefore, possible by utilizing a catalyst active in promoting this equilibrium.

As shown in Equation 1, a H₂ to NO_x ratio of 2.5 is required to convert all of the incoming NO_x to NH₃. While H₂ and NO_x are emitted by the engine during rich operation, other species are also emitted that can consume or produce H₂ in the catalyst. H₂ can be generated over the TWC by water-gas-shift of CO or steam reforming of HCs (Equations 2 and 3). O₂, which can still be present in exhaust after rich combustion, can remove H₂ via oxidation over the TWC. Thus, the concept of “effective H₂” is used to represent the H₂ in the TWC after subsequent reactions with other exhaust constituents that is available for conversion of NO_x to NH₃. The effective H₂ to NO_x ratio at the TWC inlet is shown in Figure 3, where the effective H₂ is defined as $\text{H}_{2,\text{eff}} = \text{H}_2 + \text{CO} + 2.9 \cdot \text{HC} - 2 \cdot \text{O}_2$. For all of the rich conditions, the H_{2,eff} to

NO_x ratios are significantly greater than 2.5. Thus, at the inlet there are enough reductants to convert all of the NO_x to NH₃, and as expected, higher engine out reductant concentrations at richer λ s result in higher NH₃ yields (Figure 2b). However, much higher H_{2,eff}:NO_x ratios ($\gg 2.5$) were needed to achieve high NH₃ yields.

When there is a deficiency in H₂, the reduction of NO_x becomes more selective to N₂ (Equation 4):

Nitrous oxide (N₂O) is also known to form over precious metal catalysts via the reaction in Equation 5 [12], [19]–[22]:

N₂O formation is important due to its high global warming potential; its CO₂ equivalence is 298 [19], [23], [24]. Even low levels of N₂O can have a high impact on greenhouse gas emissions, and if not carefully controlled, N₂O will reduce the overall benefit of the passive SCR approach. N₂O is primarily observed at temperatures below 200°C, although some studies have reported N₂O formation at higher temperatures [12],[22]. The Pd-only Malibu TWC evaluated here did not show any N₂O during any of the steady state operating conditions used in this work.

The results shown thus far indicate the importance of λ in the NH₃ production over the TWC. However, the rich operation necessary for NH₃ production incurs a fuel consumption penalty, and thus should be minimized. The fuel penalty relative to the stoichiometric engine operation for running the engine rich is shown in Figure 4. The fuel penalty at the point of maximum NH₃ production ($\lambda=0.96$) is 3.9% and decreases with leaner λ s. Both the fuel penalty and the desired NH₃ levels must be considered when selecting the optimum operating λ .

3.1.2 Increasing engine out NO_x through changes in spark timing

In conventional stoichiometric engine operation, a number of engine-based control parameters such as λ , EGR, and spark timing are used to reduce the engine out NO_x emissions in order to reduce the burden on the TWC to meet the emission standards. Typically, some of the engine efficiency (and fuel) is sacrificed in the process. In the approach being studied here, these constraints can be removed, as increased NO_x emissions are actually beneficial during rich engine operation, since the increased NO_x can be converted to NH_3 , thereby reducing the amount of time required to run rich.

The effect of λ on NO_x emissions is shown in Figure 1a. As the mixture is enriched, NO_x emissions drop. Excess fuel at rich mixtures prevents the full release of the thermal energy of the fuel, thereby reducing the peak cylinder temperature and decreasing NO_x emissions. Since λ is also a critical parameter in generating reductants that in turn control NH_3 selectivity, the choice of the operating λ will most likely be determined by the reductant demands. However, EGR rate and spark timing have less significant impacts on NH_3 selectivity, and therefore present opportunities for boosting NO_x production during rich operation to reduce the overall fuel consumption of a lean gasoline engine equipped with a passive SCR system.

Exhaust-gas recirculation is an important technique utilized for emission control in SI engines [7], [8], [25]–[27]. The exhaust gas recirculated back to the combustion chamber increases the proportion of inert gas in the cylinder charge mixture and also increases the heat capacity of the mixture. This results in a reduction in the flame temperature and, in turn, a drop in temperature-dependent NO_x emissions. EGR can be implemented in two ways: externally (via EGR valve) and internally (via intake and exhaust valve overlap). The engine used in this study employs both internal and external EGR for emissions control. During all of the operating points studied here, the external EGR was deactivated under rich engine operation to maximize NO_x emissions while valve timing was maintained at the OEM set points.

On SI engines, the combustion process is initiated by the spark. The timing of the spark event significantly affects engine emissions and performance [7], [8],[28]. Advancing the timing (igniting earlier in the compression stroke) increases the peak cylinder pressure, which results in higher in-cylinder temperature and hence higher NO_x emissions. Advancing the spark timing can also result in improved fuel efficiency up to the MBT timing. Figure 5 shows (a) engine torque, (b) NO_x emissions and (c) fuel consumption as a function of spark timing with the engine operating at a 2000 rpm 8 bar BMEP operating point. The OEM spark timing at this operating point is 17 crank angle degrees (CAD) before top dead center (TDC). NO_x emissions steadily increase as spark timing is advanced from the OEM timing. Advancing the spark timing also results in improved fuel efficiency. NO_x emissions increase by 22%, while fuel consumption improves by 2% as a result of advancing the spark timing to the MBT timing of 24° before TDC. To study the effects of advanced spark timing on NH₃ production, λ sweep experiments discussed in 3.1.1 were repeated with the spark timing maintained at the MBT timing. The effect of spark timing at MBT on the engine out NO_x emissions, NH₃ production, and fuel consumption as a function of λ is shown in Figure 6. Advancing the spark resulted in a 10-15% increase in engine out NO_x emissions, with most NO_x converted to NH₃ by the TWC. The fuel penalty relative to the OEM stoichiometric engine operation for running the engine rich was reduced as a result of advancing the spark timing. At the point of maximum NH₃ production ($\lambda=0.96$), the fuel penalty was reduced from 3.9% to 1.7%. Thus, optimal spark timing results in increased engine out NO_x emissions and reduced fuel consumption, both of which are beneficial for the passive SCR system.

3.1.3 Optimal parameters for multiple engine operating points

All of the results presented in Figures 1-6 were collected while the engine was operating at 2000 rpm and 8 bar BMEP. Similar trends were also observed at the other engine operating points used in this study. Table 5 summarizes operating conditions where >90% conversion of NO_x to NH₃ was obtained for

all engine operating points evaluated. High NO_x to NH_3 conversions were achieved over a wide range of temperatures (320-750°C) and space velocities (15-90K h^{-1}), which covers the majority of the engine operating conditions typically encountered on a vehicle. However, different levels of reductant were needed to achieve high NH_3 yields, as seen from the range of λ s and $\text{H}_{2,\text{eff}}/\text{NO}_x$ ratios in Table 5.

3.2 Lean/rich cycling experiments

The NH_3 formation and reductant utilization over the TWC were studied under rich/lean cycling operation representative of the conditions a passive SCR system would encounter under realistic driving. The optimal spark timing obtained during steady state experiments was employed during the rich portion of the cycles. External EGR was turned off during rich operation, while it was maintained at the OEM levels during lean. The emissions of NO_x , NH_3 , N_2O , CO, and HC at the TWC inlet and outlet during the load step experiments with rich $\lambda=0.97$ are shown in Figure 7. Note that the average TWC inlet temperature during this experiment is 480 °C, while the peak measured mid-bed temperature is 705 °C. During the lean phase of the cycle, CO and HC emissions are completely oxidized over the TWC; however, excess oxygen prevents NO_x reduction resulting in most of the NO_x passing through the TWC unreacted (not shown in the figure).

The catalyst is very effective at reducing the engine out NO_x emissions during rich operation with selectivity to NH_3 approaching 100%. The effluent NH_3 increases instantaneously as soon as the engine switches to rich. The lack of a delay in NH_3 production can be attributed to the characteristics of the TWC and the engine controller used in this investigation. The Pd-based TWC used in this study does not have a dedicated oxygen storage component, which helps explain the instantaneous NH_3 evolution. In a TWC with OSC, such as ceria, the OSC undergoes a reduction-oxidation process during rich/lean cycling. When transitioning from lean to rich, the incoming reductants react with the stored O_2 first [29], [30] delaying the NO_x to NH_3 reduction reaction [9], [31]. The transient response of the engine when it

switches from lean to rich also contributes to the rapid onset of NH_3 production. The engine transitions from lean ($\lambda=2.1$) to rich ($\lambda=0.97$) in about 1 s. However, during this 1s transient, the engine temporarily drops to a much richer $\lambda\sim 0.8$ and produces a large flux of reductants, as indicated by the spikes in engine out CO and HC emissions in Figure 6. The increased availability of reductants would quickly reduce the catalyst surface and initiate the NH_3 production. This transient, often referred to as a “tip-in”, may be beneficial in the case of a TWC with OSC where extra reductants are needed to remove the stored O_2 and reduce the delay in NH_3 production [31]. However, in the case where the TWC does not have OSC, an excessively rich λ should be avoided in order to minimize the CO and HC slip and fuel consumption.

After the initial spike in CO and HC emissions during the transition from lean to rich λ , CO continues to slip during the rich operation, while HC emissions decrease to <5 ppm. The overall cycle CO and HC conversions for the load step and fixed load cycling experiments are shown in Figure 8a and Figure 8b, respectively. HC emissions are not sensitive to changes in λ , and the TWC achieves $>99\%$ HC conversion at all points. On the contrary, the CO emissions are affected by λ , with richer λ s resulting in higher engine out CO emissions and decreasing CO conversion over the TWC. Under stoichiometric-only engine operation, the TWC achieves 99.9% HC conversion for the load step and fixed load experiments, while CO conversion was 100% during fixed load and 96.7% during load step experiments. Optimizing the engine transient response could reduce the unnecessary CO and HC spikes during the lean/rich transitions and further minimize HC emissions. The CO emissions, however, would still need to be addressed; one possible solution consists of a downstream oxidation catalyst with either significant oxygen storage or secondary air injection to remove the CO that slips from the TWC.

Similar to steady-state experiments, N_2O emissions are not observed during the rich operation; however, small traces of N_2O (<1 ppm) are detected during the lean portion of the cycles. The 20 ppm

N₂O spike during the switch from lean to rich results from the complex competitive reduction of NO_x on the catalyst surface when the TWC transitions through oxidation/reduction processes [32], [33].

For an estimation of the fuel consumption impacts of lean operation enabled by a passive SCR emissions control system, fuel consumption during lean/rich cycling is measured and compared to fuel consumption under conventional stoichiometric operation. The fuel consumption measurements are normalized to the power produced by the engine (brake specific fuel consumption or BSFC) before the change in fuel consumption is calculated. Fuel consumption improvements for the load step and fixed load cycling experiments are shown in Figure 9. The maximum fuel consumption improvement with OEM spark timing was 8.8% at rich $\lambda=0.97$ and 7.3% at rich $\lambda=0.96$ for load step and fixed load, respectively. The fuel consumption benefit is relatively flat in the load step case between λ 0.96 and 0.98, before dropping significantly at $\lambda = 0.99$. At this less-rich λ , NO_x reduction is limited by reductant availability, resulting in decreased NH₃ selectivity, longer rich times, and increased fuel consumption. Similarly, fuel consumption increases at richer λ , where NH₃ production is limited by engine out NO_x. As seen in Figure 8, the optimized spark timing results in additional fuel efficiency gains as a result of higher engine out NO_x emissions, especially for the load-step case. The ratio of lean to rich cycle times at the maximum fuel efficiency point is 4.2 during the load step experiments compared to 0.9 during fixed load experiments, which is due to higher engine out NO_x emissions during rich phase resulting in much shorter rich time and better fuel consumption benefits. This underlines the importance of acceleration events during transient drive cycle operation, which create an opportunity for higher engine out NO_x emissions and, thereby, higher TWC NH₃ production which reduces fuel consumption for a passive SCR system.

4. Conclusions

In this work, the effect of air-fuel equivalence ratio and spark timing on NO_x to NH_3 conversion over a TWC was investigated on a lean burn gasoline engine for the purpose of supplying NH_3 for a passive SCR approach. A primary focus of the study was minimizing fuel consumption associated with catalytic NH_3 generation. Air-fuel equivalence ratio impacts both engine out NO_x emissions and NH_3 selectivity. Richer air-fuel equivalence ratios increase NH_3 selectivity but decrease engine out NO_x . Advancing spark timing increases engine out NO_x and thereby, NH_3 production by the TWC during rich operation. These engine operating parameters must be carefully optimized to deliver the best fuel efficiency and desired emission levels. In addition, higher engine loads associated with acceleration events create an opportunity for higher engine out NO_x and, thereby TWC NH_3 production, which results in additional fuel efficiency gains. A fuel consumption benefit up to 9.6% relative to stoichiometric combustion was achieved through selection of optimal rich air-fuel equivalence ratio and spark timing during the load step experiments. Greater than 99% HC conversion for the system was achieved during all of the experiments; however, CO conversion was limited to 65-85% from slip during rich operation.

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Figure Captions

Figure 1. Steady state gas concentrations at (a) TWC inlet (b) TWC outlet as a function of λ with engine operating at 2000 rpm and 8 bar BMEP and catalyst operating at $\sim 700^\circ\text{C}$ inlet temperature and $64,000\text{ hr}^{-1}$ space velocity.

Figure 2. (a) NO_x and NH_3 concentrations at TWC inlet and outlet, respectively, and (b) corresponding NO_x conversion and NH_3 yield as a function of λ with engine operating at 2000 rpm and 8 bar BMEP and catalyst operating at $\sim 700^\circ\text{C}$ inlet temperature and $64,000\text{ hr}^{-1}$ space velocity.

Figure 3. $H_{2,eff}$ to NO_x inlet concentration ratio as a function of λ with engine operating at 2000rpm and 8 bar BMEP and catalyst operating at, $\sim 700^\circ\text{C}$ inlet temperature and $64,000\text{ hr}^{-1}$ space velocity.

Figure 4. Fuel consumption penalty relative to stoichiometric operation as a function of λ with engine operating at 2000 rpm and 8 bar BMEP and catalyst operating at ~ 700 °C inlet temperature and 64,000 hr^{-1} space velocity.

Figure 5. (a) Engine brake torque, (b) engine out NO_x emissions and (c) brake specific fuel consumption as a function of spark timing with engine operating at 2000 rpm and 8 bar BMEP. The OEM spark timing is 17 CAD before TDC.

Figure 6. (a) NO_x and NH_3 concentrations at TWC inlet and outlet and (b) fuel consumption penalty relative to OEM stoichiometric operation for OEM (solid marker) and advanced (empty marker) spark timing as a function of λ with engine operating at 2000 rpm and 8 bar BMEP and catalyst operating at $\sim 700^\circ\text{C}$ inlet temperature and $64,000\text{ hr}^{-1}$ space velocity.

Figure 7. Emissions of (a) NO_x and NH_3 , (b) N_2O , (c) CO and (d) HC at TWC inlet and outlet during load step rich/lean cycling experiments. Rich conditions: 2000 rpm 8 bar BMEP with $\lambda=0.97$. Lean conditions: 2000 rpm 2 bar BMEP with $\lambda=2.10$. Average temperature at TWC inlet=480 °C with maximum mid-bed temperature of 705 °C.

Figure 8. Overall cycle CO and HC conversions for (a) load step and (b) fixed load cycling experiments as a function of rich λ .

Figure 9. Fuel consumption benefits for (a) load step and (b) fixed load cycling experiments relative to stoichiometric engine operation as a function of rich λ .

Tables

Table 1. BMW 2.0-liter lean burn direct injection engine specifications

Engine Model Number	N43B20
Displaced volume	1995 cm ³
Number of cylinders	4
Stroke	90 mm
Bore	84 mm
Compression ratio	12.0:1
Rated Power	125 kW at 6700 rpm
Rated Torque	210 Nm at 4250 rpm

Table 2. EEE-Lube Cert Gasoline fuel properties.

Lower Heating Value, kJ/kg	42715
Density, kg/liter	0.742
C, weight fraction	0.8598
H, weight fraction	0.1314
Oxygen, weight %	<0.01
Sulfur, mg/kg	4
Aromatics, volume %	27.4
Olefins, volume %	0.9
Saturates, volume %	71.8
Research Octane Number (RON)	96.4
Motor Octane Number (MON)	88.4

Table 3. Dual zone Chevrolet Malibu TWC details

	Volume (liter)	Pt/Pd/Rh Loading (g/liter)	Oxygen Storage Component
Front Half	0.6	0.00/7.33/0.00	No
Back Half	0.7	0.00/1.14/0.30	Yes
Total	1.3	0.00/4.00/0.16	Yes

Table 4. Steady-state operating points used in λ sweep experiments with corresponding catalyst inlet temperatures and space velocities at $\lambda=1$

Speed (rpm)	BMEP (bar)	TWC T_{IN} (° C)	SV (hr⁻¹)
1000	2	314	15,000
1000	6	473	27,000
2000	2	524	27,000
2000	8	713	64,000
3000	2	641	38,000
3000	8	768	89,000

Table 5. Operating conditions that resulted in >90% NO_x to NH₃ conversion under steady state operation.

Speed (rpm)	BMEP (bar)	TWC T _{IN} (° C)	SV (hr ⁻¹)	λ	H _{2,eff} /NO _x
1000	2	320	15,000	0.92	23.9
1000	6	463	27,000	0.94	14.5
2000	2	529	27,000	0.97	30.8
2000	8	696	64,000	0.96	23.5
3000	2	619	38,000	0.96	23.0
3000	8	752	89,000	0.95	13.0