

Potential and Challenges for a Water-Gas-Shift Catalyst as a Combustion Promoter on a D-EGR® Engine

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ABSTRACT

In light of the increasingly stringent efficiency and emissions requirements, several new engine technologies are currently under investigation. One of these new concepts is the Dedicated EGR (D-EGR®) engine. The concept utilizes fuel reforming and high levels of recirculated exhaust gas (EGR) to achieve very high levels of thermal efficiency. While the positive impact of reformat, in particular hydrogen, on gasoline engine performance has been widely documented, the on-board reforming process and / or storage of H₂ remains challenging.

The Water-Gas-Shift (WGS) reaction is well known and has been used successfully for many years in the industry to produce hydrogen from the reactants water vapor and carbon monoxide. For this study, prototype WGS catalysts were installed in the exhaust tract of the dedicated cylinder of a turbocharged 2.0 L in-line four cylinder MPI engine. The potential of increased H₂ production in a D-EGR engine was evaluated through the use of these catalysts. Furthermore, the impact on engine performance was also examined. By using a WGS catalyst, H₂ levels can be increased significantly, leading to further improved burn durations, combustion instabilities, decreased HC emissions, and greater knock resistance which can directly translate into enhanced engine efficiency. In addition, this paper also briefly discusses the current shortcomings of the WGS technology in an engine environment.

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INTRODUCTION

Energy security and a cleaner environment are globally viewed as long-term targets. To achieve this vision, many governments are imposing new stringent emissions and efficiency standards to their local industries. In the United States, the transportation industry has to comply with two sets of parallel standards: the corporate average fuel economy (CAFE) standards and the greenhouse gas (GHG) emission standards. Based on these standards, passenger cars will be required to have a fuel economy of 54.5 mpg and emit on average 163 g/mile CO₂ by 2025 [1]. In Europe, the mandatory CO₂ emission targets will be 95 g/km by 2020 for new passenger vehicles [2]. These new regulations are putting an emphasis on further improving the efficiency of the internal combustion engine.

The impact of hydrogen or reformat, that is H₂ and CO, on spark ignition (SI) combustion has been widely documented. Alger et al. [3] demonstrated how H₂ addition shortens the combustion duration, increases combustion stability and efficiency and allows extending the EGR limit for gasoline and natural gas engines. Similar results were shown by Conte et al. [4] who investigated H₂ enrichment of a stratified single cylinder gasoline direct injection (GDI) engine. Frigo et al. [5] applied this idea to an ammonia fuelled SI engine to enhance burn rates. Several researchers have also published the improved lean stability limit through H₂ enrichment [6, 7]. Further experiments have shown knock propensity improvements when reformat is added.

Topinka et al. [8] found that when 15% and 30% of the fuel is partially oxidized into H₂, CO, and N₂, the octane number requirement of the primary reference fuel (PRF) decreases by approximately 8 and 20 octane numbers. Further results showed both CO and also H₂ were beneficial in separately increasing the knock resistance of the engine. Other researchers used a bottled reformat to approximate an achievable composition from an exhaust gas fuel reformer and compared the results to regular EGR operation [9]. The results showed improved combustion stability at the dilution limit. Furthermore, knock mitigation increased slightly and particle mass concentration decreased compared to the EGR dilution case. However, the results also showed that the estimated overall system efficiency (engine and fuel reformer) decreased at lower loads.

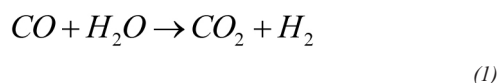
While the positive impact of H₂ on combustion and emissions is undisputed, its production is energy intensive and on-vehicle storage remains challenging. Hydrogen is mainly stored in liquid or compressed form. Both approaches, however, have major disadvantages. Liquid H₂ storage requires the handling of a cryogenic liquid to maintain temperatures around -252°C at atmospheric pressures [10]. When H₂ is not in a liquid state, it must be compressed to high pressures due to its low volumetric energy density. Generally, compressed H₂ fuel tanks will operate under pressures of 350-700 bar. In case of a pressure vessel failure, severely hazardous situations can occur [11, 12].

Instead of storing hydrogen, it can also be generated by on-board fuel reforming. One reforming method consists of a plasmatron fuel reformer. The plasmatron consists of a copper cathode and a copper tubular anode. An electrical insulator separates the electrodes. Air is used as the plasma forming gas. By means of electrical energy, the plasmatron reformer heats a fuel and air mixture to average bulk gas temperatures greater than 800 °C and injects it downstream from the electrodes where the reformation reactions occur. At the elevated temperatures, a wide range of hydrocarbon fuels can be reformed into hydrogen-rich gas [13, 14].

Extensive work also has been done in the field of steam reforming. Catalytic steam reforming is the major industrial route for hydrogen and synthesis gas production. The process uses light hydrocarbons, such as methane, to react with water in a reactor [15]. For gasoline on-board reforming, the steam reforming, partial oxidation reforming or auto-thermal reforming technique can be selected [16]. However, high octane premium gasoline requires high temperatures and long contact times for the reforming process due to their high content of aromatics [17].

Ideally, on-board fuel reformers utilize exhaust heat to drive their endothermic reactions. By doing so, some of the waste heat can be recovered and the system efficiency improved. Fowler et al. [18] used a copper-nickel catalyst applied to a 3.5 L V6 flex-fuel gasoline engine for low temperature ethanol reforming. The results showed more than 10% brake thermal efficiency (BTE) improvement was possible at low loads over the engine operating without the reformer.

The water gas shift reaction, displayed in Equation (1), is a well known chemical reaction that utilizes the reactants CO and H₂O to react to CO₂ and H₂. Historically, the main application of the industrially important reaction has been H₂ production for ammonia synthesis. A more recent application is the H₂ generation for fuel cells [19]. In a D-EGR engine, a WGS catalyst can be applied to the dedicated cylinder exhaust tract to increase H₂ concentrations and potentially improve combustion. Other reactions are promoted by a catalyst in the EGR stream. The three main reactions are steam reforming of unburned HC, dry reforming of the CO₂, and the water-gas shift reaction. The WGS reaction is the most significant at the temperatures and constituent concentrations present in gasoline engine exhaust though the other reactions also play a role.



DEDICATED EGR ENGINE

The D-EGR engine is an engine configuration where the exhaust of a sub-group of power cylinders is routed back to the intake of all the cylinders, creating EGR for all cylinders with the exhaust of a few. In a four cylinder application, the exhaust of one cylinder will be used as EGR for the entire engine, resulting nominally in 25% EGR across the operating map. This minimizes the need for active EGR control across the speed load range. By dedicating EGR production to a sub-group of cylinders, the D-EGR cylinder(s) can now operate at any equivalence ratio, since their exhaust will never exit the engine without passing through another cylinder operating at a

stoichiometric air fuel ratio (AFR). This offers options to vary the gaseous composition of the EGR. In particular, it allows the D-EGR cylinder to run rich and produce hydrogen (H₂) and carbon monoxide (CO) through in-cylinder fuel reformation. The in-cylinder reformation process reduces the heat rejection normally associated with external reformers while continuing to generate power in the dedicated cylinder(s). The presence of reformat enhances the flame speeds, combustion, and knock tolerance of all the cylinders [20] and can hence overcome combustion limitations that have historically limited SI engine efficiency at high dilution levels. Since only stoichiometric exhaust leaves the engine, a conventional three-way catalyst can be utilized to reduce pollutant emissions. The net result of this engine architecture has demonstrated very high engine efficiency with a low associated cost [21, 22]. Moreover, the D-EGR engine is capable of operating on a variety of alternative fuels, including ethanol and natural gas.

The motivation for this project was to demonstrate the benefits of additional H₂ on combustion behavior and performance on a D-EGR engine utilizing an integrated WGS catalyst for further improved hydrogen production.

EXPERIMENTAL SETUP

This study has been carried out on a turbocharged, inline four cylinder 2.0 L engine with port fuel injection. The engine was equipped with variable camshaft phasers on the intake side. In its baseline configuration, peak torque of 300 N-m was reached starting at 2250 rpm and maximum power delivery was 180 hp at 5500 rpm. One measure of the engine modifications for this work included the replacement of the production turbo charger with a dual-scroll unit designed for a 1.6 L engine to account for changing exhaust and intake conditions from the EGR dilution. Additionally, a Dual Coil Offset (DCO) high ignition energy system was employed. The ignition system was fully adjustable and is described in detail in previous publications [23, 24]. However, unless otherwise noted, the ignition energy was controlled to ~400 mJ and 5 DCO re-strikes. To take full advantage of the improved knock resistance with high levels of EGR, the stock compression ratio of 9.1:1 was increased to 12.5:1 and eventually to 13.5:1. Table 1 gives a description of the relevant physical parameters of the engine in stock form. The fuel for this study was the Haltermann EEE certification gasoline with an anti-knock index (AKI) of 92 and a lower heating value (LHV) of 42.89 MJ/kg.

Table 1. Base engine specification

Displaced volume	1998 cc
Stroke	93 mm
Bore	82.7 mm
Connecting Rod	144 mm
Compression ratio	9.1:1
Number of cylinders / valves	4 in line / 16
Maximum power	180 hp @ 5500 rpm
Maximum torque	300 Nm @ 2250 rpm
Injection	Multipoint sequential

Several different WGS catalysts were tested on the D-EGR engine. Differences in the catalysts included, but were not limited to, substrate size and material, cell density and washcoat. The catalysts were installed right after the dedicated cylinder exhaust port and before the EGR mixer. The most intensive WGS catalyst testing was performed on a production three-way catalyst (TWC) designed as a close-coupled catalyst for a 1.6 L GDI engine. As a result, most of the data presented in this paper was recorded with the production TWC. Data using the prototype WGS catalysts is marked as such. The TWC utilized a ceramic substrate whereas the WGS catalysts used metal foam filters as the substrate [25] and were catalyzed for WGS reactivity. Precious metal loadings and substrate formulations were confidential and were not identified. The specific catalyst volumes and substrate materials are given in Table 2.

Table 2. WGS catalyst volumes

	WGS cat #1	WGS cat #2	WGS cat #3	WGS cat #4
Volume	1.43 L	2.1 L	1.27 L	1.27 L
Substrate	ceramic	Metal foam	Metal foam	Metal foam
Total PGM	medium	high	high	high

An embodiment of the D-EGR concept is shown in the schematic in Figure 1. In this graphic, only one of the cylinders is used to produce the entirety of the EGR induced by the engine. An additional feature of the D-EGR setup was the UEGO sensor in the dedicated exhaust stream for fueling feedback and control. The prototype EGR mixer was designed to allow good temporal EGR mixing to evenly spread the exhaust gas expelled from one cylinder across all four.

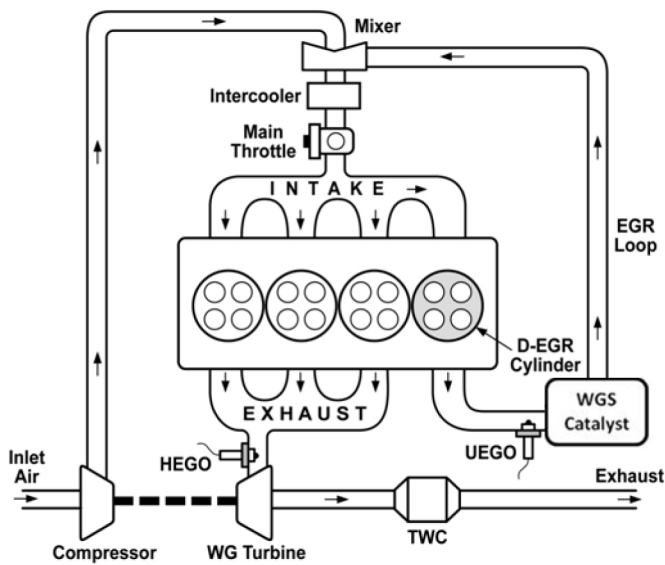


Figure 1. Schematic of a turbocharged 4-cylinder engine in a D-EGR configuration

RESULTS AND DISCUSSION

This paper has been divided into four sections. The first section discusses general findings and observations using a WGS catalyst in an engine environment. The following two sections examine the impact of an added WGS catalyst on D-EGR engine performance, emissions, and efficiency at part and high loads. Finally, the last

section provides findings about durability challenges of WGS catalyst units installed in the constantly rich operated dedicated cylinder exhaust stream.

General WGS Catalyst Observations

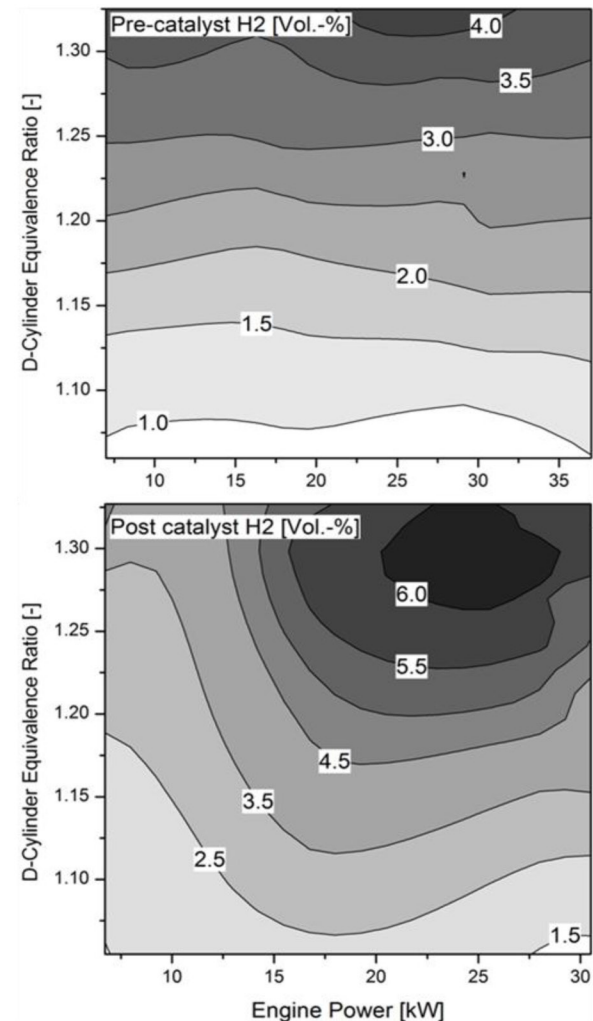


Figure 2. Pre and post catalyst H_2 vs. engine power and D-EGR fueling utilizing a production three-way catalyst (WGS cat#1) and HEEE gasoline

To study how temperatures and mass flows affect H_2 levels, plots were generated to show the H_2 concentration before and after the WGS catalyst #1 as a function of engine power (Figure 2). The H_2 concentrations upstream and downstream of the catalyst were determined by a Hewlett Packard Gas Chromatograph 5890-TDC. For the H_2 analysis, exhaust gas samples were collected utilizing a heated, stainless steel container. The exhaust gas samples were then transported to the gas chromatograph and analyzed. The top plot in Figure 2 shows the pre-catalyst H_2 concentrations and the bottom plot shows the post-catalyst concentrations for Haltermann EEE gasoline with a 1.862 hydrogen to carbon ratio. Data was recorded using the de-greened but fresh TWC. Engine power does not seem to have an effect on pre-catalyst H_2 . The amount of pre-catalyst H_2 is primarily a function of the dedicated cylinder equivalence ratio. However, engine power has an effect on the post-catalyst H_2 concentrations because D-EGR exhaust temperature and flow are proportional to engine power. The highest total H_2 concentrations were found at 1.3.

D-EGR cylinder equivalence ratio and near 25 kW brake power. At lower power levels, the exhaust gas temperatures were too low for significant CO conversion rates. Higher brake power levels featured sufficiently high catalyst temperatures, but with increasing engine speeds and loads the space velocities also increased. This trade-off between high temperatures and high space velocities resulted in a H_2 production peak of 6 Vol.-% at moderate engine power. It must be stated that the absolute post-catalyst numbers may vary and the location of the optimal H_2 islands will shift depending on substrate and coating. However, in general, the trend relationship between the parameters in this study should still be valid.

As shown above, WGS conversion efficiency depended on temperature and the activation temperature was found to be approximately 450° C for the catalyst investigated here. To examine the possible temperature range of a D-EGR engine, an operating map with dedicated cylinder exhaust port temperatures is shown in Figure 3. This map was generated using the D-EGR engine with 12.5:1 CR pistons and $\phi_{D-EGR} = 1.3$. The operating map covers full load operation up to 5000 rpm with dedicated cylinder exhaust port temperatures ranging from 400 to 650 °C. Since D-EGR exhaust gas temperatures are a function of equivalence ratio, the absolute numbers can differ depending on the amount of over fuelling. Also worth mentioning is the actual temperatures that the WGS catalyst sees will be lower due to radiation and convection losses from the port to the WGS catalyst face.

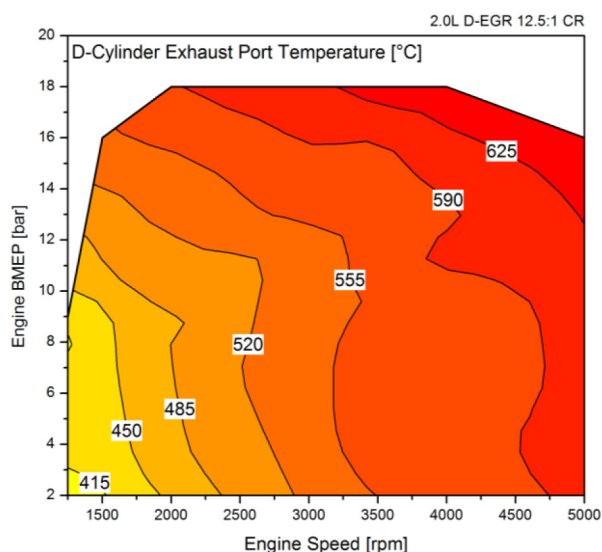


Figure 3. Dedicated cylinder exhaust port temperatures with 12.5:1 CR and $\phi_{D-EGR} = 1.3$

Since in-situ H_2 measurements are not feasible with the common emissions analyzers used in the automotive industry, it was of interest to find a surrogate to accurately predict H_2 . Therefore the next task was to investigate and measure actual H_2 production across the reactive WGS catalysts and compare it to the other exhaust gas constituents. Theoretically, the CO concentration pre and post catalyst should indicate the amount of H_2 created through the WGS reaction. H_2 concentrations in the exhaust gases were measured using a gas chromatograph. For each data point, three exhaust gas samples were

analyzed. The H_2 numbers shown are an average of these three samples. Pre- and post-catalyst emissions were measured using a Horiba 7100 exhaust gas analyzer.

Figure 4 displays measured pre-catalyst CO emissions versus equivalence ratios. Increasing the equivalence ratios elevates CO emissions through incomplete combustion. This trend is fairly linear up to $\sim \phi = 1.35$ before the CO emissions begin to deviate. The rich stability or flammability limit varied slightly with operating condition but in general was found to be around $\phi_{D-EGR} = 1.6$. Literature suggests a very similar trend for CO emissions during rich combustion [26, 27]. Since pre-catalyst CO and H_2 (compare with Figure 2) correlate well with the dedicated cylinder equivalence ratio, pre-catalyst H_2 levels can be predicted with good confidence. However, if the equivalence ratio is determined by a UEGO sensor in the dedicated exhaust runner, O_2 -sensor biasing must be taken into account. As is commonly documented, pressure has a significant effect on the O_2 -sensor measurement. Depending on the pressure conditions in the dedicated cylinder, the actual equivalence ratio can be over or under predicted. Besides the major impact of the pressure on the O_2 -sensor signal, H_2 , NH_3 are also known to bias the output of UEGO sensors [28, 29]. It is thus recommended to incorporate a correction factor to the O_2 -sensor signal if an UEGO sensor is used for dedicated cylinder fueling control or pre-catalyst H_2 prediction. The pressure correction for UEGO technologies are understood, well documented, and easily modeled. However, the correction for H_2 and other biasing constituents in rich exhaust is highly dependent on sensor technology and should be characterized independently.

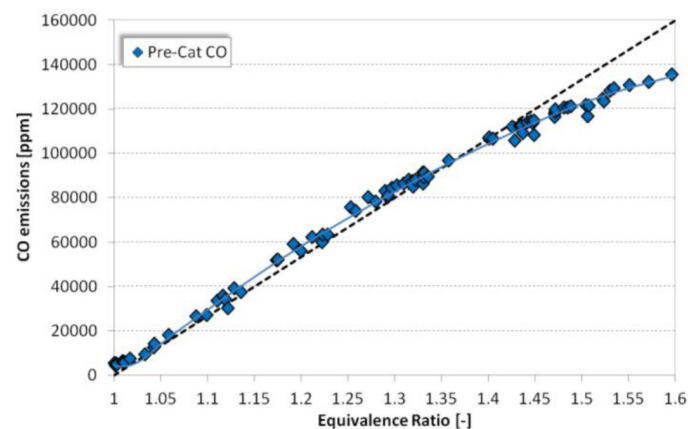


Figure 4. Pre-catalyst CO emissions versus equivalence ratio for HEEE gasoline

In Figure 5 a summary of all the measured H_2 data for two WGS catalysts is shown. Additionally, the correlation between ΔCO and ΔCO_2 emissions across the catalysts is given in Figure 6. In theory, the water gas shift reaction converts one mole CO to H_2 if no other chemical reactions occur. The black dashed line represents this 1:1 correlation between the CO reduction and H_2 formation. At CO conversion rates below 35000 ppm, this trend is valid. At greater CO conversion rates; however, the measured CO reduction was larger than the measured H_2 production. It appears that the ΔCO is diverging from the ΔH_2 at high WGS reactivity. As mentioned previously, there are other reactions occurring and they are assumed to be the primary reason for the divergence at very rich conditions. While there is some