

High Efficiency, Low Feedgas NO_x, and Improved Cold Start Enabled by Low-Temperature Ethanol Reforming

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ABSTRACT

Two major barriers to wider use of ethanol as an engine fuel are ethanol's low heating value per volume relative to gasoline and higher hydrocarbon emissions at startup. Ethanol provides about one-third lower fuel economy than gasoline on a volumetric basis if the two fuels are utilized with equal efficiency, making ethanol less attractive to consumers. In addition, it is difficult to meet emissions standards such as SULEV when using E85 or hydrous ethanol, because ethanol's low volatility and high heat of vaporization compared to gasoline result in incomplete combustion when the engine is cold.

A catalyst consisting of a copper-plated nickel sponge has recently been developed that enables ethanol to be reformed at around 300°C to a mixture of hydrogen (H₂), carbon monoxide (CO), and methane (CH₄). This low reforming temperature enables heat to be supplied from the engine exhaust. The hydrogen content in the fuel has been previously reported to enable ultralean operation ($\lambda > 2$) at high compression ratio (up to 17:1) at part load. As a result, efficiency 40% better than gasoline without dilution was achieved, which would largely offset the fuel economy penalty for ethanol. It would be expected that cold start using stored ethanol reformat, a gaseous fuel, would provide much lower startup hydrocarbon emissions than liquid ethanol or E85.

This paper reports the results of a study performed using a H₂/CO/CH₄ gas mixture simulating the output of a reformer in a single-cylinder research engine at a compression ratio of

14:1. The study addresses the practicality of achieving the desired efficiency improvements in a realistic engine-reformer powertrain. For example, the lean burn strategy used to improve efficiency in the previous study reduced engine-out NO_x, but the excess oxygen in the exhaust would disable the NO_x reduction function of three-way catalyst (TWC) exhaust aftertreatment. Use of exhaust gas recirculation (EGR), rather than lean operation, would preserve the NO_x activity of the TWC. In this study, it was found that use of ethanol reformat enables stable combustion at high cooled EGR rates (30-36%). EGR also provides hotter exhaust than high λ operation, which aids reformer function.

Another question of practical importance is what fraction of the ethanol needs to be reformed in order to maintain high dilution rates. Reforming only a portion of the fuel reduces the demand on the reformer, which would enable a smaller reformer to be installed on a vehicle, reducing cost and reformer startup time. Reforming of 50-75% of the fuel was found to be optimal at 3.5 and 6 bar net mean effective pressure (NMEP) at 1500 and 2000 rpm, although most of the efficiency benefit could be obtained when reforming only 25% of the fuel. At high load (8.5 bar NMEP), reforming is not advantageous.

Engine startup at 25°C using reformat was confirmed to be far smoother than using liquid ethanol fuel and to provide much lower hydrocarbon emissions. The amount of reformat required for startup and catalyst light-off could reasonably be stored on board a vehicle.

INTRODUCTION

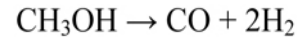
Onboard reforming of liquid fuels is a strategy for improving engine efficiency by converting a portion of the fuel to hydrogen and other gases on board the vehicle. Hydrogen increases the flammability of the fuel, enabling lean burn or high EGR strategies to be implemented while maintaining combustion stability [1].

Dilution of the fuel-air mixture with excess air or EGR reduces intake pumping work at part load by increasing the manifold absolute pressure (MAP) at a given torque. Also, both methods of dilution reduce combustion and burned gas temperatures, which results in lower heat transfer losses. Additionally, the lower burned gas temperatures result in reduced dissociation of the combustion products and lower specific heat of the gases. Collectively, these effects significantly decrease net specific fuel consumption (NSFC) and increase net thermal efficiency (NTE). The lower combustion and burned gas temperatures also result in a significant reduction in engine-out (feedgas to the exhaust aftertreatment) NO_x emissions.

The most widely-studied example has been reforming of hydrocarbon fuels to H₂ and CO [2,3,4], an approach that can also be used for fuel cell vehicles [5]. At part-load (2-4 bar BMEP), several studies have demonstrated efficiency improvements of 10-25% when reforming 30-100% of the fuel by operating at high λ [6]. Fuel consumption in the reformer offsets these gains, however. Temperatures in excess of 600°C are thermodynamically required for hydrocarbon reforming, which exceeds exhaust temperatures, particularly at high λ [7]. A portion of the fuel must therefore be combusted in order to maintain high reformer temperature and supply the heat of reaction. Introduction of air causes dilution of the reformat by nitrogen as well as CO₂ and H₂O. Nitrogen has been reported to constitute 52% of typical “plasmatron” reformat [8]. Quader *et. al.* estimated that a gasoline reformer for a V8 engine would generate about 7.2 kW of waste heat, essentially the unrecovered thermal energy carried out of the reformer by the reformat [9]. Most studies on reformed gasoline have used simulated reformat from gas cylinders and estimated reformer losses.

Reforming of methanol to CO and H₂ (eqn. 1) has received considerable attention over the last several decades because reforming can be completed at catalyst temperatures below 300°C [10, 11]. Methanol reforming can therefore be conducted without burning any methanol in the reformer to supply heat and without dilution of the reformat. Efficiency improvements of over 30% have been demonstrated at a vehicular scale with integrated reformer/ICE powertrains, although pre-ignition of the hydrogen-rich reformat fuel was reported to be a serious operational issue near $\lambda = 1$ [12,13,14,15]. In addition, the absence of a methanol

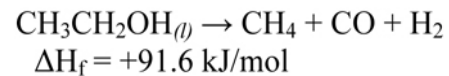
infrastructure limits the commercial prospects for this technology. There has been little research on reformed methanol ICE vehicles in the last two decades, although methanol reforming for fuel cell vehicles remains an area of interest.



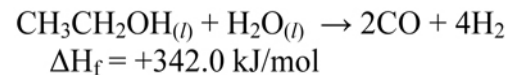
(1)

LOW-TEMPERATURE ETHANOL REFORMING

In 2005, Morgenstern and Fornango reported that ethanol could be reformed below 300°C to produce a mixture of gases (eqn. 2), referred to as “low temperature ethanol reformat” [16]. An inexpensive copper-plated nickel sponge (Raney nickel) catalyst promoted the reaction with high selectivity and good stability. At high conversion, no side reactions are significant; although some water-gas shift occurs if hydrous ethanol is used, generating additional hydrogen. Reforming occurs at a much lower temperature than that required for high hydrogen yield conventional steam reforming of ethanol (~600°C) [17]. Ethanol steam reforming, and the corresponding autothermal process, is a widely studied reaction that produces a more hydrogen-rich gas mixture (eqn 3), but as with gasoline reforming, a portion of the fuel must be burned in order to maintain reaction temperature [18, 19]. There does not appear to be any research on the use of high-temperature ethanol reformat in an engine.



(2)



(3)

Low temperature reforming of ethanol is an endothermic process, whereby the heat of formation is provided by engine exhaust gas energy (eqn 2). In this regard, low temperature ethanol reforming represents a form of exhaust heat recovery, which in theory should provide a fundamental improvement in thermal efficiency of the engine-reformer system. The net heating value (NHV) of ethanol reformat is about 7% greater than that of liquid ethanol. However, a portion of this gain in NHV is due to the fact that ethanol reformat is a gaseous fuel, whereas ethanol is a liquid fuel. In the test to determine the NHV of a liquid fuel, some of the heat released by combustion of the fuel is offset by the heat of vaporization (HoV) required to vaporize the fuel. In an engine, the heat to evaporate the fuel comes from the intake ports/valves and/or inlet air, and does not detract from the heat released during combustion. In the case of ethanol, the HoV is 31.2 kJ/mol

of heating value, or 3%. Therefore the effective increase in NHV in an operating engine for ethanol reformat relative to the ethanol from which it is derived is 4%.

A 2008 study by Hoffmann *et. al.* demonstrated that, despite its comparatively low hydrogen content (1/3 on a molar basis), low-temperature ethanol reformat enabled engine operation beyond $\lambda = 2$ at compression ratios up to 17:1 [20], allowing efficiency improvements of about 40% over a gasoline baseline to be achieved. No pre-ignition was encountered, even during stoichiometric operation, due to the lower levels of hydrogen.

This efficiency improvement is similar to that reported for reformed methanol engines, but ethanol possesses several advantages over methanol as an engine fuel. Unlike methanol, ethanol is non-toxic. The carbon in bio-ethanol represents atmospheric CO₂ that has been fixed by photosynthesis, rather than being derived from fossil fuels. In addition, a sizeable ethanol production and distribution infrastructure is in place in the US and Brazil.

Lean operation accounted for most of the efficiency gain, but increase in compression ratio and the increase in fuel value that occurs during reforming also made significant contributions. Lean operation reduced burned gas temperatures, greatly reducing feedgas NO_x emissions. However, lean operation disables the NO_x reduction function of three-way catalysts. It was unclear whether the NO_x suppression achieved using low-temperature ethanol reformat was adequate to enable a vehicle to satisfy NO_x emissions standards without additional lean NO_x exhaust aftertreatment.

PURPOSE OF THE STUDY

In this study, the performance of liquid ethanol and simulated low-temperature ethanol reformat from pre-mixed gas cylinders was assessed in a single-cylinder research engine. Optimal operating conditions were roughly identified which met the thermal demands of the reformer (sufficiently high exhaust temperatures) while satisfying emissions requirements and achieving high efficiency. More broadly, the study was designed to evaluate the potential to implement low-temperature ethanol reforming in a practical commercial vehicle. The key issues were as follows:

1). Hydrogen-rich fuels enable both lean burn (high λ) and high levels of EGR to be achieved. Three-way catalysts are compatible with EGR, assuring that low tailpipe NO_x emissions can be achieved. But efficiency is expected to be better using high λ , as demonstrated in an engine utilizing hydrogen-enriched natural gas [21]. Low-temperature ethanol reformat was tested at both high λ and at high EGR rates in order to quantify the tradeoff between higher efficiency with

lean operation and the potential to use conventional TWC NO_x aftertreatment.

2). As noted above, studies of reformed gasoline have found that reforming only 10-30% of the fuel is sufficient to provide substantial efficiency improvement. Partial reforming of ethanol on board a vehicle would be advantageous because it would enable a smaller reformer to be used. This would reduce reformer cost and the time required to bring the reformer to operating temperature. In addition, maintaining high exhaust temperature would be less crucial. Mixed-fuel operation also enables the charge-cooling properties of liquid ethanol to be exploited in combination with dilute combustion enabled by reformat.

3). Achieving low startup emissions is challenging using liquid ethanol fuel. The low vapor pressure of ethanol relative to gasoline makes it difficult to achieve ignition in a cold engine. E100 engines typically cannot cold start below 10°C. Even at higher temperatures using E85 fuel, excessive hydrocarbon emissions are typically observed during cold start due to incomplete fuel vaporization and combustion. Using ethanol reformat stored on board the vehicle for cold start is expected to enable low hydrocarbon startup emissions to be achieved. Quantification of the amount of reformat required enables assessment of the practicality of this approach.

EXPERIMENTAL

SINGLE-CYLINDER ENGINE

The engine used for this study was a single-cylinder research engine equipped with a hydraulic variable valvetrain, a gasoline PFI system, and cooled external EGR. The geometric parameters of the engine are shown in Table 1.

Table 1. Geometric parameters of the single-cylinder engine

Bore [mm]	90.2
Stroke [mm]	90.0
Displacement [l]	0.575
Compression Ratio	10:1
Valve Arrangement	2 Intake / 1 Exhaust
Valve Timing/Lift	Fully Variable
Fuel Injection System	PFI

The piston used at 10:1 compression ratio was completely flat. Gasoline data was obtained using this piston. For experiments using liquid ethanol and simulated reformat, the

compression ratio was increased to 14:1 by modifying the piston. The high compression piston had a domed geometry with three cutouts for valve-to-piston clearance. Knock-free operation of ethanol and low-temperature ethanol reformat has been demonstrated at compression ratios up to 17:1 [20], but the design of the cylinder head prevented operating above 14:1.

The engine has two inlet ports, a tangential swirl port and a neutral filling or high flow port which was disabled during this study. The ports are designed to give a torque meter swirl ratio of 2.6 with only the tangential swirl port valve open [22]. A high swirl ratio is known to be beneficial when operating at high dilution [23, 24].

A Sturman fully variable hydraulic valve actuation (HVA) system was used on the engine to control valve timings and lifts [22]. It utilizes hydraulic force controlled by high-speed digital latching valves, in place of traditional mechanical camshafts, to actuate the engine intake and exhaust valves. The use of reformed ethanol is compatible with cam-actuated valves, but HVA was experimentally convenient for this study. Fixed valve timing was used, and the valve timing was determined by maximizing intake air flow and peak cylinder pressure while motoring the engine unthrottled at 2000 rpm.

The parasitic load of the hydraulic valve actuation system is not a factor in this study, because all configurations which are compared used the same valvetrain system, and therefore are identically affected. Additionally, as is typical of single cylinder testing, all test conditions were set based on NMEP and the results are reported on a net specific basis. These parameters are independent of the levels of engine mechanical friction and parasitic losses.

Simulated low-temperature ethanol reformat, composed of equal volumes of H_2 , CO , and CH_4 supplied from pre-mixed gas cylinders at ambient temperature was directed into the air intake pipe, upstream of the mixing tank.

Cooled instead of uncooled EGR was used as a safety precaution to avoid potential backfire in the intake system given the presence of hydrogen. It should be noted that the use of uncooled EGR would be preferred at engine conditions where the engine is not knock-limited or unthrottled, because the higher temperature of the charge results in both higher MAP at a given torque due to lower density, reducing pumping work, and in improved ignitability and laminar flame speed, extending the dilute operating limit. Therefore the use of cooled EGR in this study gives a conservative estimate of potential benefits.

TEST CELL SETUP

AVL PUMA 5.5 was installed in the single-cylinder engine test cell for dynamometer control and low speed data

acquisition. In general, low speed data include process temperatures, pressures, voltages, and currents.

For high speed data acquisition, an AVL Indimeter 619 was employed. The AVL Indimeter 619 is a device with 8 channels capable of 1 MHz data acquisition rate. The test cell was equipped with AVL IndiWin software which works with the Indimeter 619 for high-speed real-time data analysis and crank angle based measurements. All combustion related parameters, such as NMEP and crank angle of 50% mass fraction burned location (CA50), were calculated by the software. Data in this paper is reported on a net basis that includes the effects of the intake and exhaust strokes in addition to the compression and expansion strokes (i.e. integrated over 720 crank angle degrees).

An AVL CEB II raw emission bench was installed in the test cell for emission measurement. This device performs continuous measurement of HC , CO , CO_2 , O_2 , and NO_x .

Aldehyde measurements were determined using a hand held device that utilizes colorimetric tubes. The exhaust gas was drawn through the pre-calibrated tubes from a port in the exhaust stream using the hand-held pump. Measurements were recorded in parts per million (ppm) and converted to g/kWh based on total exhaust flow, NMEP, and engine speed. DNPH cartridges were also used to measure aldehydes; however, this data is not reported in this paper. Steady-state operation of the engine makes the use of DNPH cartridges difficult and the data questionable.

EFFICIENCY CALCULATIONS

Denatured anhydrous ethanol (E100) was used in the study. Its NHV was determined experimentally to be 27.281 MJ/kg. The gasoline (Indolene) used as a comparator was found to have a NHV of 43.270 MJ/kg. A 1:1:1 mixture of H_2 , CO , and CH_4 (molar basis) was purchased pre-mixed in gas cylinders and used to simulate low-temperature ethanol reformat. Its heating value was calculated from the gas mixture composition. NTE was calculated based on these values, and is defined as the power output divided by the heat input, where the power output is based on the integral of the cylinder pressure vs. cylinder volume over the full engine cycle of 720°CA.

A second efficiency metric, “effective NTE”, was also calculated for experiments using a combination of E100 and simulated reformat fuel. This metric is intended to represent the efficiency of an engine-reformer system. The system boundary encloses both the engine and the reformer. In order to calculate the efficiency of the composite system, the NHV of reformat is set equal to that of ethanol. This is justified because the reformer would be heated exclusively by engine exhaust, with no additional fuel required for reformer operation.

RESULTS AND DISCUSSION

COMPARISON OF LEAN A/F AND COOLED EGR AT PART-LOAD WITH LOW-TEMPERATURE ETHANOL REFORMATE FUEL

The principal advantage of hydrogen-rich fuels is that they enable adequate combustion rates to be maintained when the cylinder mixture is diluted with exhaust or excess air. In the first part of this study, the combustion of simulated low-temperature ethanol reformat by itself was examined.

Figures 1,2,3,4 show data acquired at 1500 rpm, 3.5 bar NMEP. The 0-10% burn time at stoichiometry without dilution is extremely fast, about 10°C (Fig. 1). The 10-90% burn time of 19°C is also fast, though not as extreme as the 0-10% burn time (Fig. 2). These short burn durations are reflected in MBT spark advance of only 10°C BTDC (Fig. 3). The fast burn times are partially due to the presence of H₂ in ethanol reformat, which enhances ignitability and laminar flame speed, and partially due to the high compression temperature associated with 14:1 CR and the high turbulence level associated with 2.6 swirl ratio.

As expected, burn durations gradually increase with increasing λ or EGR, and MBT spark timing shifts to more advanced values. The increasing dilution eventually causes an increase in combustion instability, as measured by the coefficient of variation (COV) of NMEP (Fig. 4). The dilution limit is conventionally defined as the point at which COV of NMEP reaches 2%. Similar to Hoffman *et al.* [20], it was found that this occurs at about $\lambda = 2.5$ for the lean A/F approach and at about EGR = 36% for the cooled EGR approach at this speed-load point. In terms of the mass of dilution, an EGR rate of 36% corresponds to λ of 1.6. Thus, the use of excess air allows much greater dilution before combustion becomes unstable compared to cooled EGR. This is primarily because excess air contains oxygen as well as nitrogen, whereas EGR at stoichiometry contains nitrogen, water vapor, and CO₂, which are inert. NTE values for the lean A/F and EGR strategies are shown in Figure 5, and are based on the NHV of reformat. The NTE at the combustion stability limit with excess air is much higher than that with cooled EGR, because of the much greater amount of dilution with excess air.

Both approaches provide large efficiency improvements versus gasoline without dilution, 33% for the lean A/F strategy, and 20% for the cooled EGR strategy. About 6% of this benefit is due to the increased CR enabled by the high effective octane of liquid ethanol and ethanol reformat. Further, these efficiency improvements will increase by 7% for the effective NTE for low-temperature ethanol reformat (effective NTE is based on the heating value of the ethanol

from which the reformat is derived). Of course, the addition of dilution would improve the NTE of gasoline, but optimization of the gasoline case was not included in the scope of this study. Typical values for improvement of gasoline fuel consumption with dilution via external EGR at this speed-load point are about 3-4% [24].

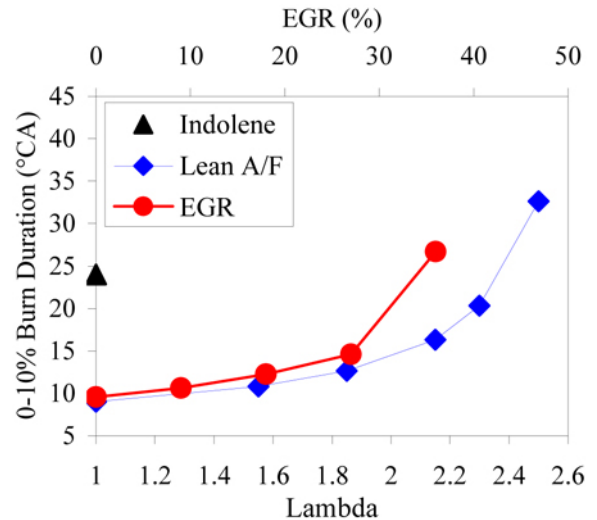


Figure 1. 0-10% Burn Duration vs. λ and EGR rate for reformat at 1500 rpm, 3.5 bar NMEP.

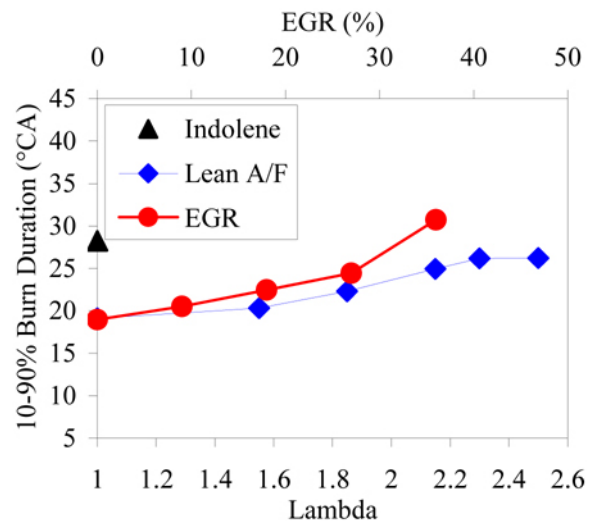


Figure 2. 10-90% Burn Duration vs. λ and EGR rate for reformat at 1500 rpm, 3.5 bar NMEP.

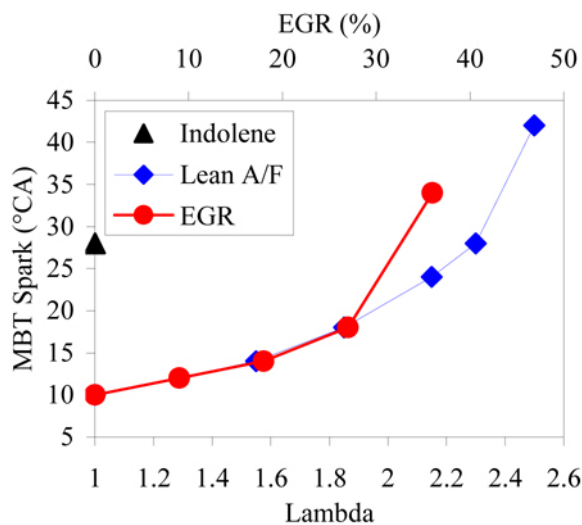


Figure 3. MBT spark timing vs. λ and EGR rate for reformat at 1500 rpm, 3.5 bar NMEP.

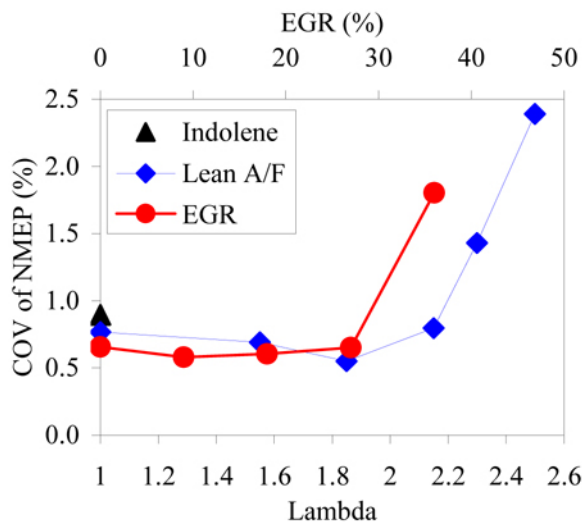


Figure 4. COV of NMEP vs. λ and EGR rate for reformat at 1500 rpm, 3.5 bar NMEP.

has the practical consequence of significantly reducing the thermal efficiency advantage of lean A/F compared to EGR (Fig. 5).

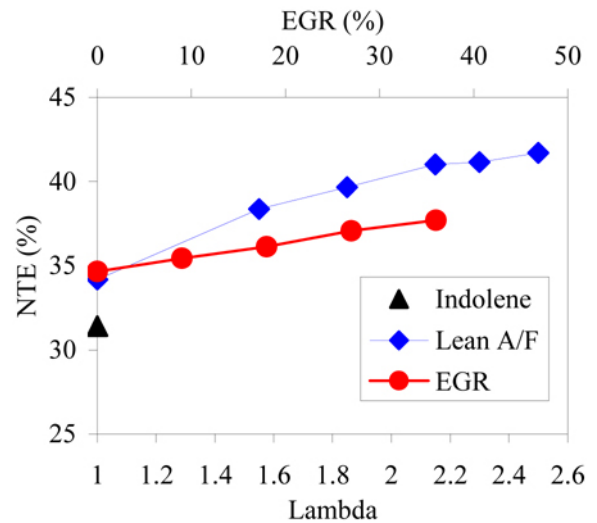


Figure 5. NTE vs. λ and EGR rate for reformat at 1500 rpm, 3.5 bar NMEP.

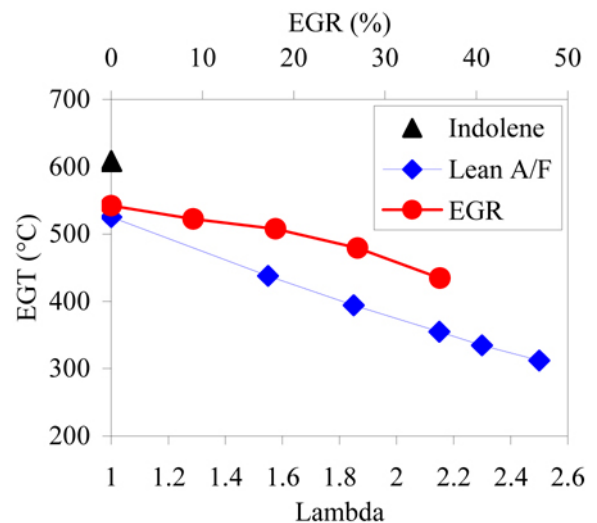


Figure 6. EGT vs. λ and EGR rate for reformat at 1500 rpm, 3.5 bar NMEP.

In addition to combustion stability, another constraint on dilute operation is imposed by the need for exhaust hot enough to maintain reformer catalyst temperatures of about 300°C. Figure 6 shows exhaust temperatures at 1500 rpm, 3.5 bar NMEP using the two strategies. Using cooled EGR, exhaust temperatures are 430°C or above throughout the range studied, which is expected to be adequate for a practical reformer. While the minimum tolerable exhaust temperature will depend on the performance of the reformer, exhaust temperatures of at least 400°C were defined as a constraint in these experiments in order to provide a temperature difference between exhaust and reformer catalyst of about 100°C to drive heat transfer from exhaust to catalyst. An exhaust temperatures constraint of 400°C imposes a limit of $\sim 1.8 \lambda$ when using the lean A/F strategy. This constraint

Feedgas NO_x , CO, and HC emissions are shown in Figure 7 for the two strategies. Both strategies are effective for reducing feedgas NO_x . As noted previously however, NO_x can be further reduced by conventional TWC exhaust aftertreatment only when maintaining stoichiometry. Using high A/F, NO_x levels at $\lambda = 1.85$ are quite low (0.9 g/kWh), although not as low as is achieved using 36% EGR (0.3 g/kWh). While a NO_x level of 0.9 g/kWh is much lower than the NO_x level at $\lambda = 1$ (19.6 g/kWh), this level is not low enough to satisfy emissions requirements without lean NO_x