

Evaluation of H₂/N₂ as an Alternative to H₂/He for Flame Ionization Detector Mix Fuel

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ABSTRACT

The Flame Ionization Detection (FID) is the most sensitive and widely used technology for the measurement of total hydrocarbons (THC). In the automotive emission testing of hydrocarbons, the fuel used for the flame in the FID analyzer is a mixture of hydrogen and helium in the ratio of 40:60. The Environmental Protection Agency (EPA) revised 40CFR part 1065 in April 2014 to include nitrogen as a balance gas alternative to helium for FID fuel mixtures used in the automotive industry. In addition to the balance gas alternative, the FID fuel blend tolerance was decreased from 40±2% to 40±1% (0.39 to 0.41 mol/mol) hydrogen to minimize the impact on analyzer response. The feasibility of nitrogen as a FID fuel balance gas was studied and compared with a helium balance gas to understand the relative impact on emission testing. The study evaluated multiple hydrogen concentrations ranging from 38-42% in both balance gases. The FID fuel was also evaluated to determine the impact of hydrocarbon contamination (0-100ppb) on the instrumental response. Hydrocarbon detection was found to be more sensitive to deviations in the fuel composition with nitrogen as a balance gas than with helium. With hydrogen composition at 40±1%, the FID response drifts up to ±6% with nitrogen compared to ±2% with helium as the balance gas. It was observed that the accuracy of the hydrocarbon analysis could be improved further by reducing the blend tolerance of hydrogen with nitrogen as a balance gas relative to helium. Background research on the impact of nitrogen as a balance gas is limited and this evaluation is aimed to study the potential of nitrogen as a replacement to helium in the coming years for FID analyses.

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INTRODUCTION

The analytical technique for determination of total hydrocarbon (THC) emissions in vehicle exhaust gases has been based on Flame Ionization Detection (FID) for more than 40 years [1]. An important parameter in FID analyzers performance is the fuel gas used. Globally, the mixture of fuel used in these FID analyzers in vehicle emission testing is typically hydrogen (H₂) and helium (He) in the ratio of 40:60. Reschke [2] and Teague *et al.* [3] determined that this 40:60 ratio provided the best sensitivity and relative response in their research conducted on various levels of H₂ in the mix fuel. Increase in the H₂ ratio in the mix fuel increased the FID sensitivity to oxygen (O₂) present in the sample. However, the flame was not stable if the H₂ ratio decreased to about 35%. Blend tolerance of the mix ratio is regulated, but depends on the regulations of the country or region. In USA, these measurements must meet the Environmental Protection Agency (EPA) requirements of the Code of Federal Regulations 40 (CFR 40) part 1065, dedicated to Engine Testing Procedures which allowed a mixture of 40±2 % hydrogen in helium balance up until 2014. The EPA revised FID fuel regulations to decrease the tolerance

of the H₂ ratio to 40±1 % (0.39 to 0.41 mol/mol) in the mix fuel using either He or Nitrogen (N₂) balance gas. Moreover, THC concentration in the fuel has been decreased from 100 ppbC₁ to 50 ppbC₁.

Limited availability of helium coupled with global supply interruptions, and have challenged He users to think of alternative solutions wherever possible. Inclusion of N₂ as an alternative to He in the FID fuel mix is a step forward to deal with the uncertain supply of He as seen in the past few years.

FID analyzers are based on the principal that a regulated flow of sample gas passes through the flame and the hydrocarbon components are ionized in the burner, producing electrons and positive ions. These ions are collected by polarized electrodes which creates a current flow. This current flow is proportional to the rate at which carbon atoms enter the burner [4]. The magnitude of the current is approximately proportional to the number of carbon atoms in a wide variety of hydrocarbon (HC) molecules in the sample [5]. The flame is sustained by regulated flows of air and fuel gas. The FID

is generally robust, linear, and sensitive to organic gases and vapors. The FID response is based on a C1 equivalent per volume. HC speciation is not a characteristic of an FID, it quantitates the number of carbon atoms in the HC. Vehicle emissions consist of complex mixtures of hydrocarbons including alkanes, alkenes, alkynes, cyclic HC, and many more functional groups. Ideally these HC should behave similarly in the FID however, in practice, their response is not necessarily uniform [1, 2, 3]. Oxygen present in the detector also contributes to the variation of signal response among HC's [1, 6, 7].

Reschke [2] suggested a sample flow of about 5 cc/min, fuel flow of 100-120 cc/min, and an air flow rate to be 4 times the fuel flow rate for optimum response of the FID analyzer. Lower sample flows were found to be less sensitive to the fuel flow rates. It was also suggested that the relative response optimization should be considered in view of the expected O₂ level of the sample, the response time needed, and the sensitivity required. Maximum sensitivity could be obtained through optimization of the flow settings for the sample, fuel, and air [4]. Reschke demonstrated how air, sample or fuel flow rates could affect relative response per carbon on FID irrespective of the H₂/He or H₂/N₂ fuel as well as any variation in pressure [2].

The purpose of this study was to evaluate N₂ FID fuel balance gas as an alternative to He for THC measurements at low levels. Nitrogen does not have a related scarcity issue and is therefore more economical than He. The research was focused on the comparative impact of both of the balance gases (N₂ or He), as well as the deviations in the fuel composition on the FID response. Moreover, signal influence was also assessed as a function of the total hydrocarbon contamination in fuel.

EXPERIMENTAL SET UP

A flame ionization detector based Rosemount Analytical Model 400A analyzer was used in this study. The special sample capillary and fuel restrictor supplied by Rosemount Analytical for premix fuel gas was installed in the analyzer so that it can operate on either H₂/He or H₂/N₂ without having to make any hardware modifications. This analyzer had three inlets: fuel, air, and sample as shown in Figure 1. The sensor was a burner in which a regulated flow of sample gas at about 7 cc/min passed through a flame sustained by the adjusted flows of about 100 cc/min mix fuel gas and 400 cc/min air for optimized signal. The fuel in this study was a mixture of either H₂/He or H₂/N₂ in the ratio of 40:60. An internal sample bypass feature provided high velocity sample flow through the analyzer to minimize system response time. An internal temperature controller maintained the analyzer interior at a constant 50°C to ensure stable and drift free operation. The analyzer provided concentration in percentage of a full scale calibrated linearly from 0 to 100%. The measured concentration of THC was given as a C1 equivalent. For example, 10 ppm of C₃H₈ would give a concentration of 30 ppmC1 equivalent. In this study, the analyzer was calibrated in the range of 0-40 ppm, so 75% full scale of

10 ppm C₃H₈ yields 30 ppmC1. Hill and Negi [8] evaluated the Beckman 400A FID analyzer for the accuracy performance and found it suitable for even sub-ppm level non-methane hydrocarbon measurements to meet the super-ultra-low-emission-vehicle (SULEV) emission measurement.

The analyzer was calibrated using either H₂/He or H₂/N₂ fuel certified as CFR 40 part 1065 (Air Liquide America Specialty Gases) with the blend tolerance of 0.4% absolute and THC less than 50 ppb. Alphagaz Air Auto (Air Liquide America Specialty Gases), certified with less than 50 ppb THC concentration, was used for the burner air. Compressed air was purified using a VICI T200-2 HC trap which ensured a THC concentration < 3 ppb at the outlet. An onsite blending panel was set up to provide varying ratios of fuel mixtures using purified gases. The switching of the fuel source from cylinder to the blending panel was facilitated through a 3-way valve without interruption of the flow. The hydrogen was supplied with a Microtorr MC 190-90FV trap at the upstream of panel to ensure THC specification remained less than 10 ppb at the outlet.

To ensure the purity of N₂ and He, upstream purifiers were used. The H₂ ratio in the fuel mixture was controlled in the range of 38-42% with calibrated Bronkhorst mass flow controllers (MFCs). The blending panel was validated by comparison with a mixture with a known accuracy and precision before conducting any experiments. The mix fuel ratio was studied in the range of 38-42% H₂ with balance of either He or N₂ to cover the global perspective on the vehicle emission testing, such as the EPA's updated regulation and European regulations. For the second part of the experiment, both balance gases for the fuel mix were precisely contaminated individually with CH₄, using a calibrated MFC before blending with H₂. About 1 ppm of CH₄ in He and N₂ balance were used for contamination to be consistent with both of the fuel balance gases. The FID fuel was studied in the range of 0 to 100 ppb of hydrocarbon contamination.

The MFCs used in the experiment were checked using a soap film flow meter to ensure the precision and accuracy compared to the set up values with the certified accuracy of ±0.5%. The uncertainty calculated on H₂ ratio for the blending panel was within 1.5% compared to the given 1% uncertainty on the H₂ ratio for the fuel cylinder. The 1.5% uncertainty on the 40% H₂ mix fuel was well within the range of 39 - 41% of H₂ in the regulated fuel mix ratio. The results indicated that the MFCs were capable of providing good accuracy for these experiments.

Master class span gas (10.2 ppm C₃H₈) and sample gas (10.2 ppm C₃H₈ or 10.2 ppm CH₄) in N₂ balance were obtained from Air Liquide America Specialty Gases with 2% accuracy. Both the span gas and sample gas cylinders were validated for accuracy on a Varian GC-FID in the lab before conducting the experiments.

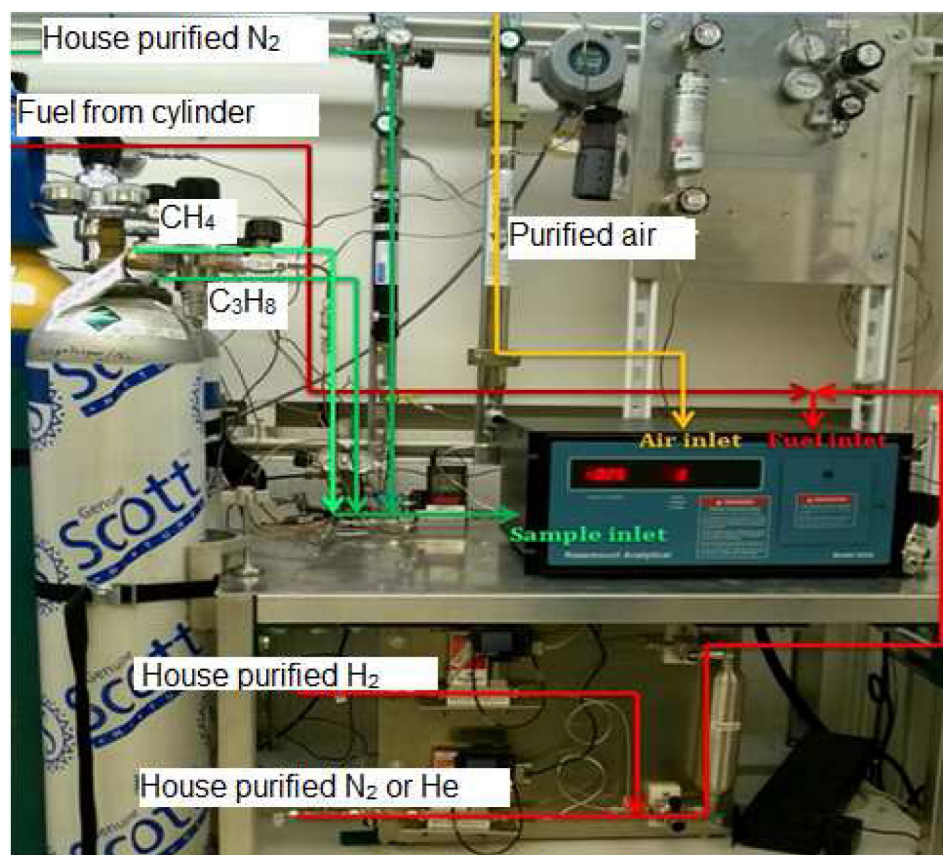


Figure 1. Experimental setup

EXPERIMENTAL PROTOCOL

The experiment was divided into two parts. In the first part, seven replicate experiments were conducted with the H_2/He fuel and seven replicates with the H_2/N_2 fuel. Each replicate consisted of the following steps: 1) The analyzer was zeroed with N_2 and then calibrated with propane with either the fuel cylinder 40/60 H_2/He or H_2/N_2 ; 2) The fuel source was switched to the blending panel and the influence of the H_2 ratio was evaluated with sample gases (C_3H_8 and CH_4). The H_2 ratios were tested from 38% to 42% at 0.5% increments; 3) Results obtained with the blended mixture at the 40/60 ratio were compared to those with the reference mixture of the cylinder to validate the blending system.

In the second part, five replicate experiments were conducted with 40/60 H_2/He or H_2/N_2 fuel. This time the H_2 ratio was kept constant at 40%. Each replicate consisted of the following steps: 1) The blending panel was set to deliver 40/60 H_2/He or H_2/N_2 ; 2) The analyzer was zeroed with N_2 and calibrated with propane; 3) The fuel was doped with HC concentrations ranging from 0 ppb C_1 to 100 ppb C_1 at 20 ppb C_1 increments. For each contamination concentration, baseline (pure N_2) and sample gases (C_3H_8 and CH_4) were measured.

VALIDATION OF BLENDING PANEL

The Rosemount analytical FID analyzer equipped with a sample capillary and a fuel restrictor to operate on the fuel mixture was tested and adjusted for various parameters to optimize the response following

the supplier recommendations. The FID analyzer was zeroed with N_2 to be consistent with the balance gas of the sample and span. Nitrogen was used to zero the analyzer using the zero potentiometer on the analyzer. After the zero point calibration, the analyzer was calibrated with 10.2 ppm C_3H_8 (30.6 ppm C_1) span gas using the span potentiometer on the scale of 0–40 ppm to adjust the value. This calibration was performed with the fuel mix cylinder at 40:60 ratio of H_2/He . The fuel mix source was then switched to the blending panel using a 3-way selection valve. The blending panel was already configured flowing 40:60 ratio of fuel mix similar to the ratio of the fuel cylinder. The response of C_3H_8 and CH_4 sample gases were also analyzed on the fuel source of blending panel. Zero and sample values were measured on multiple days to ensure the system stability and variation between fuel source of cylinder and blending panel. As shown in Figures 2 and 3, the span gas response on the blending panel matches very well with certified calibration value obtained with the fuel cylinder. Vertical bars on green crosses represent standard deviations of the measured values of all 7 replicates with the blending panel. The theoretical value represents the given certified sample concentration (30.6 ppm C_1 for C_3H_8) of the fuel mix cylinder. The vertical and horizontal bars on theoretical value represents the accuracy of the sample cylinder ($\pm 2\%$) and the accuracy of the fuel cylinder H_2 composition ($\pm 1\%$), respectively. The span gas measured with the fuel supplied by the blending panel matched very well within the uncertainty level with the certified values.