

Hydrocarbon Speciation of a Lean Burn Spark Ignited Engine

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ABSTRACT

A research program at West Virginia University sought to identify and quantify the individual hydrocarbon species present in alternative fuel exhaust. Compressed natural gas (CNG) has been one of the most widely researched fuels proposed to replace liquid petroleum fuels. Regulated CNG non-methane hydrocarbon emissions are often lower than hydrocarbon emissions from conventional liquid fuels because of the absence of heavier hydrocarbons in the fuel. Reducing NO_x and non-methane organic gas (NMOG) emission levels reduces the ozone forming potential (OFP) of the exhaust gases. A Hercules GTA 3.7 liter medium duty CNG engine was operated at seven load and speed set points using local supply CNG gas. The engine was operated at several rated, intermediate and idle speed set points. The engine was operated while the air/fuel ratio value was varied. The lighter load tests as well as the lean operation tests showed an increase in the hydrocarbon emissions as a result of unburnt fuel passing through the engine. As the lambda value approached stoichiometric operation, NO_x increased and the HC decreased. Hydrocarbons were captured using a dedicated sampling system drawing a sample from a full scale dilution tunnel via a rotary vane pump through a mass flow controller and collected in a tedlar bag. The sample was then analyzed by a gas chromatograph for identification and species were quantified utilizing retention indices. Upon close analysis of the data, the production and destruction of compounds present in engine exhaust can be related to the test fuel and background dilution air. The intent of this research was to identify the formation of products such as ethene that arise from incomplete combustion.

INTRODUCTION

Compressed natural gas (CNG) has been one of the most widely researched fuels proposed to replace liquid petroleum based fuels. Under certain conditions, the use of CNG fuel has proven potential to reduce regulated emissions compared to conventionally fueled engines. CNG has a research octane value of approximately 130 which allows a dedicated engine to operate at a higher compression ratio relative to a spark ignited engine running on gasoline with much lower octane ratings. Increasing the compression ratio allows an engine to

operate more efficiently. CNG also has an excellent lean flammability limit allowing for lean burn operation which reduces production of carbon monoxide (CO) and oxides of nitrogen (NO_x) in the exhaust and raises thermal efficiency at part load. Regulated CNG non-methane hydrocarbon emissions are lower than that of conventional liquid fuels because of the absence of heavier hydrocarbons in the fuel. Reducing non-methane organic gas (NMOG) emission levels reduces the ozone forming potential (OFP) of the exhaust gases: ground level ozone is of concern for both environmental and health effects. In this study, tests were performed to evaluate the effects of varying the engine loading and the air/fuel ratio on the hydrocarbon compounds present in the exhaust of a spark ignited lean burn engine. The engine tested was a medium duty Hercules CNG-fueled engine intended to compete in the diesel engine market. Prior studies have addressed speciation from stoichiometric light duty CNG engines, but there is a dearth of information on hydrocarbon emissions from lean-burn systems. Data showed that varying the load and varying the air/fuel ratio can influence the production of particular hydrocarbon compounds in the exhaust as well as the total hydrocarbon amount. The two major objectives of this research were to expand the data base of hydrocarbon speciation and to evaluate the compounds present in CNG engine exhaust which have the potential to form ground level ozone.

ENGINE AND CONTROLS

The engine used in this experimental research was a Hercules 3.7 liter 4 cylinder natural gas engine. The engine was turbocharged, intercooled and spark ignited with a compression ratio of 10:1. The commercially available version of this engine employed a GFI Compuvalve fuel management system that used open loop maps based upon volumetric efficiency and desired lean air/fuel ratios. The GFI unit also controlled spark timing with an Altronics ignition system. Prior research (1) included the adaptation of the engine control to accept oxygen sensors capable of operation in the lean range. The adapted GFI system used for this study is therefore able to respond to changing gas compositions or varying volumetric efficiencies in closed-loop feedback mode, thus avoiding excursions from desired air/fuel ratio target

values. Closed-loop control is particularly desirable when the fuel gas may vary from the anticipated Wobbe number (1) although pipeline gas is generally consistent in this regard (2). The engine were coupled to a 400 hp air-cooled eddy current dynamometer for the emissions testing. Desired torque and engine speed was maintained via the engine throttle using a microprocessor-controlled proportional, integral and derivative (PID) algorithm.

EXPERIMENTAL SET-UP AND PROCEDURES

The Hercules GTA 3.7 liter spark ignited engine was tested using a 95.6% (MOL%) methane CNG fuel. Engine and fuel specifications are shown in Appendices A and B respectively. The engine was operated in closed-loop control as discussed above. Steady-state tests were performed to determine the effect of varying the load and air/fuel ratio (air/fuel ratio was normalized as the lambda value (λ)) on total (HC, CO, NO_x) exhaust emissions and individual hydrocarbon compounds. The lambda value was varied, using one speed and load set point, to represent the effect of a maladjusted or improperly maintained engine.

$$I = \frac{(A/F)_{actual}}{(A/F)_{stoich}} = \frac{1}{f} > 1 \text{ if lean} \quad (1)$$

where f is the equivalence ratio

Engine exhaust samples were drawn from a full scale dilution tunnel meeting specifications outlined in the Code of Federal Regulations (CFR) title 40 (3), with the exception that the tunnel and engine intake air was not conditioned for these tests. The total flow was regulated in the tunnel by critical flow venturies to a volumetric flowrate of approximately 660 liters per second (1400 cfm). Regulated exhaust gases, namely total hydrocarbon (HC), oxides of nitrogen (NO_x), and carbon monoxide (CO) and unregulated carbon dioxide (CO₂) were recorded for each test. Rosemount model 402, 955 and

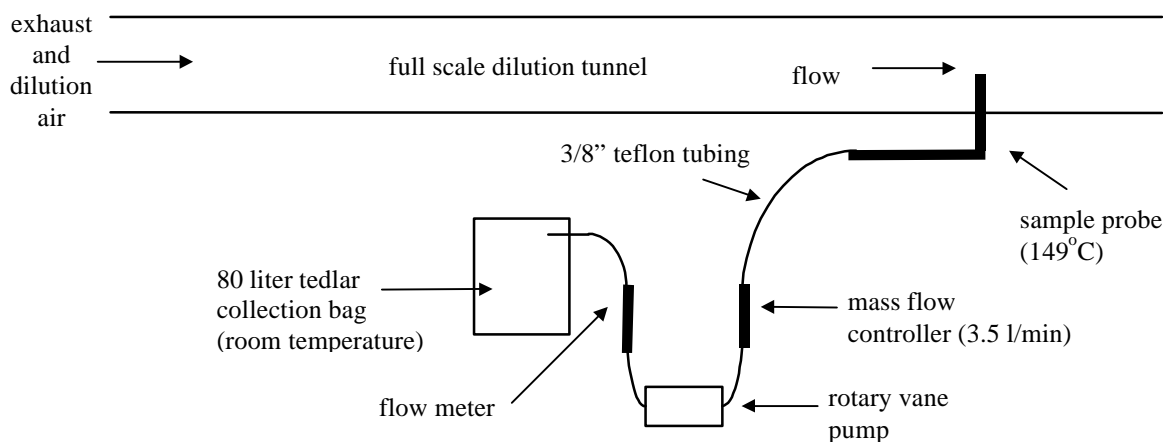
respectively. For hydrocarbon speciation, gaseous samples were drawn by a rotary vane pump from the dilution tunnel and flow was maintained at 3.5 liters per minute by a Sierra mass flow controller. Samples were collected at room temperature in an 80 liter tedlar bag. A small amount of each sample was then transferred to a 3 liter tedlar bag. The 3 liter tedlar bags, containing the samples, were stored in a black plastic bags prior to analysis in order to minimize reactions caused by exposure to ultra-violet light. A layout of the sampling train is shown in Figure 1.

GC: Development of a GC Identification Method

Gas chromatography (GC) analysis was performed on each of the samples in order to identify and quantify the hydrocarbon compounds present in the exhaust. A Varian 3600 GC with a J&W GS alumina column was used. A GC temperature ramp method was developed from previous CNG research performed at WVU to identify the specific compounds present in the engine exhaust samples. The method focused on compounds eluting with retention times from methane to octane. A co-elution of propene and isobutane resulted in the initial GC method used. The temperature ramp was then modified to separate the co-elution. Compounds were quantified using standard gases. The methane peak was quantified using a response factor specifically for methane while all other compounds were quantified using an average response factor. Response factors for non-oxygenated compounds other than methane are known to differ by less than 6 to 8 percent (4,5,6). The response factors were calculated on a per carbon basis (4) as reported by the Auto/Oil Air Quality Research Program (AQIRP) study. Specifications for the column, temperature ramp and GC operating conditions are shown in Table 1.

In reporting the mass quantity of speciated hydrocarbons, the fractions (relative quantities) of hydrocarbon constituents from the GC work were used, but they were normalized to yield the mass quantity integrated from continuous data using the

Figure 1: Sampling train layout



868 analyzers were used for HC, NO_x and CO/CO₂ analysis

Rosemount 402 flame ionization detector. Such an approach

is possible because the quantity of heavy hydrocarbons present in the exhaust is negligible with respect to the compounds in the methane to octane range.

Table 1: Specifications for the column, temperature ramp

GC Oven Temperature	Rate of Temperature Change	Hold time (min.)
40°C	hold constant	2.5
40°C to 100°C	20°C / minute	-----
100°C to 140°C	2°C / minute	-----
140°C to 200°C	20°C /minute	-----
200°C	hold constant	15

column length: 50m
column inner dia.: 0.53 mm

Injection parameters:

volume of sample injected = 5 ml
injection loop temperature = 120°C
detector: FID temperature = 250°C
carrier helium gas flowrate = 9.5 ml/min.
(measured at 40°C)

OZONE FORMING POTENTIAL

In 1990, standards for reactivity-based emissions were adopted in California. These emission standards were calculated by adjusting speciated quantities of exhaust hydrocarbons by using maximum incremental reactivity (MIR) and maximum ozone reactivity (MOR) factors. The basic definition of reactivity is the tendency of an organic gas to contribute to the formation of ozone in specific atmospheres containing NO_x. MOR scales are concerned with the concentration of NO_x present in the atmosphere. The MIR and MOR scales were developed by simulation experiments in a smog chamber by Carter (8). MIR scales are concerned with the tendency of hydrocarbons to form ground level ozone. Hydrocarbons cannot form significant amounts of ozone without the presence of NO_x (7). Methane is argued to have vanishingly small ozone forming potential, although it is acknowledged to be a greenhouse gas. Ground level ozone causes great concern for both environmental and health effects (9). A list of OFP MIR factors for each of the compounds identified is shown in Appendix C.

RESULTS

Test Matrix: Test identification number

The tests completed in the test matrix were each identified by the date and run number. For example, the first I50 run was labeled 08119701 (month; day; year; run number). A complete list of test runs and their parameters is shown in Table 2.

Table 2: Test Matrix

Test Number	Mode of Operation	Lambda Value
08119701	I50	1.32
08119702	I50	1.32
08119703	I50	1.32
08119704	I50	1.55
08119705	I50	1.10
08119706	I10	1.32
08119707	R50	1.32
08119708	R10	1.32
08119709	I100	1.32
08119710	Idle	1.32
08119711	R100	1.32

Intermediate speed means peak torque speed if the peak torque speed occurs between 60 and 75 percent of the rated speed. If the peak torque speed is less than 60 percent of rated speed, intermediate speed means 60 percent of rated speed. If the peak torque speed is greater than 75 percent of rated speed, intermediate speed means 75 percent of rated speed as defined by the CFR title 40. (3)

Rated speed means the speed at which the manufacturer specifies the maximum rated horsepower on an engine as defined by the CFR title 40. (3)

Regulated emissions:

It was important to obtain consistent regulated and CO₂ emissions results to verify the stability of the engine operation over time. Three I50 test runs were chosen as the base points for this research as well as to establish quality control of the data. Regulated (HC, CO and NO_x) and CO₂ emissions results were calculated in grams per mode. Each mode represented a 180 second test run, except in the case of the rated tests, where 60 seconds was used. However, in tabulating the data, rated emissions were increased threefold to reflect 180 seconds of operation. Background levels of regulated emissions were determined using bag samples and were subtracted using dilution factors calculated from the formula recommended in the CFR title 40 subpart N (3). The initial I50 runs were analyzed and good agreement of the regulated emissions was found.

Calculation of GC totals:

GC results in raw form were reported in parts per million carbon (ppm C). It was desired to partition the hydrocarbon emissions results on a mass basis. GC results were converted to mass using the ppm C of each compound, molecular weight per carbon for each compound, mode duration and the hydrocarbon response factor.

When using hydrocarbon results from two hydrocarbon analyzers (GC versus the HFID), it is important to know how the analyzers were calibrated. The heated flame ionization detector (HFID) of the Rosemount 402 analyzer was

calibrated using propane. The GC was calibrated with both methane and propane to reveal their relative response factors. To correct for the difference in the methane and propane response factors, the HFID was calibrated on 99.9 ppm by mass propane. Then 101.0 ppm by mass methane was introduced to the analyzer. The calculated response of the analyzer for the methane introduced was 33.7% of full scale. The experimental value was found to be 35.6% of full scale for three consecutive tests, thus resulting in an adjustment for methane of 5.3 percent, relative to propane response. In the case of the GC, for species other than methane, the response

mass per mode for the GC results is shown in the following table 3. Table 3 is only a partial list of the compounds detected for the test run. Background data in Table 3 has already been corrected for tunnel dilution factors.

COMPARISION OF TEST RESULTS

The first objective for comparison was to demonstrate data quality by showing repeatability of the base test data. The three base tests would then be averaged for comparison against varying the load and lambda value. Rated torque tests

Table 3: Example of GC results conversion to mass per mode (08119701)

Test Mode	I50						Corrected CH ₄	Fully Corrected			
Lambda Value	1.32				Ratio of species	Ratio of species	Ratio of species	Ratio of species	Regulated HFID HC		
Test Number	density	GC result	Backgnd GC result	Difference	to the total	to the total	to the total	to the total	less background	total HC	HC corrected
Test Unit	(g/mol C)	(ppm C)	(ppm C)	(ppm C)		(mass)	(mass)		(g/mode)	(g/mode)	(g/mode)
methane	16	32.18567	4.5017	27.6840	0.8775	14.0398	14.7839	0.8938	3.1000	2.7709	2.6314
ethane	15	1.3184	0.0694	1.2490	0.0396	0.5939	0.5939	0.0359		0.1113	0.1113
ethene	14	1.5166	0.0633	1.4533	0.0461	0.6449	0.6449	0.0390		0.1209	0.1209
propane	14.667	0.2772	0.0312	0.2460	0.0078	0.1144	0.1144	0.0069		0.0214	0.0214

for propane was employed, as discussed above. It is acknowledged that the GC is not capable of detecting some oxygenated species.

The background hydrocarbon compounds, found from GC analysis of background bags, were subtracted from their respective GC sample compounds. For this purpose it was necessary to employ a dilution factor. However, the dilution factor prescribed in the CFR, title 40 (3) presupposes the stoichiometry and fuel composition used in the testing. For the present research, in adjusting the individual species, the dilution factor was calculated with precise knowledge of the natural gas composition and the air/fuel ratio used. However, the differences between mass emissions of a chemical species calculated using the actual and the CFR methods were small: at most 0.05 percent. Appendix E shows examples of typical compound concentrations found in background samples taken during the test matrix. The percentage of each compound in the total hydrocarbon quantity detected (by volume) was determined and the percentage (by volume) of each compound was then multiplied by the appropriate molecular weight per carbon to obtain the representative mass. To correct for the methane response factor, the methane mass total was divided by the 1.053 difference to arrive at the new methane mass. The percentage mass for each compound was then multiplied by the emissions laboratory HC analyzer total to arrive at the compound's concentration by mass. The methane was then multiplied by the 1.053 difference to reflect the correct methane response. An example of the process to calculate the

were 60 seconds long versus 180 seconds for all other tests. When comparing results on a mass per mode basis, the equivalent rated torque results for 180 seconds are shown in parentheses .

Repeatability of the base I50 tests:

Once the GC data were converted to mass per mode, comparisons of test to test and the effects of variations of load and lambda value could then be made. Table 4 shows the compound results for three repeat I50 tests. Hydrocarbons in the range of methane to butane account for 97% of the total mass of each of these tests and were shown to have small variations in the results. However, higher variations were found for compounds with higher molecular weights and low mass values. No attempt was made to attribute these variations to either the engine variation or GC error.

Table 4: Repeatability of base I50 test results ($\lambda = 1.32$)

Test Number	08119701	08119702	08119703
methane	2.63	2.57	2.62
ethane	0.11	0.11	0.11
ethene	0.12	0.12	0.13
propane	0.021	0.020	0.019
propene	0.021	0.021	0.026
isobutane	0.0060	0.0043	0.0045
butane	0.0098	0.0041	0.0038
propadiene	<i>NP</i>	<i>NP</i>	<i>BDL</i>
acetylene	0.013	0.012	0.014
t-2-butene	<i>NP</i>	<i>BDL</i>	<i>BDL</i>
1-butene	0.0046	0.0037	0.0049
2M-propene	0.0064	0.0059	0.0062
2M-butane	0.0017	0.0042	0.0031
pentane	0.00094	0.00044	0.00031
1,3-butadiene	0.0035	0.0028	0.0024
benzene	<i>NP</i>	0.0034	<i>NP</i>
toluene	0.0090	<i>NP</i>	0.0032
Total (g/mode)	2.96	2.88	2.95

BDL – below detection limit*NP* – no peak detected*Effect of varying the lambda value:*

The influence of air/fuel ratio (as lambda value) was investigated. The “richer condition” ($\lambda = 1.10$) was determined by increasing and decreasing the lambda value until the maximum NO_x production limit was found. Note that the “richer condition” refers to the lambda value approaching the stoichiometric condition, though it is still in the lean region of operation. The “leaner condition” was determined by increasing the A/F ratio until audible misfire was detected. A continuous total hydrocarbon emissions trace was viewed as the test was performed to note visually the onset of misfire: tailpipe hydrocarbon emissions rise sharply at point of misfire. A lambda value of 1.55 was used for the lean condition. The goal was to reach a misfire region without operating the engine near failing limits. It was clearly seen that the elevated hydrocarbon compounds in the exhaust, caused by the “leaner condition”, were largely the constituents of the raw test fuel passing through the engine (see Appendix B). These compounds, as well as the totals, differed slightly in the “richer condition” and the desired set condition suggesting that the target value of 1.32 was well selected. An operating point of $\lambda = 1.10$ would be disfavored due to the associated high NO_x output and the inability to reduce this NO_x level with catalysts under lean operating conditions.

Exhaust hydrocarbon speciation data for these tests is shown in Table 5. The higher hydrocarbons associated with running as $\lambda = 1.55$ confirm that the misfire limit was approached.

Comparison of varying the load applied to the engine:

The engine was operated at idle (790 rpm), 1600 and 2500 rpm. Loads were 10%, 50% and 100% loads for both the 1600 rpm (intermediate speed) and 2500 rpm (rated speed) test runs. The idle test did embody a light power load due to the nature of air-cooled eddy current dynamometers. When comparing runs of “heavy” loads to “light” loads at the same speeds, the “heavier” load run had lower total work specific mass emissions. As shown in Table 6, the intermediate speed with a light load (I10) produced 4.4 times higher emissions than that of the intermediate speed, full load (I100) run, and 2.8 times higher emissions than the intermediate speed, half load (I50) run. Rated speed comparisons agreed with the intermediate speed comparisons: the light load run emissions were 2.6 and 3.4 times those of the R50 and R100 runs respectively. Idle emissions compared on a g/mode basis showed that the test fuel was passing through the engine largely as unburnt hydrocarbons.

Table 5: Effects of varying the lambda value (I50 tests)

Test Number	08119701-03 (g/mode)	08119704 (g/mode)	08119705 (g/mode)
Lambda Value	1.32	1.55	1.10
methane	2.61	6.60	2.14
ethane	0.11	0.32	0.058
ethene	0.12	0.25	0.12
propane	0.020	0.053	0.017
propene	0.023	0.036	0.027
isobutane	0.0049	0.010	0.0030
butane	0.0056	0.011	0.0027
propadiene	<i>BDL</i>	<i>NP</i>	0.0016
acetylene	0.013	0.019	0.025
1-butene	0.0044	0.0069	0.0053
2M-propene	0.0062	0.0078	0.011
2M-butane	0.0030	0.0064	0.00033
pentane	0.00056	0.0022	<i>NP</i>
1,3-butadiene	0.0029	0.0025	<i>NP</i>
benzene	0.0034	<i>NP</i>	0.0048
toluene	0.0061	<i>NP</i>	0.0038
Total (g/mode)	2.93	7.33	2.42

*BDL – below detection limit**NP – no peak detected***Table 6:** Intermediate, rated and idle test runs in g/mode with each mode at 180 seconds of operation ($\lambda = 1.32$)

Test Number	08119701-03 average	08119706	08119707	08119708	08119709	08119710	08119711
Test Mode	I50	I10	R50	R10	I100	Idle	R100
methane	2.61	2.14	3.45	2.94	3.99	1.93	4.44
ethane	0.11	0.10	0.11	0.12	0.16	0.097	0.16
ethene	0.12	0.18	0.23	0.21	0.11	0.048	0.23
propane	0.020	0.019	0.015	0.024	0.036	0.024	0.030
propene	0.023	0.049	0.032	0.029	0.013	0.011	0.038
isobutane	0.0049	0.0042	0.0022	0.0039	0.0083	0.0060	0.0059
butane	0.0056	0.0034	0.0025	0.0043	0.0085	0.0049	0.0055
propadiene	<i>BDL</i>	0.0022	0.0019	0.0030	<i>BDL</i>	<i>NP</i>	<i>BDL</i>
acetylene	0.013	0.014	0.027	0.021	0.010	0.0037	0.025
1-butene	0.0044	0.0011	0.0049	0.0040	0.0017	0.0024	0.0067
2M-propene	0.0062	0.013	0.0072	0.0054	0.0092	0.0087	0.0038
2M-butane	0.0030	0.0016	0.0042	0.0020	0.0041	0.0014	0.0020
pentane	0.00056	<i>BDL</i>	<i>NP</i>	<i>NP</i>	0.0020	0.00045	0.00037
1,3-butadiene	0.0029	0.0092	<i>NP</i>	<i>NP</i>	<i>NP</i>	<i>NP</i>	<i>NP</i>
benzene	0.0034	0.0024	0.0055	0.0053	0.0015	0.0021	0.0067
toluene	0.0061	0.0060	0.0040	0.0025	0.0044	0.0016	0.0052
Total (g/mode)	2.93	2.58	3.90	3.37	4.35	2.14	4.95
Total (g/bhp-hr)	1.20	4.23	0.91	2.36	0.95	NA	0.69

*BDL – below detection limit**NP – no peak detected**NA – not applicable*

Ozone formation:

Ozone forming potential is an important issue to consider when analyzing CNG exhaust. Compounds with high MIR values tend to be alkenes, alkynes (such as acetylene) and aromatics. When methane is neglected in the exhaust sample, the majority of the remaining compounds have significant MIR values, which is why they are customarily regulated as “non-methane organic gases”. For this study, methane contribution to ozone formation was included in the results although it is not customarily regulated. Table 7 below shows the comparison of results from the average of three I50 tests, an I10 and an I100 test at the same lambda value. Results are reported in grams ozone per mode, grams ozone per gram

NMOG and grams ozone per brake horsepower hour in order to compare test to test variations as well as to other speed and load test runs. Table 8 shows the total results for all the tests performed in both grams ozone per mode, grams ozone per gram NMOG and grams ozone per bhp-hr. The authors concede that oxygenated species such as aldehydes were not accounted for in this research, and that oxygenates will also contribute to the ozone forming potential of the exhaust. For the species detected, over all operating conditions, the mass of ozone produced per mass of NMOG emitted was projected to vary between 2.84 and 5.16. It was observed that the g O₃/g NMOG ratios varied in sympathy with A/F ratio at the I50 operating point.

Table 7: Projected ozone formation ($\lambda = 1.32$)

Test Number	08119701-03 average	08119706	08119709
Test Mode	I50	I10	I100
methane	0.026	0.021	0.040
ethane	0.029	0.027	0.041
ethene	0.90	1.34	0.77
propane	0.0097	0.0090	0.017
propene	0.21	0.46	0.12
isobutane	0.0050	0.0042	0.0085
butane	0.0057	0.0035	0.0086
propadiene	<i>BDL</i>	0.024	<i>BDL</i>
acetylene	0.0067	0.0072	0.0051
t-2-butene	<i>BDL</i>	0.016	<i>NP</i>
1-butene	0.039	0.098	0.015
2M-propene	0.033	0.068	0.049
2M-butane	0.0041	0.0022	0.0057
pentane	0.00058	<i>BDL</i>	0.0020
1,3-butadiene	0.032	0.10	<i>NP</i>
benzene	0.0014	0.0025	0.00062
toluene	0.017	0.0095	0.012
Total (g O₃)	1.32	2.21	1.10
Total (g O₃/g NMOG)	4.07	5.16	3.01
Total (g O₃/bhp-hr)	0.54	3.62	0.23

BDL – below detection limit

NP – no peak detected

Table 8: Ozone forming potential (OFP) of all tests performed in matrix

Test Number	08119701	08119702	08119703	08119704	08119705	08119706	08119707	08119708	08119709	08119710	08119711
Test Mode	I50	I50	I50	I50	I50	I10	R50	R10	I100	Idle	R100
Lambda Value	1.32	1.32	1.32	1.55	1.10	1.32	1.32	1.32	1.32	1.32	1.32
Total g O₃	1.31	1.24	1.41	2.52	1.34	2.21	2.17	2.00	1.10	0.60	2.22
Total (g O₃/g NMOG)	3.98	3.99	4.25	3.45	4.76	5.16	4.89	4.59	3.01	2.84	4.33
Total (g O₃/bhp-hr)	0.54	0.51	0.58	1.03	0.55	3.62	0.51	1.40	0.23	<i>NA</i>	0.31

NA – not applicable

Ethene:

Ethene (ethylene) in the exhaust was of particular interest in this research. The test fuel, which was analyzed by a local laboratory, had no ethene present as shown in Appendix B. This result was confirmed by our in house laboratory. A small amount of ethene was detected in the background sample. As a 1992 turbocharged medium duty engine, the Hercules engine was not required to have a closed crankcase ventilation system. Although the crankcase emissions were vented outside the laboratory, it is possible that a trace of crankcase emissions was entrained in the background air. However, detected levels of exhaust ethene were at 25 times the background level. Ethene is therefore produced during the combustion process: this has been well documented in a recent study (10).

Ratios of Exhaust Constituents:

One way to compare the ethene production in varying the lambda value and load tests is to look at the ethene to methane ratio. The ethane (C_2H_6), ethene (C_2H_4), ethyne (C_2H_2 ; acetylene) and propene (C_3H_6) ratios are shown in Table 9. It is of interest that ethene, propene and ethyne have lower ratios for the idle and I100 cases. The idle case can be explained by

the mild combustion temperatures and pressures associated with low throttle operation, where the combustion is clearly sufficiently mild as not to produce these pyrolysis products. Yet the highest values of ethene, propene and ethyne occurred at light load (I10 and R10). A University of Dayton report (10) discusses thermal decomposition of methane: at temperatures over $850^\circ C$, ethene and propene were reported as significant byproducts, with yields of up to 10% for ethene and 1% for propene. They found that ethene was destroyed at $1050^\circ C$ and propene at $1000^\circ C$. This is offered as explanation for the lower ratios seen at high load operation. One may conclude that our light load conditions, R10 and I10, were associated with sufficiently hot in-cylinder temperatures to yield these byproducts, but were not so hot during combustion to destroy them. Higher load cases yield higher in-cylinder temperatures which would eliminate some of the ethene, propene and ethyne. It should be noted, however, that inhomogeneous charge and temperature variations in time and space in the cylinder, as well as cylinder to cylinder variations in the Hercules engine (11), will provide for a broad spectrum of temperatures associated with pyrolysis and combustion. When the data for ethene are considered not as ratios with methane, but as quantities in g/bhp-hr, similar trends are found, as seen in Table 10.

Table 9: Ethane, ethene, acetylene and propene ratios to methane

Test Number	08119701	08119702	08119703	08119704	08119705	08119706	08119707	08119708	08119709	08119710	08119711
Test Mode	I50	I50	I50	I50	I50	I10	R50	R10	I100	Idle	R100
Lambda Value	1.32	1.32	1.32	1.55	1.10	1.32	1.32	1.32	1.32	1.32	1.32
C_2H_6/CH_4	4.23%	4.28%	4.25%	4.89%	2.72%	4.83%	3.14%	4.09%	4.00%	5.02%	3.57%
C_2H_4/CH_4	4.59%	4.56%	5.10%	3.83%	5.68%	8.59%	6.56%	7.09%	2.65%	2.52%	5.08%
C_2H_2/CH_4	0.50%	0.48%	0.53%	0.29%	1.17%	0.66%	0.77%	0.72%	0.25%	0.19%	0.56%
C_3H_6/CH_4	0.81%	0.83%	0.98%	0.54%	1.26%	2.28%	0.93%	0.98%	0.33%	0.57%	0.85%

Table 10: Ethene, propene and acetylene g/bhp-hr trends (g/bhp-hr)

Test Number	08119701	08119702	08119703	08119704	08119705	08119706	08119707	08119708	08119709	08119711
Test Mode	I50	I50	I50	I50	I50	I10	R50	R10	I100	R100
Lambda Value	1.32	1.32	1.32	1.55	1.10	1.32	1.32	1.32	1.32	1.32
C_2H_4	0.050	0.048	0.055	0.10	0.050	0.30	0.053	0.15	0.023	0.032
C_2H_2	0.0054	0.0051	0.0056	0.0079	0.010	0.023	0.0062	0.015	0.0022	0.0035
C_3H_6	0.0088	0.0088	0.011	0.015	0.011	0.081	0.0075	0.020	0.0028	0.0053

Aromatics:

The presence of aromatics in the samples raised a point of interest. The test fuel was re-analyzed in house and confirmed that aromatics were present in small quantities. The University of Dayton report (10) confirmed that in an oxygen-free environment, organic byproducts such as ethane, n-butane, benzene and ethyl benzene could be produced at temperatures greater than 850°C. As seen in Table 6, the quantities were small when detectable. As discussed in the ethene section, a small amount of benzene and toluene may have resulted from engine “blow by” to the background dilution air, although effort was made to vent the crankcase emissions from the laboratory.

CONCLUSIONS

A Hercules engine was operated on natural gas fuel of 95.6% methane (MOL%) composition. Engine speed, engine load and air/fuel ratio were varied, and both regulated emissions and speciated hydrocarbon emissions were measured. Effect of air/fuel ratio was evident in that a lean condition, near the misfire limit, yielded a higher fraction of unburned fuel in the exhaust than did the standard operating condition. Richer operation, near the NO_x peak, provided lower overall hydrocarbon emissions. In comparison to higher loads, idle operation yielded little ethene, propene and ethyne in relation to methane, but light load conditions yielded high relative quantities of these constituents. Data was processed to yield projected ozone forming potential of the exhaust. The less lean operation showed high ozone forming potential relative to standard and misfire air/fuel ratios. Also, light load operation yielded high ozone forming potential primarily due to the increased quantity of ethene, propene and ethyne present in the exhaust.

Future investigation will include varying the fuel composition as well as the effects of exhaust gas recirculation (EGR) on the compounds present in the engine exhaust.

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Appendix A:

Hercules 3.7 liter GTA engine

Displacement	226 cu. in.	3.7 liters
Bore and Stroke	4" x 4-1/2"	101.6 x 114.3 mm
Number of Cylinders	4	
Firing Order	1-2-4-3	
Compression Ratio	10:1	
Fueling	CNG: GFI	
Ignition	Altronics	
Horsepower (hp)	130 @ 2800 rpm	
Torque (ft-lb)	320 @ 1600 rpm	

Appendix B: Test fuel specifications

Gas Analytical Services, Clarksburg WV

Sample: Wall Gas		Date: 08/13/1997	
Component	MOL %	MASS %	
methane	95.6123	93.129%	
ethane	2.6288	4.801%	
propane	0.406	1.137%	
i-Butane	0.058	0.205%	
n-Butane	0.083	0.293%	
i-Pentane	0.023	0.101%	
n-Pentane	0.016	0.070%	
nitrogen	0.016	0.027%	
CO ₂	0.016	0.043%	
hexanes +	0.038	0.194%	
Analytical Results at Base Conditions			
BTU/SCF (Dry):	1035.079		
BTU/SCF (Saturated):	1017.988		
PSIA:	14.730		
Temperature (°F):	60.000		
Z Factor (Dry):	0.99787		
Z Factor (Saturated):	0.99783		
Analytical Results at Contract Conditions			
BTU/SCF (Dry):	1035.079		
BTU/SCF (Saturated):	1017.988		
PSIA:	14.730		
Temperature (°F):	60.000		
Z Factor (Dry):	0.99787		
Z Factor (Saturated):	0.99783		
Calculated Specific Gravities			
Ideal Gravity:	0.5808		
Real Gravity:	0.5818		

Appendix C: MIR values from reference (8), as used in this research.

Compound	MIR value (mg O ₃ / mg NMOG)
methane	0.01
ethane	0.26
ethene	7.28
propane	0.48
propene	9.39
isobutane	1.02
butane	1.02
propadiene	10.89
ethyne = acetylene	0.51
trans-2-butene	9.94
1-butene	8.90
2-methyl propene	5.31
2-methyl butane	1.38
isobutylene	8.90
pentane	1.03
1,3-butadiene	10.88
benzene	0.42
toluene	2.72

State of California, Air Resources Board, “Proposed Reactivity Adjustment Factors for Transitional Low Emission Vehicles”

Appendix D: Regulated and CO₂ emissions

Idle emissions were actually at light load due to the nature of the non-motoring dynamometer. Values at idle are in grams per hour (g/hr).

Test Number	Test Mode	Lambda Value	HC (g/bhp-hr)	CO (g/bhp-hr)	CO ₂ (g/bhp-hr)	NO _x (g/bhp-hr)
8119701	I50	1.32	1.27	0.90	443.16	6.76
8119702	I50	1.32	1.24	0.89	440.40	6.53
8119703	I50	1.32	1.27	0.88	437.88	6.84
8119704	I50	1.55	3.15	1.40	455.60	0.77
8119705	I50	1.1	1.04	0.65	448.97	17.11
8119706	I10	1.32	4.41	2.54	723.11	1.72
8119707	R50	1.32	0.95	0.94	469.39	6.22
8119708	R10	1.32	2.47	2.02	611.97	4.75
8119709	I100	1.32	1.00	0.52	380.39	11.80
8119710	Idle	1.32	44.8 (g/hr)	11.2 (g/hr)	3579 (g/hr)	3.8 (g/hr)
8119711	R100	1.32	0.73	0.65	428.74	14.29

Appendix E: An example of compounds present in the background air.

Test Mode	150
Lambda Value	1.32
Test Number	08119701
Test Unit	(ppm C)
methane	4.502
ethane	0.069
ethene	0.063
propane	0.031
butane	0.025
2M-propene	0.032
2M-butane	0.033
pentane	0.028
benzene	0.029
toluene	0.059
Total	4.871