Effect of Variable Fuel Composition on Emissions and Lean Blowoff Stability Performance

Analysis of Nine Industrial Combustion Applications

Appendix C - Burner Configuration #3: C65 Microturbine
Burner Configuration # 3: C65 Microturbine

Emissions and Stability Performance

CEC Agreement No. 500-13-004

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Burner Configuration # 3: C65 Microturbine

EXECUTIVE SUMMARY

A summary of the emissions and stability results for Burner Configuration #3, C65 Microturbine Generator (MTG), is presented in Table 1. The table is coded with colors and trend indicators to provide a simple overview of how fuel composition impacts the performance of Burner Configuration #1.

Table 1. Summary of emissions and stability

<table>
<thead>
<tr>
<th>Fuel class/2</th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen enriched natural gas (CH₄+H₂)</td>
<td>Biogas (CH₄+CO₂)</td>
<td>Mixtures with heavier hydrocarbons (C1/C2/C3)</td>
<td></td>
</tr>
<tr>
<td>NOₓ</td>
<td>↑ @↑H₂</td>
<td>↓@↑CO₂</td>
<td>↑@↑C₂,C₃..</td>
</tr>
<tr>
<td>CO</td>
<td>↓ @↑H₂</td>
<td>↑@↓CO₂</td>
<td>↑@↑C₂,C₃..</td>
</tr>
<tr>
<td>Stability</td>
<td>↑ @↑H₂</td>
<td>Slightly ↓@↑CO₂</td>
<td>↓@↑C₂,C₃..</td>
</tr>
</tbody>
</table>

/1 Cells highlighted with red represent negative impacts on emissions or stability. Conversely, cells highlighted with green represent positive effects.

/2 Fuel Class I: Hydrogen Containing Fuels  
Fuel Class II: Diluted Fuels  
Fuel Class III: Fuels with Higher Hydrocarbons

The example below illustrates how the table can be read:

<table>
<thead>
<tr>
<th>Emissions</th>
<th>Hydrogen enriched natural gas (CH₄+H₂)</th>
<th>Reading</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOₓ</td>
<td>↑ @↑H₂</td>
<td>NOₓ increases (↑) when adding (@) (↑) H₂</td>
</tr>
<tr>
<td>CO</td>
<td>↓ @↑H₂</td>
<td>CO decreases (↓) when adding (↑) H₂</td>
</tr>
</tbody>
</table>
The following mixtures are interchangeable with natural gas according to the Wobbe Index and the interchangeability indices for flashback, lifting and yellow tipping established by the American Gas Association (AGA). Table 2 presents a summary indicating the expected increase (↑) or reduction (↓) of NOx and CO concentration at a fixed 3% O2 concentration in the exhaust. The percent change indicated in the table represents the change compared to the results for natural gas (Assumed as 100% CH4).

<table>
<thead>
<tr>
<th>Fuel Mixture</th>
<th>Equivalence Ratio</th>
<th>NOx [ppmdv]</th>
<th>CO [ppmdv]</th>
</tr>
</thead>
<tbody>
<tr>
<td>76% CH4 - 24% H2</td>
<td>0.46</td>
<td>↑ 100%</td>
<td>↓ 50%</td>
</tr>
<tr>
<td>94% CH4 - 6% C2H6</td>
<td>0.47</td>
<td>↑ 4%</td>
<td>↑ 4%</td>
</tr>
<tr>
<td>95% CH4 - 5% C3H8</td>
<td>0.47</td>
<td>↑ 3%</td>
<td>↑ 4%</td>
</tr>
<tr>
<td>98% CH4 - 2% CO2</td>
<td>0.47</td>
<td>↓ 2%</td>
<td>↑ 1%</td>
</tr>
</tbody>
</table>

/3 % change compared to 100% methane

**Key Features**

The configuration studied in this report is the C65 microturbine by Capstone Turbine Corp.

![Figure 1. C65 combustor outline with injector cross section. Figure copied from [1]](image-url)
planes of injection followed by a dilution zone (Figure 1). The C65 MTG features a single stage compressor and single stage turbine on a common shaft as well as an annular combustor configuration. The Capstone combustor incorporates a globally swirl stabilized combustion process with fuel injectors that are canted slightly from purely radial orientation. The MTG includes a recuperator that provides preheated air to the combustor at a temperature of 840±10 K, regardless of the turbine load and/or the ambient temperature. The pressure ratio is nominally 4:1 and recuperation of the exhaust gas for preheating the incoming combustion air is incorporated to increase the overall efficiency.

The following list includes C65 important key features regarding emissions and stability:

- Flame interaction
- Heat recirculation
- Recirculation of products
- Air preheating-heat recovery
- Six turbulent premixed jet

The specifications of the equipment are presented in Table 3. The Capstone C65 Micro Turbine Generator (MTG) has been previously tested in UCICL with alternative fuels and natural gas; some experimental results are readily available.

Figure 2 shows the C65 installed at the UCICL facility.
### Table 3. Equipment specification

<table>
<thead>
<tr>
<th>Units</th>
<th>Max fire rate</th>
<th>Max Efficiency</th>
<th>Flame type</th>
<th>Max Generator output</th>
<th>Compression ratio</th>
<th>Equivalence ratio ((\phi))</th>
<th>Air preheating</th>
<th>Application</th>
<th>Fuel(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>kW (Btu/hr)</td>
<td>222</td>
<td>27%</td>
<td>6 Turbulent premixed jets</td>
<td>60</td>
<td>---</td>
<td>4:1</td>
<td>840 ±10 K</td>
<td>Gas turbine</td>
<td>NG, biogas and Hydrogen enriched natural gas, NG mixed with heavier hydrocarbons</td>
</tr>
<tr>
<td>%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

- The equivalence ratio is controlled to guarantee the temperature of 1050±50 K at the turbine inlet.
- The control temperature – Adiabatic flame temperature is 1850 K (constant regardless the fuel composition) the equivalence ratio is adjusted to guarantee the flame temperature.
- The temperature entrance turbine is 1050±50 K.

---

**Virtual AeroThermal Field - Computational Fluid Dynamics**

This section presents the details about the CFD simulation and the results that are used to build the chemical reactor network. Total emissions are a primary function of temperature, oxygen concentration, and the time the species spend under those conditions. The temperature profile, flow field and concentration of species are presented and analyzed in this section. The methodology to build a CRN consists on using the results of CFD simulations to divide the combustor volume into zones represented by idealized reactor elements. Zones of the combustor where the gases flow in one direction are modeled using PFRs; highly turbulent zones or zones with strong mixing are modeled with PSRs. At the end of the section an equivalent CRN representing similar but simplified fluid dynamics of the chamber is presented. The CRN is also similar regarding the volume the reactors occupy in the combustion chamber, and the energy balance of the system.

**1.1. Domain and Mesh**

A virtual chamber is used to model the fluid dynamics, heat transfer and heat release from the reaction. In this case, the details regarding stability and emissions are not sought—only a relatively time efficient calculation that can be used to guide the sectioning of the chamber into individual reactors. The combustor is simulated with a 3D model. Steady state, Reynolds-Averaged-Navier-Stokes (RANS) simulations are conducted using the Software ANSYS Fluent, version 15.0. A non-
structured mesh is used. The mesh consists of 1'000,000 cells, with a maximum aspect ratio of 27 and minimum orthogonal quality of 0.58. The geometry and names of the boundary conditions are presented in Figure 3. A summary of the mathematical models governing the experiment is presented in Table 4.

![Figure 3. Geometry and boundary conditions of the virtual combustion chamber](image)

| Table 4. CFD models |
|--------------------|-----------------|
| Mesh               | 3D – non structured – 1'000,000 cells |
| Solver             | Steady Pressure based |
| Viscous model      | K-ԑ standard with enhanced wall functions |
| Radiation          | P1 |
| Species model      | Partially Premixed combustion - turbulent flame speed model - Zimmont |
| Density            | Incompressible ideal gas model |
| pressure velocity coupling | SIMPLE: relationship between velocity and pressure corrections to enforce mass conservation and to obtain the pressure field |

1.2. Boundary conditions
The boundary conditions are set to match the energy balance of the actual system. This approach is useful to describe more precisely the energy flow through the combustor, which leads to a more accurate result for temperature field.

- All the inlets are set at a temperature of 835K. The equivalence ratio for each fuel composition is set to guarantee a constant adiabatic flame temperature equal to 1850K.
- The results for temperature distribution on the two planes of injectors are presented in Figure 4.
- Compression ratio is 4:1.
- The efficiency of the system is assumed to be oblivious to the fuel composition. Efficiency~≈28% at maximum load, e.g. the six injectors are in operation and the fire rate per injector is 222kW/6 injectors = 37kW/injector. The actual efficiency of the MTG as a function of the generated electric output is presented in Figure 5.
- For the operation with NG, the equivalence ratio is fixed at 0.46 to guarantee an AFT=1850K. See Figure 6.
  - For the operation with [90% H2]/[10%CH4] the equivalence ratio is 0.41 to guarantee an AFT=1850K.
  - The same AFT was found for 80%CH₄-20%C₃H₈ for an equivalence ratio of 0.46.
  - For 15% C₂H₆-85% CH₄, the equivalence ratio to hold constant the same AFT is 0.46.
- The energy balance guarantees an approximately constant temperature at the exit of the combustor (turbine inlet) ~1050 to 1100K.
- The maximum firing input is held constant at 222kW.

Figure 4. Temperature contours of the MTG operating with natural gas and at full load.

Figure 5. Efficiency of the C65 MTG as a function of the electric power generated.
Chemical Reactor Network

The chemical reactor modeling is found to be a valuable tool in the evaluation of pollutant formation and the blow-out performance of combustion systems. The methodologies of the development vary between authors [2]. In this study, the chemical reactor network is constructed based on the computational fluid dynamics (CFD) results presented above. The concept of modeling a combustor using chemical reactors such as perfectly stirred reactors (PSR), plug flow reactors (PFR) was first introduced by S. L. Bragg [3]. A reactor network is defined to model the pollutant formation with a detailed chemistry. On the other hand the introduction of a complex reaction mechanism in 3D turbulent combustion codes is still too CPU time intensive to be applied in an industrial context. CFD solvers could not be efficiently used to solve chemical equations due to the stiffness of the underlying reaction scheme and the great number of species that it contains [4].

1.3. Zonal distribution

In order to develop the CRN, the first step is divide the combustor volume into the distinct regions or zones. Each of the zones is characterized by the particular physical properties of the flow and the flame behavior. The two basic models used to build the network of reactors are the perfectly stirred reactor (PSR) and the plug flow reactor (PFR).

- A PSR (i.e., a continuously stirred tank reactor) presumes that mixing to the molecular scale occurs. Highly turbulent regions, premixed flows, and turbulent premixed reactions can be modeled with this reactor. In this reactor, the chemical reaction occurs homogeneously.
- A PFR assumes that the flow moves as a “plug” and the chemical reaction proceeds one-dimensionally, longitudinal mixing in the reactor is assumed to be zero. One limitation of this model is that it can’t receive more than one stream. The composition at the entrance of the reactor has to be defined.

The chemical reactor network presented in Figure 7 depicts the flow distribution extracted from the CFD analysis; it also indicates the heat losses (red lines) associated with the flames. The reaction network presented in this paper was designed using the set reactor models (PSR, mixers, exhaust, splitters) available in Chemkin Pro 15131. The effect of the heat loss is of fundamental interest for the CRN methodology since the chemistry of the Nitrogen is highly sensitive to the temperature, therefore to the heat transfer. The heat losses indicated in the...
reactor network account for the radiation losses and the convective currents at lower temperatures around the flame; 3% heat losses were estimated for the flame at the conditions in the combustor. Since the flames in the turbine are ultra-lean and premixed we expect very low heat losses from the flame as a consequence of the species radiating heat to the walls; most heat losses in the combustion chamber are associated to the combustion products convecting heat to the walls and not from the direct heat transfer from the flame.

- The first block (or block 1) includes the total mass flow inlet of premixed gas that is necessary to achieve an electrical power output equal to 60kWe. The flow rate of premixed gas was set using the actual thermal efficiency at full power, in this case ~ 27%. In the same block, the flow rate is divided into three blocks (Blocks 2, 4 and 5). Since the turbine configuration displays flame symmetry, it was possible to set a block of two perfectly stirred reactors (PSR) to represent each pair symmetrical flames. Each pair of flames is grouped into Blocks 2, 4 and 5, respectively and is represented by two PSRs in series. The first reactor of the series represents the primary reaction zone or the core of the reactions (the reactions taking place inside the blue cone), where the effects of the surroundings are negligible; the second reactor in each block symbolizes a post flame zone, which is a region at high temperature where the first PSR injects its products; additionally, Blocks 4 and 5 account for the effect of the exhaust gases that were produced in Block 2. The splitter in the CRN divides the exhaust products from Block 2 into three flow streams; two of these portions are directed toward the two second PSRs of the fourth and fifth Blocks, in that manner the effect of the exhaust gas that come from the plane of two injectors is accounted with this CRN configuration. This could be considered to account for the flame interaction between flames that located within the same plane. From the analysis of the CFD results neglecting the effect of recirculation patterns in the plane of two injectors is a reasonable assumption; however the same assumption may not be as valid for the plane of four injectors where it is expected that the exhaust gases emitted by the flames in the two plane of 2 injectors and the preceding coplanar flame have a significant effect on the combustion process. The exhaust recirculation effect (both from the preceding flame and from the preceding plane) is accounted by using a portion of the exhaust gases from the Block 2. Block 6 represents a post flame region where the streams of all the previous reactors are mixed again before they are diluted with air coming from Block 7 (dilution air inlet). Finally, Block 8 accounts for the mixing process and the reactions after the dilution air is injected. NOx emissions corrected to 15% O2 are analyzed in the exhaust products of Block 8.
1.4. Reactor Network Variables
Each PSR in the network requires the following input variables:

- Residence time \( (R_t) \), which is the average amount of time the species spend in a particular system. This variable can be related to the volume \( (V) \) of the reactor, the average gas density \( (\rho) \) and the mass flow \( (\dot{m}) \) through the following expression: \( R_t = \frac{\rho V}{\dot{m}} \)
- Mass flow through the reactor \( (\dot{m}) \)
- Initial temperature
- Pressure
- Heat losses

The PFRs require the following input variables:

- Length.
- Diameter. This can be a function of the distance.
- Initial temperature
- Pressure
- Heat losses
A summary of the variables used in the CRN model for the MTG Configuration #3 are presented in Table 5.

<table>
<thead>
<tr>
<th>Table 5. Input variables used in the CRN model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel classes (% by Vol.)</td>
</tr>
<tr>
<td>• 100% CH4</td>
</tr>
<tr>
<td>• up to 90% H2 (Balance CH₄)</td>
</tr>
<tr>
<td>• Up to 65% CO₂ (Balance CH₄)</td>
</tr>
<tr>
<td>• Up to 100% C₂H₆ (Balance CH₄)</td>
</tr>
<tr>
<td>• Up to 100% C₃H₈ (Balance CH₄)</td>
</tr>
<tr>
<td>Equivalence ratio (ER)</td>
</tr>
<tr>
<td>Variable: Set to guarantee an adiabatic flame temp=1850K with all fuel classes</td>
</tr>
<tr>
<td>Mass flow rate</td>
</tr>
<tr>
<td>Variable: set to guarantee 222kW fire rate at the ER @ 1850 AFT</td>
</tr>
<tr>
<td>Secondary air dilution</td>
</tr>
<tr>
<td>Fixed constant 0.3</td>
</tr>
<tr>
<td>Mass flow Split in block 3</td>
</tr>
<tr>
<td>80% to post flame, 10% to block 4 and 10% to block 5</td>
</tr>
<tr>
<td>Pressure (atm)</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>Inlet temperature (K)</td>
</tr>
<tr>
<td>835</td>
</tr>
</tbody>
</table>

1.5. Effect of Fuel Composition on Emissions

![Figure 8, Comparison of the temperature contours (four injectors plane) for three fuel compositions. The boundary conditions are set up to guarantee a constant adiabatic flame temperature 1850K](image)

In this section, the evaluation of the effect of the fuel composition on the emissions is assessed using the CRN methodology. The fire input to the burner is held constant at 222kW. Also the control strategy requires a fixed temperature at the turbine inlet. This would mimic typical operation gas turbine generator, in which the goal is achieve the maximum temperature while ensuring the integrity of the turbine blades. A comparison of the temperature contours at the four injectors plane and for three fuel compositions is presented in Figure 8, notice that the boundary conditions
are set up to guarantee a constant adiabatic flame temperature (1850K). The figure shows shorter flames for the hydrogen mix and longer flames for natural gas and biogas mixtures.

For this specific configuration a longer flames can provide the following characteristics:

- More mixing with surroundings
- Increased flue entrainment
- Possible flame interaction
- Recirculation of radicals and recirculation of combustion products
- Increases heat transfer (convection and radiation) to the wall

The results for emissions are presented as part per million (ppm) or part per billion (ppb) of pollutant corrected at 15% oxygen on a dry basis. This presentation is representative of the measures in the field for gas turbines and it is also typical of units found in regulatory or permit limits. Volumetric fractions such as “ppm” indicate a relative proportion of the pollutant in the pool of species. When the emissions are plotted against equivalence ratio they represent the dependency of the emissions on the relative proportion of available oxygen.

The emissions are also presented in the form of emission index, which measures the emissions on a mass basis.

The emission index is usually presented in one of the following forms:

- as mass of pollutant emitted per mass of fuel burned:
  \[
  \frac{g_{NOx}}{kg_{Fuel\_burned}}
  \]

- Pollutant emitted per energy contained in the fuel:
  \[
  \frac{g_{NOx}}{kWh_{Fuel\_burned}}
  \]

- Pollutant emitted per electricity generated. In this case the emission index includes the efficiency of the system and it would be read as:
  \[
  \frac{g_{NOx}}{kWh_{electricity\_generated}}
  \]

The CRN results for emissions were obtained using Chemkin Pro 15131 and the GRI 3.0 reaction mechanism [5]. While it is recognized that the specific chemistry mechanism used can influence the absolute values of the emissions predicted [6], the trends are generally insensitive to the mechanism used.
1.5.1. Fuel class I - Hydrogen enriched natural gas

The fuel class I is hydrogen enriched natural gas. The fuel compositions are presented in Table 6. The equivalence ratio that guarantees constant adiabatic flame temperature is presented in Figure 9 as a function of the mole fraction of hydrogen in the mix. Notice that the addition of Hydrogen to the fuel increases the flame temperature, therefore the mixture is diluted with more air to counteract this effect. Notice that the exhaust and adiabatic flame temperature are constant for all the fuel compositions.

<table>
<thead>
<tr>
<th>Hydrogen enriched natural gas</th>
<th>Wobbe index (BTU/scf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% CH4 – 90% H2</td>
<td>1095</td>
</tr>
<tr>
<td>30% CH4 – 70% H2</td>
<td>1095</td>
</tr>
<tr>
<td>50% CH4 – 50% H2</td>
<td>1144</td>
</tr>
<tr>
<td>70% CH4 – 30% H2</td>
<td>1205</td>
</tr>
</tbody>
</table>

Figure 9. Equivalence ratio (read left axis), exhaust (before turbine) and Adibatic flame Temperature (read right axis) vs. Mole fraction of H2 in the fuel mixture (horizontal).

The emissions trends for CO, NOx, UHC, and VOC were obtained using the reactor network analysis and are presented on a concentration of part per million (ppm) on a dry basis corrected @ 15% O2 vs equivalence ratio (see Figure 10). For some of these mixtures, experimental data were available and were used to compare and refine the CRN models. Also, The CRN emission results for emissions in the form of emission index are presented in Figure 11. Emission index (EI) measures emissions on a mass basis. Other pollutant species such as Nitrous Oxide (N2O) and Formaldehyde (CH2O) can also be quantified using the reactor network, an example of results for the last two species is shown in Figure 12. Formaldehyde can be found among the products of incomplete combustion (PIC), and nitrous oxide is one of the reactive species of the nitrogen chemistry at fuel lean conditions.
Figure 10. Concentration of NOx/CO (see left axis-notice part per Million) & UHC/VOC (see left axis-notice part per Billion) against mole fraction of H2 in the mixture. Experimental data (geometric figures) and CRN (lines). Experimental results by therkelsen et al. [1] and Brückner-Kalb et al. [7]

Figure 11. Emission index (EINOx and EICO) as a function of the mole fraction of H2 in the fuel mix.
A summary of the key points regarding the behavior of NOx emissions for Fuel Class I include:

- The experimental and CRN results show that the addition of hydrogen up to 90% to NG leads a significant shift on the concentration of NOx emissions at a constant flame temperature.
- Also the addition of H₂ promotes the formation of intermediate species like OH and H, which form more NOx through the NNH, thermal and N₂O routes compared to pure hydrocarbon flame. On the other hand, the prompt path is initiated by rapid reactions of hydrocarbon radicals with molecular nitrogen; therefore the addition of H₂ to the fuel reduces the formation of NOx through the prompt route.
- The trends for nitrous oxide (N₂O) indicate residual values under 1ppmdv @ 15% O₂. The measurement of subppm emissions requires precise instruments, which makes it more difficult to detect. Still N₂O is a powerful greenhouse gas with a global warming potential 298 times higher compared to CO₂ and a lifetime in the atmosphere of 114 years².
- The results in form of emission index display the same trends as the concentration results in ppmdv. However, the emission index form allows an easy estimation, for example, of the mass of pollutant emitted per year; in contrast the concentration form gives a relative idea of volume occupied by the pollutant on a dry basis (after removing the water from the

²epa.gov/climatechange/ghgemission/gases/n2o.html
combustion products), which again biases the results for the Hydrogen samples, since hydrogen enriched fuels produce more water than carbon dioxide when compared to any hydrocarbon.

Regarding the emissions of CO, UHC and VOC, which can be referred as products of incomplete combustion (PICs). The key points regarding the behavior of PICs for Fuel Class I include:

- At constant flame temperature, the addition of hydrogen to the fuel reduces the emissions of PICs.
- The high reactivity of hydrogen helps to complete the oxidation reactions avoiding incomplete combustion products. Moreover, the additional hydrogen displaces carbon from the fuel, so inherently less CO, UHC and VOC can form.
- The predicted levels of VOC and UCH are below 20 ppb @ 15% O₂.
- The predicted levels of CO are below 100ppm @ 15% O₂ and decreases with the addition of hydrogen.
- The predicted levels of Formaldehyde (CH₂O), which can be considered a VOC and UHC where found in the order of part per billion. Formaldehyde can cause irritation of the skin, eyes, nose and throat. High levels of exposure may cause some types of cancer³.

1.5.2. Fuel class II- Landfill / digester biogas

The test fuels for Fuel Class II are shown in Table 7. These fuels represent those that would be found in landfills or anaerobic digestion processes. The final fuel (96% CH₄-4% CO₂) reflects one which would be meet minimum Wobbe Index requirements.

<table>
<thead>
<tr>
<th>Fuel class III: landfill-digester-biogas</th>
<th>Wobbe index (BTU/scfm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35% CH₄ – 65% CO₂</td>
<td>312</td>
</tr>
<tr>
<td>60% CH₄ – 40% CO₂</td>
<td>599</td>
</tr>
<tr>
<td>80% CH₄ – 20% CO₂</td>
<td>895</td>
</tr>
<tr>
<td>96% CH₄ – 4% CO₂</td>
<td>1279</td>
</tr>
</tbody>
</table>

The equivalence ratio that guarantees constant adiabatic flame temperature (1850K) is presented in Figure 13 as a function of the mole fraction of CO₂ in the mix. Notice that the addition of CO₂ to the fuel reduces the flame temperature, therefore less excess of air is required to counteract this effect. Notice that the exhaust and adiabatic flame temperature are constant for all the fuel compositions.

³www2.epa.gov/formaldehyde
For the fuel class II, the CO, NOx, UHC, and VOC trends were obtained using the reactor network analysis and are presented on a concentration of part per million (ppm) on a dry basis corrected @ 15% O2 vs equivalence ratio (See Figure 14). For some of these mixtures, experimental data were available and were used to compare and refine the CRN models. Also CRN results for emissions in the form of emission index are presented in Figure 15. A sample with reactor network results for Nitrous oxide and formaldehyde is presented in Figure 16.

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**Figure 13.** Equivalence ratio (read left axis), exhaust (before turbine) and Adibatic flame Temperature (read right axis) vs. Mole fraction of CO₂ in the fuel mixture (horizontal).

**Figure 14.** NOx, CO, VOC and UHC emission concentration [ppmdv corrected at 15% O₂] as a function of the Equivalence ratio for natural gas and biogas fuels. Experimental results by Hack et al. [8]
A summary of key results of the impact of CO2 addition to Natural gas on emissions of NOx and CO is as follows:

- Figure 12 presents volumetric concentration of NOx in ppm dv @ 15% O2 vs. equivalence ratio. It is clear from that figure that the concentration of NOx decreases with the
The addition of CO₂ to the fuel, with the highest levels of diluent producing the lowest NOx and highest level of CO. Since the results represent the emission at the same temperature (1850K) it can be concluded that dilution with CO₂ acts as heat sink cooling down the reactions. A similar heat sink effect can be achieved by using a larger excess of air or lean combustion. Also, the dilution of the reactions with CO₂ depletes the formation of radicals such as OH, this is the same concept applied to systems with exhaust gas recirculation and internal recirculation of gases to reduce NOx emissions.

- The effect of diluting the fuel with CO₂ is similar to using a leaner mixture (air excess), although the presence of CO₂ is expected to have a greater impact on reaction temperatures than N₂ because it has a greater specific heat. As a result, it might be expected that each species may impact emissions somewhat differently. CO₂ was used as the only diluent during the testing. More details about the experiments operating the MTG on CO₂/natural gas mixtures can be found in [9].
- Fuel dilution follows the same physics behind the injection of water or steam to the reaction zone and the strategy of ultra-lean combustion. By diluting the fuel with 8.8% CO₂ a reduction of NOx emissions by 28% (from 6 to 4.3 ppmv of O₂) was achieved. The NOx depletion reaches an asymptote as the volumetric concentration of CO₂ in the fuel increases from 36 to 44%.
- The dilution of natural gas with CO₂ increases the production of CO and reduces the flame temperature of the reactions at constant equivalence ratio.
- The addition of fuel diluent (CO₂) depletes the formation of O-atoms, OH radicals, and N₂O that form NOx through the thermal route and N₂O route. This depletion of radicals can be observed in Figure 17. Where the increase of CO₂ concentration indicates a proportional reduction on the radicals O, H, and N₂O. Similarly, the relative importance of each NOx pathway was analyzed using CRN (See Figure 18).
- The addition of CO₂ hinders the formation of NOx through the thermal and N₂O routes, while the NNH and prompt mechanisms are not significantly affected.

![Figure 17. Relative increase reduction of important radicals (compared to 100% CH₄) leading the formation of NOx through N₂O Intermediate mechanism (CRN conditions: preheating 835K, Pressure: 4 atm-GRI 3.0)](image-url)
The key points associated with the impact of CO₂ on VOC and UHC emission are as follows:

- The emissions of UHC and VOC are below 1ppmdv @15% O₂

The key points associated with the emissions of N₂O and CH₂O are:

- The results for N₂O emissions show a decreasing trend when adding CO₂ to the fuel (at constant flame temperature). The predicted levels of N₂O are under 1ppmdv @ 15% O₂.
- N₂O is produced in flames due to 1. Oxidation of amine radicals (mainly NH and less significant CN₂). 2. In lean regions of gas flames. 3. In fluidized bed furnaces (T approx. 850°C).
- In general, the combustion of solid and liquid fuels emit more N₂O than gaseous fuels. The nitrogen attached to the fuel acts as a precursor of N₂O products.
- The predicted levels of Formaldehyde are below 0.01 ppmdv @ 15% O₂.
- Diluting the fuel with CO₂ the O and H atoms involved in the intermediate N₂O route are depleted with the addition of CO₂, and, as a result, the production of N₂O is also depleted. With the strategy of analysis presented in this study it is possible to conclude that the addition of diluents such as CO₂ to the fuel hinders the formation of NOₓ through the N₂O route under the conditions of the micro turbine generator. Similar results might apply to other applications such as those found in Diesel engines.

Finally, other emissions such as NO₂ levels were analyzed using the CRN model. It has been observed that, at low temperature conditions such as at start up and low load, brown exhaust
plumes can result due to emission of NO₂ from the combustion system. It is believed that HO₂, which is formed in low temperature regions, can oxidize NO present in higher temperature regions. NO₂ is related to the HO₂ radical that can be formed by the third-body reaction H+O₂+M⇌HO₂+M. The concentration of HO₂ in the CRN revealed that the presence of diluents such as CO₂ does not lead to a difference in the generation of HO₂. However, the presence of diluents reduces the concentration of other radicals such as H and OH, and dilutes the O₂ that is necessary in the third body reaction that leads to NO₂. For the current conditions, the CRN indicates that the concentration of NO₂ in the exhaust represents less than 8% of the total NOₓ emissions.

1.5.3. Fuel class III-Mixtures with heavier hydrocarbons

The effect of blending natural gas with ethane and propane is examined in this section. Fuel mixtures of methane with heavier alkane gases were assessed with the reactor network. The first fuel is a mixture of ethane (C₂H₆) balanced with methane and the second blend is propane (C₃H₈) balanced with methane; both compositions are expressed by their volumetric concentrations. These mixtures represent expected variation in natural gas content within the United States [10].

The fuels tested in terms of mixtures of natural gas with heavier hydrocarbons are shown in Table 8. The analysis of the pure gases, 100% Ethane (C₂H₆) and 100% Propane (C₃H₈), was also included for a direct comparison with NG.

<table>
<thead>
<tr>
<th>Mixtures with heavier hydrocarbons</th>
<th>Wobbe index (BTU/scf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75% CH₄ – 25% C₂H₆</td>
<td>1399</td>
</tr>
<tr>
<td>85% CH₄ – 15% C₂H₆</td>
<td>1360</td>
</tr>
<tr>
<td>75% CH₄ – 25% C₃H₈</td>
<td>1489</td>
</tr>
<tr>
<td>85% CH₄-15% C₃H₈</td>
<td>1416</td>
</tr>
<tr>
<td>100% C₂H₆</td>
<td>1663</td>
</tr>
<tr>
<td>100% C₃H₈</td>
<td>1954</td>
</tr>
</tbody>
</table>

The equivalence ratio that guarantees constant adiabatic flame temperature (1850K) is presented in Figure 19 as a function of the mole fraction of C₂H₆ or C₃H₈ in the mix, where the balance fraction is CH₄. Notice that the variation of the equivalence ratio is only -0.01, φ~0.47 for CH₄ and φ~0.46 for C₂ and C₃. This is the addition of C₂H₆ or C₃H₈ slightly increases the flame temperature at a constant air to fuel ratio.
The CRN results for NOx and CO emission on a concentration basis are shown in Figure 20. The figure includes trends for both mixtures of CH\textsubscript{4} with C\textsubscript{2}H\textsubscript{6} or C\textsubscript{3}H\textsubscript{8}, the numerical results are also compared to the some available experimental results obtained by Hack & McDonell in 2008 [8]. Similarly, the results for VOC and UHC on a concentration basis are presented in Figure 21. Also CRN results for emissions in the form of emission index are presented in Figure 22. A sample with reactor network results for Nitrous oxide and formaldehyde is presented in Figure 23.
Figure 21. NOx emissions in ppmv @ 15% O₂ vs mole fraction of C₂H₆ or C₃H₈ in the mix with natural gas.

Figure 22. EINOx (Right vertical axis) and EICO (Left axis) vs mole fraction of C₂, C₃ hydrocarbons mixed with natural gas.
A summary of key impacts of fuel composition on NOx are as follows:

- The addition of heavier hydrocarbons to methane yields an increase of the concentration of NOx as presented in Figure 20 and Figure 22. At temperatures below 1900K, the thermal NOx pathway is not expected to produce most of the NOx. Below this temperature, other NOx pathways play a significant role. In this case, the N$_2$O pathway plays a significant role in the overall levels of NOx emitted from lean premixed reactions with equivalence ratios less the 0.80. The N$_2$O reaction is also pressure dependent. At high pressures NO formation via N$_2$O becomes important. The pressure influence on NO formed from this mechanism is evidenced in the reaction O + N$_2$ + M $\leftrightarrow$ N$_2$O + M; with "M" representing a chemically unchanged third body species. Per Le’ Chatelier’s principle, increasing pressure drives the equation to the right, thus enabling NO formation through the subsequent reactions.

- At an equal flame temperature, the addition of ethane or propane enhances the production of NOx. The trends indicate that the addition of ethane to natural gas has a more significant effect on increasing the NOx emissions than a similar addition of propane.

- The results for the pure fuels (100% C$_2$H$_6$ or C$_3$H$_8$) also indicate an increase of NOx for heavier hydrocarbons.

The key result regarding the impact of mixing natural gas with heavier alkane fuels on CO, VOC and UHC emissions is as follows:

- The addition of heavier alkanes enhances the emissions of carbon monoxide. At equal flame temperature (1850K) CH$_4$ produces the least amount of CO.

- The addition of ethane to natural gas slightly increases the production of CO. Propane has a more significant effect on the formation of CO relative to Ethane and Methane.
For the conditions of the experiment the concentration of UHC remains below 0.2ppmdv @ 15% O\textsubscript{2} for all the fuel composition. Propane displays a tendency to emit more UHC when compared to Ethane and Methane.

The addition of heavier hydrocarbons enhances VOC emissions. The trends indicate that heavier alkanes will tend to emit larger quantities of VOC compared to the simplest hydrocarbon (CH\textsubscript{4}).

Finally, Figure 23 shows the emission trends for formaldehyde and N\textsubscript{2}O.

The emissions of N\textsubscript{2}O are not dependent on the fraction of heavier hydrocarbons. The results indicate a constant value ~ 1 ppmdv@15%O\textsubscript{2} for all Fuel class III.

Conversely, the results for formaldehyde show a positive effect regarding the addition of ethane and propane. The trends indicate that heavier hydrocarbons emit lower levels of CH\textsubscript{2}O when compared to natural gas. The results indicate the lowest levels of CH\textsubscript{2}O for 100% C\textsubscript{3}H\textsubscript{8}.

### 1.6. Stability analysis

Many physical considerations have been used in correlating blowout, but they all lead to the same form of correlation in terms of a Damkhoher number, \( Da = \frac{\tau_{\text{rec}}}{\tau_{\text{chem}}} \). The generally accepted idea is that blowout occurs when the characteristic chemical time becomes longer than the characteristic residence time. e.g. \( Da=1 \). Due to the wide band of turbulent time scales that exists within combustors it is possible for oxidation of different fuel elements to occur in different combustion regimes.

CRNs have been applied to a variety of combustion topics, such as determining overall reaction kinetic rates, NO\textsubscript{x} formation, and turbulent flame phenomena. PSRs idealize the mixing behavior such that they model a situation where combustion products are back-mixed with reactants so quickly that the reaction zone is distributed uniformly in the control volume. For the combustor in this experiment the exhaust gas recirculation promotes turbulent mixing of reaction zones that produce back-mixing conditions that approach the stirred reactor idealization. Success in correlating behavior for lean blow out with a PSR has been shown elsewhere [11]. Evaluation of lean blowoff using a CRN is carried out following the approach of Strakey et. al [12] This method involves performing one PSR simulations for the experimental conditions (i.e., inlet temperature, equivalence ratio, pressure, mass flow rate, fuel class), without heat losses or diffusion effects. For those conditions the residence time of the reactors is varied until the reactions extinguish. The residence time at blowoff is \( \tau_{\text{res}} \). Page et. al., found that the residence time \( (\tau_{\text{rec}}) \) at blowoff is sensitive to the reaction mechanism. Although the differences are not sufficient to significantly affect the results [11]. For the conditions tested by Page et al, \( \tau_{\text{rec}} \) was found to be 0.053 with GRI 3.0 and 0.064 Galway C5[13].

Also the chemical time \( \tau_{\text{chem}} \) at the experimental operating conditions can be found using the following equation:
\[ \tau_{chem} = \frac{\alpha}{(S_L)^3} \]

Where \( \alpha \) is the thermal diffusivity and \( S_L \) is the laminar flame speed at the inlet operating conditions; \( \alpha = f(T, P, \phi, Fuel\ type) \) and \( S_L = f(T, P, \phi, Fuel\ type) \).

Lean blowoff happens when the chemical time is equal to the residence time or \( Da=1 \). So mixtures approaching \( Da=1 \) will blowoff. Figure 24 shows the variation of the Damkohler number as a function of the mole fraction of the alternative fuel balanced with \( CH_4 \). Notice that when increasing the mole fraction of hydrogen and biogas \( Da \) decreases and tends to move further from \( Da=1 \). This behavior indicates those two mixtures would be more resistant to blowoff. Conversely, mixtures with heavier alkanes show \( Da \) increases with a larger mole fraction of heavier hydrocarbons. The addition of \( C_2H_6 \) and \( C_3H_8 \) moves the curve closer to the blowoff stability limit.

Figure 24. Damkohler number as a function of the mole fraction of \( H_2, CO_2, C_2H_6, C_3H_8 \) - Balance \( CH_4 \). Figure 25, 26, 27, 28 show the equivalence ratio at blowoff for hydrogen enriched NG, biogas, ethane enriched NG and the propane mix, respectively. The results are presented as a function of the mole fraction of the alternative fuel balanced with natural gas. Notice that the red line represents the equivalence ratio used to guarantee AFT=1850K.
Figure 25. Lean blowoff stability limit for Hydrogen enriched natural gas compared to the equivalence ratio to reach AFT 1850K.

Figure 26. Lean blowoff stability limit for biogas compared to the equivalence ratio to reach AFT 1850K.

Figure 27. Lean blowoff stability limit for mixtures CH₄ with C₂H₆ to the equivalence ratio to reach AFT 1850K.
Figure 28. Lean blowoff stability limit for mixtures CH$_4$ with C$_2$H$_6$ to the equivalence ratio to reach AFT 1850K.

A summary with the stability limits found for the configuration # 3 is presented in Table 9.

<table>
<thead>
<tr>
<th>Fuel class I - Hydrogen enriched natural gas</th>
<th>LBO limit$^1$</th>
<th>Fuel class III: Mixtures with heavier hydrocarbons</th>
<th>LBO limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% CH$_4$ – 90% H$_2$</td>
<td>0.31</td>
<td>75% CH$_4$ – 25% C$_2$H$_6$</td>
<td>0.428</td>
</tr>
<tr>
<td>30% CH$_4$ – 70% H$_2$</td>
<td>0.34</td>
<td>85% CH$_4$ – 15% C$_2$H$_6$</td>
<td>0.424</td>
</tr>
<tr>
<td>40% CH$_4$ – 60% H$_2$</td>
<td>0.36</td>
<td>75% CH$_4$ – 15% C$_3$H$_8$</td>
<td>0.42</td>
</tr>
<tr>
<td>50% CH$_4$ – 50% H$_2$</td>
<td>0.37</td>
<td>75% CH$_4$ – 25% C$_3$H$_8$</td>
<td>0.43</td>
</tr>
<tr>
<td>70% CH$_4$ – 30% H$_2$</td>
<td>0.39</td>
<td>100% C$_3$H$_8$</td>
<td>0.45</td>
</tr>
<tr>
<td>100% CH$_4$</td>
<td>0.42</td>
<td>100% C$_2$H$_6$</td>
<td>0.436</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fuel class III - biogas</th>
<th>LBO limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>35% CH$_4$ – 65% CO$_2$</td>
<td>0.45</td>
</tr>
<tr>
<td>60% CH$_4$ – 40% CO$_2$</td>
<td>0.433</td>
</tr>
<tr>
<td>80% CH$_4$ – 20% CO$_2$</td>
<td>0.43</td>
</tr>
<tr>
<td>96% CH$_4$ – 4% CO$_2$</td>
<td>0.42</td>
</tr>
</tbody>
</table>

$^1$ LBO limit: Equivalence ratio at lean blow out
$^2$ pure methane is presented here as a reference of the stability limits for natural gas.

A summary of key points regarding the role of fuel composition on lean stability limits follows:

- The addition of hydrogen to natural gas widens the stable operating region. While for pure natural gas the LBO limit happens at an equivalence ratio equal to 0.42, for a hydrogen enriched natural gas up to 90% H$_2$-10% CH$_4$ this limit is 0.31. Several studies have focused on H$_2$ /CH$_4$ flames and shown that small additions of H$_2$ substantially enhance the mixture’s resistance to extinction or blowout. For example, fundamental studies show that the extinction strain rate of methane flames is doubled with the addition of 10% H$_2$ [14].
- The stability range of the synthetic gases is wider compared to natural gas.
• The dilution of natural gas with diluents like CO$_2$ or N$_2$ reduces the stability limits. These diluents in the fuel impact the flame stability in at least three ways, through changes in (1) mixture specific heat and adiabatic flame temperature, (2) chemical kinetic rates, and (3) radiative heat transfer. The addition of N$_2$ apparently has straightforward effects, as it is only manifested through the first item above, an influence that can be easily quantified with standard equilibrium calculations.

• The addition of CO$_2$ to NG up to 65% doesn’t affect significantly the stability of the system. In this case diluting the fuel with CO$_2$ is similar to using a leaner mixture with natural gas. For a biogas up to 65% CO$_2$ the equivalence ratio at blowoff is 0.45. For pure natural gas this limit is 0.42.

• H$_2$O and CO$_2$ additions, however, exert additional subtle effects through the latter two items. As noted by the second point, CO$_2$ and H$_2$O do not act as passive diluents in the fuel but interact kinetically reducing the flame speed of the mixtures with CO$_2$ dilution [14].

• The addition of heavier hydrocarbons to natural gas reduces the stability limits. Damkhoier number increases and approaches the unity with the addition of C$_2$H$_6$ and C$_3$H$_8$ as a consequence the operating point @ 1850K is closer to the blowoff limit for these type of mixtures.
Appendix A: Interchangeability analysis

In this section an interchangeability analysis is presented. For the analysis we take into account the Wobbe index and the rule 30. The former regulates the content of other constituents of the natural gas distributed in California.

According to rule 30 the gas shall have a minimum Wobbe Number of 1279 Btu/scf and shall not have a maximum Wobbe Number greater than 1385 Btu/scf. The gas shall meet American Gas Association’s Lifting Index, Flashback Index and Yellow Tip Index interchangeability indices for high methane gas relative to a typical composition of gas in the Utility system serving the area.

Acceptable specification ranges are:

<table>
<thead>
<tr>
<th>AGA Indices</th>
<th>Acceptable specification ranges</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lifting Index ($I_L$)</td>
<td>$I_L \leq 1.06$</td>
</tr>
<tr>
<td>Flashback Index ($I_F$)</td>
<td>$I_F \leq 1.2$</td>
</tr>
<tr>
<td>Yellow Tip Index ($I_Y$)</td>
<td>$I_Y \geq 0.8$</td>
</tr>
</tbody>
</table>

Regarding the fuel composition, rule 30 specifies:

Carbon Dioxide: The gas shall not have total carbon dioxide content in excess of three percent (3%) by volume.

Inerts: The gas shall not contain in excess of four percent (4%) total inerts (the total combined carbon dioxide, nitrogen, oxygen and any other inert compound) by volume.

Since the Wobbe Index is only concerned with matching heat release for a given burner, other indices have been developed to assess the interchangeability of other flame properties such as lifting, yellow tipping, flash back, air supply, incomplete combustion, and burner load [1].

In 1946 the American Gas Association (AGA) carried out extensive experimental research on fuel gas interchangeability [15]. AGA Tests were done on a specially developed partial premixing Bunsen-type burner and focused on establishing criteria for blending "supplemental" or “peaking gases” with base load supplies or adjustment gases; those adjustment gases were the three most historically representative natural gases available in the U.S at that time [10]. Based on this experimental work, AGA developed several empirical indices to address the effects of fuel interchange on Yellow Tipping ($I_Y$), Flame Lifting ($I_L$) and Flash Back ($I_F$). The methodology to calculate these indices is presented in the AGA bulletin#36 of 1946 [15]. These indices may not be applicable to the typical complex turbulent premixed flames found in current practical systems. The inaccuracies expected from applying AGA indices to current fuels may be even greater, since current fuels of interest include coal derived syngas, landfill and biomass gases, imported liquefied natural gas (LNG) and hydrogen augmented fuels whose composition is completely different to those natural gases used to set the stability criteria. Nonetheless, these indices were considered as the most advanced methods and effective tools to predict interchangeability in the United States and should be considered as a starting point.
Considerations before applying the AGA indices:

- AGA Tests were done on a specially developed partial premixing Bunsen-type burner. The results of these experiments may not be feasible for other kind of systems where the conditions are different to those of the atmospheric burner.
- AGA developed a set of preferable limits for each of the three indices. Those limits establish if a fuel is interchangeable with the adjustment gases under each criterion (flashback, lifting and yellow tipping).
- AGA set the preferable limits for three adjustment natural gases. Thus, the same limits may not be suitable if other adjustment gases are selected as reference fuels.

Interchangeability under the criterion of Flashback (AGA)

Mixtures of CO-H₂, CH₄-H₂, CH₄-C₂H₆, CH₄-C₃H₈ and biogases (CH₄-CO₂) were analyzed with AGA criteria. Flashback indices were calculated for every mixture. Pure gases such as H₂, CO and CH₄ were analyzed and are depicted with single markers in Figure A-. Every point in the figure represents a mixture; the volumetric content varies every 10% (by volume) starting with the pure substance.

- According to the Wobbe Index only a narrow region (1279-1385) is interchangeable. This region excludes most mixtures and is bounded by two vertical lines.
- According to AGA if the flashback index is lower than 1.2 (I_f<1.2) the fuels are interchangeable. 100% CH₄, all mixtures of methane with propane and ethane, biogas up to 30% CO₂ and mixtures of CH₄ with H₂ up to around 20% H₂ are flashback interchangeable.
with the original adjustment natural gases. Most of these mixtures are outside of the interchangeable region defined with the Wobbe Index.

- Mixtures CH₄-H₂ with a concentration of H₂ higher than 20% are prone to flashback, therefore they are not interchangeable with the adjustment gases. Enrichment of the methane with H₂ makes the mixture more prone to flashback; a higher concentration of H₂ increases the pool of OH and H radicals that makes the mixture more reactive, this translates into a higher flame speed that entails a higher flashback propensity.

- No mixtures of CO-H₂ are feasible to interchange with the adjustment gases. Since all their flashback indices are higher than 1.18; according to the AGA index all these mixtures would experience flashback. Again the higher reactivity of CO and H₂, when compared to that of CH₄, makes these mixtures more likely to flashback.

Interchangeability under the criterion of Lifting (AGA)

![AGA Lifting Index](image)

AGA lifting indices were calculated for CO-H₂ and CH₄-H₂ mixtures and pure fuels (H₂, CO and CH₄). The results indicate that CH₄-H₂, CH₄-C₂H₆ and CH₄-C₃H₈ mixtures are not susceptible to experience lifting.

- The addition of hydrogen, with its high reactivity, tends to reduce the lifting index of a mixture. According to this, all the mixtures CH₄-H₂ are interchangeable under the lifting index.

- Notice that pure CO and mixtures of CO-H₂ failed under the flashback criterion, and for mixtures H₂-CO with CO content higher than 40%, they fail again under the lifting condition. These results show that the AGA indices are not suitable to predict the interchangeability of natural gas with this kind of fuels. Besides, the range of Wobbe indices for these mixtures is...
far from the region expected for natural gas. As mentioned before, these indices were intended to predict the interchangeability between natural gasses.

- Most biogas mixtures fall in the non-interchangeable region. Only biogas up to 3% CO$_2$ is interchangeable under the lifting condition.
- Even though all CH$_4$-H$_2$ mixtures are interchangeable under the lifting criterion, only 100% CH$_4$ and mixtures up to 20% H$_2$-80%CH$_4$ were interchangeable under the flashback criterion, therefore only the mixtures that are interchangeable under all the criteria are really interchangeable.

Interchangeability under the criterion of yellow tipping (AGA)

![Figure A-3. AGA Yellow tipping index. Analysis of interchangeability for mixtures CH$_4$-H$_2$ and CO-H$_2$.](image)

- The yellow tipping index for CO-H$_2$ mixtures yield a division by zero, which in this case may represent that $I_Y$ tends to infinity. For that reason the mixtures CO-H$_2$ and pure CO and H$_2$ are not presented in Figure A-3. This implies that those mixtures are not likely to display yellow tips in their flames.
- The addition of CO$_2$ increases the yellow tipping index. This trend indicates that the addition of CO$_2$ to the fuel will reduce the yellow tipping propensity, when compared to natural gas.
- The addition of C$_2$H$_6$ and C$_3$H$_8$ to the fuel reduces the yellow tipping index. These fuels increase the propensity of the flame to produce yellow tips. Mixtures up to 8% C$_2$H$_6$ in CH$_4$ and up to 4.5% C$_3$H$_8$ are acceptable under the yellow tipping criteria since for those mixtures $I_Y = 0.8$

Emissions of Interchangeable mixtures compared to natural gas
The following mixtures are interchangeable with natural gas according to the Wobbe Index and the interchangeability indices for flashback, lifting and yellow tipping established by the American Gas Association (AGA).

### Table A-1. Summary of emissions for interchangeable mixtures (AGA)

<table>
<thead>
<tr>
<th>Fuel Mixture</th>
<th>Equivalence Ratio For ( AFT )=1850K</th>
<th>( \text{NO}_x ) [ppmdv]</th>
<th>CO [ppmdv]</th>
</tr>
</thead>
<tbody>
<tr>
<td>76% CH(_4) - 24% H(_2)</td>
<td>0.46</td>
<td>↑ 100%</td>
<td>↓ 50%</td>
</tr>
<tr>
<td>94% CH(_4) - 6% C(_2)H(_6)</td>
<td>0.47</td>
<td>↑ 4%</td>
<td>↑ 4%</td>
</tr>
<tr>
<td>95% CH(_4) - 5% C(_3)H(_8)</td>
<td>0.47</td>
<td>↑ 3%</td>
<td>↑ 4%</td>
</tr>
<tr>
<td>98% CH(_4) - 2% CO(_2)</td>
<td>0.47</td>
<td>↓ 2%</td>
<td>↑ 1%</td>
</tr>
</tbody>
</table>

Using the CFD to CRN methodology, the \( \text{NO}_x \) and CO emissions for the fuel mixtures presented above were compared to the emissions of pure natural gas at a equivalence ratio that guarantees \( AFT \)=1850K. The preheating temperature and pressure are 835K and 4atm, respectively.

- A mixture of 76% CH\(_4\) and 24% H\(_2\) is interchangeable according to the Wobbe Index and the AGA interchangeability indices. The CRN results indicate that the addition of hydrogen to natural gas increases the concentration of \( \text{NO}_x \) by 100% in comparison to pure natural gas and the production of CO is reduced by 50%.
- The interchangeable mixture of 94% CH\(_4\) and 6% C\(_2\)H\(_6\) increases the concentration of \( \text{NO}_x \) by only 4% and the concentration of CO is increased by 4%.
- The dilution of natural gas with a small amount of CO\(_2\) increases the production of CO by 1% and reduces the concentration of NO\(_x\) by 2%.
Appendix B: NOx pathways

There are several routes to form NOx pollutants and these may be broadly catalogued as thermally-generated, flame-generated, or fuel-bound NOx.

1. Thermal NOx - Thermal NOx is formed by oxidation of nitrogen in air and requires sufficient temperature and time to produce NOx. A rule of thumb is that below approximately 1700K, the residence time in typical gas turbine combustors is not long enough to produce significant thermal NOx. Where temperatures higher than 1700K cannot be avoided, it is necessary to limit residence time to control NOx formation, which favors very short combustor designs. Thermal NOx production also increases with the square root of operating pressure, making it more difficult to reduce in higher-pressure aero-derivative gas turbines. The three principal reactions (the extended Zeldovich mechanism) producing thermal NOx are:

\[
\begin{align*}
N_2 + O &\rightarrow NO + N \\
N + O_2 &\rightarrow NO + O \\
N + OH &\rightarrow NO + H
\end{align*}
\]

2. Fuel NOx - Fuels that contain nitrogen (e.g., coal) create “fuel NOx” that results from oxidation of the already-ionized nitrogen contained in the fuel. Crude oils contain 0.1 to 0.2 % nitrogen on a mass basis, but levels as high as 0.5 % are found in some oils. In refining the oil, this nitrogen is concentrated in the residual fractions, that is, in that portion of the oil that is most likely to be burned in large combustion systems such as power plants or industrial boilers rather than used as transportation fuels. Coal typically contains 1.2 to 1.6 % nitrogen [16].

3. Prompt NOx - This third source is attributed to the reaction of atmospheric nitrogen, N\textsubscript{2}, with radicals such as C, CH, and CH\textsubscript{2} fragments derived from fuel, where this cannot be explained by either the aforementioned thermal or fuel processes. Occurring in the earliest stage of combustion, this results in the formation of fixed species of nitrogen such as NH (nitrogen monohydride), HCN (hydrogen cyanide), H\textsubscript{2}CN (dihydrogen cyanide) and CN- (cyano radical) which can oxidize to NO [16]. In fuels that contain nitrogen, the incidence of prompt NOx is especially minimal and it is generally only of interest for the most exacting emission targets. This other route occurs at low temperatures, fuel rich conditions and short residence times. This mechanism was first identified by C.P Fenimore in 1971 while studying NO formation in fuel–rich hydrocarbon flames. Fenimore concluded that the NO formed early in the flame was the result of the attack of a hydrocarbon free radical on N\textsubscript{2}, in particular by:

\[CH + N_2 \rightarrow HCN + N\]
NO from N₂O Under favorable conditions, which are elevated pressures and oxygen-rich conditions, this intermediate mechanism can contribute as much as 90% of the NOx formed during combustion. This makes it particularly important in equipment such as gas turbines and compression-ignition engines. Because these devices are operated at increasingly low temperatures to prevent NOx formation via the thermal NOx mechanism, the relative importance of the N₂O-intermediate mechanism is increasing. It has been observed that about 30% of the NOx formed in these systems can be attributed to the N₂O-intermediate mechanism [17].

At high pressures NO formation via N₂O becomes important. The pressure influence on NO formed from this mechanism is evidenced in the reaction O + N₂ + M ↔ N₂O + M; with “M” representing a chemically unchanged third body species. Per Le’ Chatelier’s principle, increasing pressure drives Equation 1 to the right, thus enabling NO formation through the subsequent reactions.

\[ O + N₂ + M \leftrightarrow N₂O + M \]

\[ N₂O + H \leftrightarrow NO + NH \]

\[ O + N₂O \leftrightarrow NO + NO \]
Appendix C: Transport properties

Figure C-1. Thermal diffusivity of the premixed gases at the inlet conditions (4 atm and 835K, AFT = 1850K)

Figure C-2. Laminar flame speed of the premixed gases at the inlet conditions (4 atm and 835K, AFT = 1850K)
Figure C-3. Chemical time of the premixed gases at the inlet conditions (4 atm and 835K, AFT = 1850K)

Figure C-4. Blowoff time of the premixed gases at the inlet conditions (4 atm and 835K, AFT = 1850K)
References


