Energy Research and Development Division

FINAL PROJECT REPORT

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

Analysis of Nine Industrial Combustion Applications

Appendix I - Burner Configuration #9: Slot Burner

California Energy Commission
Edmund G. Brown Jr., Governor

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Burner Configuration # 9: Slot Burner

Emissions and Stability Performance

CEC Agreement No. 500-13-004

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Executive Summary
A summary of the emission and stability results for the slot burner configuration is presented in Table 1. The table is coded by different colors to indicate how the fuel compositions impact the performance of the slot burner.

| Table 1 Summary of Fuel Composition Effects on Emissions and Stability /1 |
|-----------------|-----------------|-----------------|
| Fuel type /2    | I               | II              | III              |
| Hydrogen Enriched Natural Gas (CH$_4$+H$_2$) | Biogas (CH$_4$+CO$_2$) | Mixtures with heavier hydrocarbons (C$_2$H$_6$, C$_3$H$_8$) |
| NOx             | ↑ @↑H$_2$       | ↓ @↑CO$_2$      | ↑ @↑C$_2$H$_6$, C$_3$H$_8$. |
| CO              | ↓ @↑H$_2$       | ↑ @↑CO$_2$      | ↑ @↑ C$_2$H$_6$, C$_3$H$_8$. |
| Stability       | ↑ @↑H$_2$       | ↓ @↑CO$_2$      | ↑ @↑ C$_2$H$_6$, C$_3$H$_8$. |

/1 Cells highlighted with red represent negative impacts on emissions or stability with an increase in components other than natural gas. Conversely, cells highlighted with green represent positive effects.

/2 Fuel Class I: Hydrogen Enriched NG Fuels
Fuel Class II: Biogas
Fuel Class III: Fuels with Higher Hydrocarbons

The example below illustrates how the table can be interpreted:

<table>
<thead>
<tr>
<th>Emissions</th>
<th>Hydrogen enriched natural gas (CH$_4$+H$_2$)</th>
<th>Reading</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOx</td>
<td>↑ @↑H$_2$</td>
<td>NOx increases (↑) when adding (@) H$_2$</td>
</tr>
<tr>
<td>CO</td>
<td>↓ @↑H$_2$</td>
<td>CO decreases (↓) when adding (↑) H$_2$</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 NO$_x$ and CO concentration at a fixed 3% O$_2$ concentration in the exhaust. The percent change indicated in Table 2 represents the change compared to the results for natural gas (Assumed as 100% CH$_4$).

| Table 2 Summary of Emissions of AGA Interchangeable Mixtures |
|------------------|------------------|------------------|------------------|
| Fuel Mixture     | Equivalence Ratio at 3% O$_2$ | NO$_x$ [ppmvd] | CO [ppmvd] |
| 76% CH$_4$ - 24% H$_2$ | 0.87             | ↑ 8%            | ↓ 6%          |
| 94% CH$_4$ - 6% C$_2$H$_6$ | 0.87             | ↑ 3%            |              |
| 95% CH$_4$ - 5% C$_3$H$_8$ | 0.87             | ↑ 5%            |              |
| 98% CH$_4$ - 2% CO$_2$ | 0.87             | ↓ 3%            | ↑ 2%          |
1. Introduction

The purpose of this study is to assess the performance of the slot burner operating on different natural gas compositions. Fuel and air are mixed before the combustion and the slot burner studied in this report is considered a premixed combustion. The operability issue associated with the premixed flame is an important concern in industry. Indeed, it is crucial to determine whether the flame can be stabilized under various operating conditions or it will be extinguished. Once the flame is stabilized, pollutant emissions can be determined to evaluate the applicability if using different fuels. To achieve these objectives, the stability (lean blow-off limit) and emission of the slot burner has been studied using CRN (Chemical Reactor Network). The other stability issues such as flashback for high hydrogen content fuels cannot be evaluated by this model.

2. Burner Model Characteristics

The slot burner studied in this report is the Extruded Band Burner BB102A by Flynn Burner Corp (Figure 1). This type of burner is generally used in food processing industry and has been designed to operate on natural gas, propane, and butane. Fuel and air are mixed within the venturi before entering the extruded burner with the length of 36 inches. The premixed fuel/air mixture is finally injected into the atmosphere through the ribbon slot, where the flame stabilizes by sudden expansion. The firing rate of the burner is 4,000 Btu/inch of flame space with a stable turndown to 200 Btu/inch. A summary of the equipment specifications is presented in the following table.

![Figure 1 Schematic of the slot burner [1]](image)

<table>
<thead>
<tr>
<th>Table 3 High Velocity Burner Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Thermjet TJ0100 high velocity burner by Eclipse Inc.</strong></td>
</tr>
<tr>
<td>Units</td>
</tr>
<tr>
<td>Maximum input rating</td>
</tr>
<tr>
<td>Minimum input rating</td>
</tr>
<tr>
<td>Flame type</td>
</tr>
<tr>
<td>Air preheating</td>
</tr>
</tbody>
</table>
### Table 1: Burner Configuration #9—Slot Burner

<table>
<thead>
<tr>
<th>Approx. Flame Velocity</th>
<th>m/s (Ft/s)</th>
<th>Min: 3(6.5) High: 15(50)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Application</td>
<td>Boiler</td>
<td></td>
</tr>
<tr>
<td>Fuel(s)</td>
<td>Designed for: NG, Propane, and Butane Gases tested in this evaluation: Mixed fuels: biogas (up to 80% CO₂ by vol.), hydrogen enriched NG (up to 90% H₂ by vol.), NG with Heavier Hydrocarbons</td>
<td></td>
</tr>
</tbody>
</table>

### 3. Fluent Computational Fluid Dynamics (CFD)

This section presents the relevant details about the CFD simulation and the parameters used to build the subsequent chemical reactor network designed in Chemkin. The stream function, temperature, and velocity contours are presented and analyzed in this section. The methodology to build a CRN is contingent on the results of CFD simulations to divide the combustor volume into zones represented by idealized reactor elements. Combustor zones consisting of 1-D gas flow are modeled using Plug-Flow Reactors (PFRs), whereas highly turbulent (well-mixed) zones are modeled with Perfectly-Stirred Reactors (PSRs). Using Chemkin, a simplified ideal chemical reactor network is established from the identified zones, equivalent volumes, and energy balance within the CFD model.

The CFD generated model was formed in Ansys Fluent, v 16.0. The slot burner can be modeled as a jet burner with periodic boundary conditions instead of considering the actual slot burner with 36 inches length. Figure 2 illustrates the geometry used to model the slot burner with the implemented boundary conditions. Front and back faces of the cube show the periodic boundary conditions surrounded by pressure outlet boundary condition. The general CFD model specifications are listed in Table 4 CFD Model Specifications.

![Figure 2 Fluent 2D Geometry of High Velocity Burner and Chamber](image-url)
The CFD model was primarily utilized for observing the temperature profiles of the different fuel compositions to give a preliminary verification of the overall similarity of combustor volume zones to be used in the CRN. The major boundary conditions defining the energy balance can be summarized as:

- Target exhaust temperature of 1300 F (~ 1000 K)
- Reference ER @10% excess air conditions
- Constant firing rate of 80,000Btu/hr (23kW)

Using boundary conditions and described models, the following stream function, velocity, and temperature profiles were obtained.

As it is expected, there is clear no recirculation region in the flow field. The ambient air entrainment can be observed from the streamlines as the jet flows downstream. Indeed, the mass flow rate of the jet increases along the axial axis.
The velocity contour is like the stream function profile and the jet velocity is maximum at the centerline. The flow velocity increases where the reaction occurs due to the lower density and this is the reason why the maximum velocity remains approximately constant further downstream.

These profiles were generated at constant fire input (23 kW), heat transfer boundaries and fixed geometry. Thus, the profiles above were used to model the sizes of the different reactors in the network. Because the flow dynamic behavior doesn’t depend on the fuel compositions, the size and configuration of the reactor network was set up as a constant. The only variable for the networks is the fuel composition and flowrates of premixed gas at variable equivalence ratio.
4. Chemical Reactor Network
Chemical reactor networks are utilized for determination of pollutant formation and blow-off performance of modelled combustion systems. For this burner configuration, the chemical reactor network is built in Chemkin Pro 15131 based off of the CFD results that are represented in figures 3-5.

4.1. 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 are 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.

In order to establish the necessary zones for PSR or PFR designation we use both the stream function and temperature profiles from CFD. As mentioned before, there is no recirculation region for the modeled slot burner. Hence, the flame front is estimated by PSR where the actual combustion occurs. Then, the downstream reaction can be modeled by a PFR.

The allocation of zones is depicted in Figure 6. The first section is the fuel and air inlet. PSR illustrates the main flame zone where the main reaction and immediate post-flame occurs. PFR represents the one-dimensional flow of the gases leaving the flame front.

![Figure 6 Diagram of Chemkin CRN to CFD Model Relation](image)
4.2. Chemical Reactor Network Parameters

According to the GTI experiments the guidelines for model design of the high speed burner are:

- Exhaust temp goal: 1300 F or 1000 K
- NOx emissions target @3%O2: 15 – 45ppmv
- CO emissions target @3%O2: 5 – 40ppmv
- Firing Rate 80,000Btu/hr (23kW)

In order to adhere to these guidelines there were certain variables in the Chemkin model that were adjusted accordingly:

PSR parameters:

- Temperature estimate (K)
- Pressure (atm)
- Residence time (ms)
- Heat Loss (kJ/s)

PFR parameters:

- Start/End Axial Position (mm)
- Diameter (mm)
- Pressure (atm)
- Temperature (K)
- Heat Flux (kJ/cm-s)

For the PSRs the most important variables were the residence time and heat losses. Volume reflected the general size of the zones represented. As seen in Table 5 that summarizes the PSR inputs, PSR experiences a maximum of 5% total heat losses since further heat losses in the main flame can cause premature blow-off or prevent the reaction to initiate.

<table>
<thead>
<tr>
<th>Reactor name</th>
<th>Representative zone</th>
<th>Residence time (ms)</th>
<th>Temperature (K)</th>
<th>Pressure (atm)</th>
<th>Heat Loss (kJ/s)</th>
<th>Heat losses (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSR_1</td>
<td>Cold inlet stream</td>
<td>3</td>
<td>290</td>
<td>1</td>
<td>1.15</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 6 below reflects the PFR input. The diameter and overall length are specified for the region found by the stream function profile in section 4-0. The PFR has a large heat loss.

<table>
<thead>
<tr>
<th>Reactor name</th>
<th>Representative Zone</th>
<th>Diameter (mm)</th>
<th>Length (mm)</th>
<th>Pressure (atm)</th>
<th>Temperature (K)</th>
<th>Heat Flux (kJ/cm-s)</th>
<th>Heat losses (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFR_1</td>
<td>1-D flow</td>
<td>15</td>
<td>200</td>
<td>1</td>
<td>2000</td>
<td>0.75</td>
<td>65</td>
</tr>
</tbody>
</table>

The finalized specifications and outputs of the slot Burner model are summarized below in Table. 7. Assuming 100% efficiency of the 80,000 Btu/hr firing rate, the heat losses were
variable to achieve the experimental results. Total combined heat losses from the main flame (PSR), the continued reaction (PFR) were 65%. With the target exhaust temperature was 1000K. Finally, the experimental NOx emissions @3%O₂ were between 15-35ppmvd and model output was 30.6ppmvd.

<table>
<thead>
<tr>
<th>Heat Input (kW)</th>
<th>Total Combined Heat Loss (%)</th>
<th>Exhaust Temp (K)</th>
<th>NOx ppmvd @3%O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>65</td>
<td>1000</td>
<td>30</td>
</tr>
</tbody>
</table>
5. Effect of Fuel Compositions on Emissions

In this section, the evaluation of the effect of the fuel composition on the emissions is assessed using the CRN methodology. The power input to the burner is held constant at 23kW (80,000Btu/hr), while the air flow rate is varied to control the flame temperature. The results are presented as part per million (ppmvd) of pollutant corrected at 3% oxygen on a dry basis. This presentation (ppmvd) is representative of the measures in the field and is also typical of units found in regulatory or permit limits. While this presentation is important and common, when comparing results among significantly different fuel types, it can create some challenges in the interpretation of the results comparing fuels.

The CRN results for emissions and lean blow off limits were obtained using Chemkin Pro 15131 and GRI 3.0 reaction mechanism [7]. While it is recognized that the specific chemistry mechanism used can influence the absolute values of the emissions predicted [8], the trends are generally insensitive to the mechanism used.

5.1. Fuel Class I: Hydrogen-Enriched Natural Gas

Table 8 summarizes the H₂-enriched NG test fuels used and their respective Wobbe Indexes. Hydrogen is often added to natural gas to raise the heating value and lower CO and products of incomplete combustion (PICs) emissions. However, as discussed in the summary of conclusions, this causes shorter flame length and higher localized temperatures that increases NOx emissions.

<table>
<thead>
<tr>
<th>Hydrogen enriched natural gas</th>
<th>Wobbe index (MJ/Nm³)</th>
<th>Wobbe index (BTU/scf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% CH₄ – 90% H₂</td>
<td>42.4</td>
<td>1136</td>
</tr>
<tr>
<td>30% CH₄ – 70% H₂</td>
<td>42.4</td>
<td>1136</td>
</tr>
<tr>
<td>50% CH₄ – 50% H₂</td>
<td>44.3</td>
<td>1188</td>
</tr>
<tr>
<td>80% CH₄ – 20% H₂</td>
<td>47.9</td>
<td>1283</td>
</tr>
</tbody>
</table>

Figure 7 presents the NOx emissions of the hydrogen enriched natural gas cases by concentration.
A summary of the key points regarding the behavior of NOx emissions for Fuel Class I include:

- At a fixed flame temperature, the addition of hydrogen to natural gas increases the production of NOx per energy consumed. 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 a 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 combined result is an increased production of NOx for the hydrogen enriched fuels.

- The NNH reactions enhanced by the addition of H₂ include: NH + N = N₂ + H; NH + NO = N₂ + OH; NNH = N₂ + H; NNH+M= N₂ + H + M; NNH + O₂=HO₂+N₂; NNH + O = OH + N₂; NNH + H = H₂+N₂; NNH + OH = H₂O+N₂; and NNH + CH₃=CH₄+N₂ [9].

- The thermal route is enhanced by the addition of H₂ since the mechanism is comprised of the three following reactions: N₂ + O = N + NO; N + O₂=NO + O; and N + OH = NO + H.

- Again, since the addition of hydrogen to the fuel enhances the production of H and OH species, the effect of hydrogen addition on the N₂O Intermediate mechanism can be explicated by the following reactions: O + N₂ + M = N₂O + M; N₂O + H = NO + NH; O + N₂O = NO + NO.

- At a fixed equivalence ratio the addition of hydrogen to natural gas increases the concentration of NOx on a dry basis. Hydrogen enriched fuels produce more water as a result of the complete oxidation of H₂, for these fuels when the emissions are presented on a dry basis (water is removed from the sample) a significant shift towards a higher NOx concentration for the hydrogen enriched flames is observed. However, one of the
reasons for the NOx increase is the dry basis format itself. For comparison, on a wet basis and stoichiometric combustion with air, the maximum percentage of water in the combustion products for a methane flame is 19% with 9.5% CO₂ and N₂ balance, whereas the maximum percentage of water for pure hydrogen is 34.7% with 0% CO₂ and balance N₂. Consequently removing the water from the sample will yield relative higher concentrations for the hydrogen enriched flames.

Figure 8 show the CO emissions results for hydrogen enriched natural gas cases by concentration.

A summary of the key points regarding the behavior of CO emissions for Fuel Class I include:

- The addition of hydrogen to the fuel reduces the emission of carbon monoxide (CO). Again the higher 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 can form.

5.2. Fuel Class II: Biogas

Biogas is produced from the breakdown of organic matter typically through anaerobic digestion. This form of gas will typically be found in landfills or wastewater treatment plants. The higher content of CO₂ in the gas generally raises CO emissions. Due to lower heating value caused by the dilution of the fuel with CO₂, there is generally less NOx produced since there are lower reaction temperatures. The compositions of biogas used in this study are summarized below in Table 9. Figure 9 depicts the CRN results for the biogas cases in NOx emission concentration.
Table 9  Biogas Fuel Compositions and Wobbe Indexes

<table>
<thead>
<tr>
<th>Fuel class III: landfill-digester-biogas</th>
<th>Wobbe index (MJ/Nm3)</th>
<th>Wobbe index (BTU/scfm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35% CH₄ – 65% CO₂</td>
<td>12.1</td>
<td>323</td>
</tr>
<tr>
<td>50% CH₄ – 50% CO₂</td>
<td>18.4</td>
<td>493</td>
</tr>
<tr>
<td>60% CH₄ – 40% CO₂</td>
<td>23.2</td>
<td>621</td>
</tr>
<tr>
<td>80% CH₄ – 20% CO₂</td>
<td>34.7</td>
<td>929</td>
</tr>
</tbody>
</table>

Figure 9. Equivalence Ratio vs. NOx Emissions for Biogas mixtured-fuel class II.

A summary of key results for the effect of natural gas with CO₂ on the emissions of NOx are as follows:

- Figure 9 presents volumetric concentration of NOx in ppmvdv @ 3% O₂ vs. equivalence ratio. It is clear from that figure that the concentration of NOx decreases with the addition of CO₂ to the fuel, with the highest levels of diluent producing the lowest NOx. However, the content of CO₂ in the fuel is one of the reasons for more diluted emissions and lower biogas flame temperatures when compared to natural gas. The lower flame temperatures are just an effect of the dilution with CO₂ that acts as heat sink cooling down the reactions. 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 to reduce the NOx emissions.
Figure 10 shows the results for CO emissions. The mixture with higher CO₂ concentration shows a higher level of CO compared to natural gas.

The key points associated with the impact of diluent on CO emission are as follows:

- On a volumetric basis (ppmdv), CO emissions begin to increase sharply for equivalence ratios higher than 0.9. The increase in CO is more pronounced for more diluted mixtures and the most diluted case exhibits the highest CO concentrations.
- Regarding the stability of the flame, the addition of CO₂ to NG shortens the stability range of the flame. Biogas flames blowoff at higher equivalence ratios and closer to the
stoichiometry than natural gas flames. In general a peak of CO marks the lean blowoff limit (LBO).

5.3. Fuel Class III: NG with Heavier Hydrocarbons

Natural gas compositions are not always purely methane. Some mixtures include heavier hydrocarbons such as ethane (C₂H₆) and propane (C₃H₈). Compositions with higher concentrations of these heavier hydrocarbons are more likely to exist as a liquid at atmospheric conditions. Table 10 summarizes Fuel Class III compositions and respective Wobbe indexes. Figure 11 illustrates the CRN results for NOx emissions in a concentration basis in ppmvdv and in emission index form, respectively.

<table>
<thead>
<tr>
<th>Mixtures with heavier hydrocarbons</th>
<th>Wobbe index (MJ/Nm³)</th>
<th>Wobbe index (BTU/scf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75% CH₄ – 25% C₂H₆</td>
<td>54.1</td>
<td>1452</td>
</tr>
<tr>
<td>85% CH₄ – 15% C₂H₆</td>
<td>52.6</td>
<td>1411</td>
</tr>
<tr>
<td>75% CH₄ – 25% C₃H₈</td>
<td>57.6</td>
<td>1545</td>
</tr>
<tr>
<td>85% CH₄ – 15% C₃H₈</td>
<td>54.8</td>
<td>1469</td>
</tr>
</tbody>
</table>

Figure 11. Equivalence Ratio vs. NOx Emissions in ppmvdv @ 3% O₂ for Heavier Hydrocarbon Mixtures

A summary of key impacts of fuel composition on NOx are as follows:

- On a volumetric basis, the addition of heavier hydrocarbons to methane yields an increase of the concentration of NOx.
Below are the CRN results for CO emissions.

![Figure 12. Equivalence Ratio vs CO Emissions in ppmvd @ 3% O₂ vs. for Heavier Hydrocarbon Mixtures](image)

The key points associated with the impact of diluent on CO emission are as follows:

- An increases of ethane ($C_2H_6$) and propane ($C_3H_8$) increases the CO emission for all the range of equivalence ratios. It is also clear form the figure that this increases is more pronounced at higher equivalence ratios.

6. Stability Analysis
Lean blowoff (LBO) is one of the most important parameters for low NOx combustor design. It is also difficult to predict as it is inherently transient. LBO occurs when heat generated by the reactions is not enough to ignite the incoming mixture of fresh reactants. In low-NOx combustor design, this limit is often bound by the onset of combustion instability in the form of LBO. As the flame temperature is decreased to reduce NOx, the chemical reactions slow to the point where temperature becomes the rate limiting factor and the onset of LBO is triggered. It is possible to use the CRN methodology to predict LBO by adjusting equivalence ratios in key reactors. For lower equivalence ratios or gases with high inert content (lower energy content) the kinetic simulation becomes unstable and does not converge. These results also coincide with the lowest NOx levels. This is consistent with the design goal of lean systems to operate as close to the stability limit as possible to minimize NOx. Another indicator is an increase in CO preceding the LBO limit.

A summary of the stability limits found for the burner configuration # 5 is presented in Table 11.
## Table 11 Lean Blow-Off Stability Limits

<table>
<thead>
<tr>
<th>Fuel class I – Hydrogen enriched natural gas</th>
<th>LBO limit&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Fuel class III: Mixtures with heavier hydrocarbons</th>
<th>LBO limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% CH₄ – 90% H₂</td>
<td>0.36</td>
<td>75% CH₄ – 25% C₂H₆</td>
<td>0.5</td>
</tr>
<tr>
<td>30% CH₄ – 70% H₂</td>
<td>0.42</td>
<td>85% CH₄ – 15% C₂H₆</td>
<td>0.51</td>
</tr>
<tr>
<td>50% CH₄ – 50% H₂</td>
<td>0.45</td>
<td>75% CH₄ – 25% C₃H₈</td>
<td>0.49</td>
</tr>
<tr>
<td>80% CH₄ – 20% H₂</td>
<td>0.49</td>
<td>85% CH₄ – 15% C₃H₈</td>
<td>0.5</td>
</tr>
<tr>
<td>100% CH₄</td>
<td>0.51</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Fuel class II - Biogas**

<table>
<thead>
<tr>
<th>LBO limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>35% CH₄ – 65% CO₂</td>
</tr>
<tr>
<td>50% CH₄ – 50% CO₂</td>
</tr>
<tr>
<td>60% CH₄ – 40% CO₂</td>
</tr>
<tr>
<td>80% CH₄ – 20% CO₂</td>
</tr>
</tbody>
</table>

<sup>1</sup> LBO limit: Equivalence ratio at lean blow out

<sup>2</sup> Pure methane is presented here as a reference of the stability limits for natural gas.
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 [3].

In 1946 the American Gas Association (AGA) carried out extensive experimental research on fuel gas interchangeability [2]. 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 [2]. 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 [11]. 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)

![Flashback index diagram](image)

- 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 . 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)**

![Figure A-2. 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% CO₂ is interchangeable under the lifting condition.
• Even though all CH₄-H₂ mixtures are interchangeable under the lifting criterion, only 100% CH₄ and mixtures up to 20% H₂-80%CH₄ 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 CH₄-H₂ and CO-H₂](image)

- The yellow tipping index for CO-H₂ mixtures yield a division by zero, which in this case may represent that \( I_y \) tends to infinity. For that reason the mixtures CO-H₂ and pure CO and H₂ 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 CO₂ increases the yellow tipping index. This trend indicates that the addition of CO₂ to the fuel will reduce the yellow tipping propensity, when compared to natural gas.
- The addition of C₂H₆ and C₃H₈ to the fuel reduces the yellow tipping index. These fuels increase the propensity of the flame to produce yellow tips. Mixtures up to 8% C₂H₆ in CH₄ and up to 4.5% C₃H₈ 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)](image)
Using the CFD to CRN methodology, the NOx and CO emissions for the fuel mixtures presented above were compared to the emissions of pure natural gas at a fixed equivalence ratio of 0.87. That equivalence ratio corresponds to a reading of 3% oxygen in the exhaust gases on a dry basis.

- A mixture of 76% CH4 and 24% H2 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 NOx by 8% in comparison to pure natural gas and the production of CO is reduced by 6%.
- The interchangeable mixture of 94% CH4 and 6% C2H6 increases the concentration of NOx by only 2% and CO by 3%.
- The dilution of natural gas with a small amount of CO2 increases the production of CO by 3% and slightly reduces (2%) the concentration of NOx.
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:

\[
\begin{align*}
\text{N}_2 + \text{O} & \rightarrow \text{NO} + \text{N} \\
\text{N} + \text{O}_2 & \rightarrow \text{NO} + \text{O} \\
\text{N} + \text{OH} & \rightarrow \text{NO} + \text{H}
\end{align*}
\]

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 [4].

3. Prompt NOx - This third source is attributed to the reaction of atmospheric nitrogen, N₂, with radicals such as C, CH, and CH₂ 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), H₂CN (dihydrogen cyanide) and CN⁻ (cyano radical) which can oxidize to NO [4]. 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 N₂, in particular by:

\[
\text{CH} + \text{N}_2 \rightarrow \text{HCN} + \text{N}
\]

4. 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 [5].

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.

\[
\begin{align*}
O + N₂ + M & \leftrightarrow N₂O + M \\
N₂O + H & \leftrightarrow NO + NH \\
O + N₂O & \leftrightarrow NO + NO
\end{align*}
\]
7. References


