GAS TURBINES: EMISSIONS, COMBUSTION AND FUELS

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Abstract

Pipeline natural gas, while dominantly composed of methane, also contains various amounts of diluents, hydrogen, and hydrocarbons. The objective of this report is to describe how variations in fuel composition influence gas turbine emissions, operability, and operational range (turndown). A key point of this report is that these fuel composition sensitivities are not described by a single parameter, such as Wobbe index, but by different parameters depending upon the specific issue. For example, the autoignition time is an important parameter influencing autoignition risk, while flame speed has important influences on combustion instability and blowoff risk. This report explains these sensitivities, as well as approaches for identifying and mitigating operational risk.

1 – Introduction

Fuel composition influences gas turbine emissions, operability, and operational range (turndown). Some of these issues are well understood and utilize well developed engineering knowledge, such as required line or orifice sizes needed to pass a given fuel flowrate in order to supply the combustor with a given heating rate. There are a number of other issues, however, which are substantially less well understood, which involve complex interactions between fundamental combustion phenomena and fluid mechanics. Relatedly, there are a number of operability issues related to operating the combustor in a safe, efficient, and reliable manner. This includes ensuring the combustor reliably holds the flame so that it neither flashes back nor blows out, and burns the fuel in a "quiet," steady fashion. While the Wobbe Index and modified Wobbe Index are standard fuel properties which are used to capture certain fuel composition influences, they really do not describe anything beyond the fuel heating value, and do not describe the different kinetic properties which influence operability and emissions. This paper presents a summary of these issues, with a more detailed treatment in PRCI report (1).

Fuel Composition Impacts on Gas Turbine Performance

This section reviews the Wobbe index, the influence of fuel composition on the Wobbe index, and the effect of variation in fuel composition on overall gas turbine performance. Subsequent sections will detail these effects at a more granular component level.

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In general, varying fuel composition can have impacts on gas turbine power output, and compressor stability. The Wobbe index is a standard quantity used to quantify heat content effects. While the Wobbe Index does not capture all aspects of fuel composition variability, it is important to have a basic understanding of its impact on gas turbine performance. The equation below defines the Wobbe Index (as provided by OEMs) as the ratio of the lower heating value (LHV) to the square root of the specific gravity (SG) of the fuel. In essence, the Wobbe index and modified Wobbe index measure the fuel heat content that is delivered *for a given pressure source and fuel delivery system*.

$$
WI = \frac{LHV}{\sqrt{SG}}\tag{1}
$$

Key Operability Issues

3.1 – Blowout

Blowout, also interchangeably referred to as blowoff, refers to when the flame becomes detached from the location where it is anchored and is physically "blown out" of the combustor. Blowout is often referred to as the "static stability" limit of the combustor. Blowout occurs when the time required for chemical reaction becomes longer than the combustion zone residence time. It is an issue because the chemical kinetic rates and flame propagation speeds vary widely with fuel composition. For example, many candidate fuels have similar heating values but also have chemical kinetic times that vary by an order of magnitude.

Blowout events can require a lengthy, and often expensive system shut down, purge cycle, and restart. Developing physics-based correlations of blowout behavior is complicated by lack of understanding of the detailed phenomenology of the blowout process, such as the dynamics of near blowout flames or the flame characteristics at the stabilization point. Several different theories or physical considerations have been used in past blowout correlation studies. As noted by Glassman (2) and Shanbogue *et al*. (3), these lead to similar correlations that relate the blowout limits to a Damköhler number, i.e., ratio of a residence and chemical kinetic time, *τres/τchem*.

$$
Da = \frac{\tau_{res}}{\tau_{chem}}\tag{2}
$$

The residence time is generally scaled as d/U_{ref} , where *d* and U_{ref} denote a characteristic length scale (e.g., a recirculation zone length) and velocity scale, respectively. While historical studies have utilized a range of empirically derived formulae for the kinetic time in the "loading parameter", modern workers have access to sophisticated kinetics software which allows one to make good inferences about fuel composition, pressure, preheat temperature, effects on kinetic rates, etc. For example, a common method of estimating chemical time scales is to use the following macro time-scale for a premixed flame.

$$
\tau_{chem} = \frac{\alpha}{S_L^2} \tag{3}
$$

where S_L and α denote the laminar flame speed and thermal diffusivity, respectively $(4, 5)$. Note that this is a different chemical time scale than the autoignition time that will be discussed later, which is controlled by different chemical reactions. Putting this together, the reactor based theory predicts that blowout limits should scale with the Damköhler number:

$$
Da = \frac{\tau_{res}}{\tau_{chem}} = \frac{S_L^2 d}{\alpha U_{ref}} \tag{4}
$$

3.2 – Flashback

The opposite problem to blowoff is *flashback*, where the flame physically propagates upstream of the region where it is supposed to anchor and into premixing passages that are not designed for high temperatures. Flashback is a serious safety risk because of overheat and subsequent failure of fuel nozzle components.

In swirling flows *four* different flashback mechanisms exist: *turbulent flame propagation in the core flow*, *flashback due to combustion instabilities*, *flashback in the boundary layer,* and *flashback in the core flow due to alteration of vortex breakdown dynamics* (6). The first three types can occur in swirling as well as non-swirling premix burners, whereas the fourth mechanism requires a swirling flow in the mixing zone. Fuel composition effects influence these mechanisms very differently. Hydrogen and hydrogen blends have a particularly high susceptibility to flashback, due to their high flame speeds and small quenching distances.

The fuel-sensitive parameter for both flashback and blowoff is the same, S_L^2/α . Clearly, the critical value of this parameter is different for these two phenomena, but the same calculations described in the blowoff section can provide insights into fuel effects for flashback and blowoff.

3.3 – Combustion Instabilities

Combustion instability refers to damaging oscillations in the combustor. They cause wear and damage to combustor components and can even lead to liberation of hardware into the gas path. Combustion instability conditions can be strongly influenced by the fuel composition. A necessary, but not sufficient, condition for an instability to occur is that the unsteady pressure and heat release oscillations must be in phase (or, more precisely, that their phase difference is less than 90°). Fuel composition variations affect combustion instabilities by altering this pressure-heat release phasing

Two mechanisms are known to be particularly significant in premixed systems: these are fuel/air ratio oscillations and vortex shedding. Fuel/air ratio oscillations and vortex shedding become important when the resulting heat release perturbation is in phase with the pressure fluctuation. This can be expressed by the following relationship:

$$
\tau_{conv} = kT \tag{5}
$$

where τ_{conv} refers to the time required for either the equivalence ratio perturbation or the vortex to convect from its point of formation to the "center of mass" of the flame, *T* refers to the acoustic period, and *k* is an integer constant whose value depends upon the combustion chamber acoustics $(7, 8)$. Variations in fuel composition influence this relationship, by changing the flame length and flame stabilization location. The effect on the convective time can be better understood from the following equation which expresses the convective time as the sum of the convective time in the premixer (τ_{pm}) and the convective time in the combustor (τ_{comb}) :

$$
\tau_{conv} = \tau_{pm} + \tau_{comb} \tag{6}
$$

$$
\tau_{conv} = \left[\frac{L_{pm}}{u_{pm}}\right] + \left[\frac{L_f}{\alpha u_{comb}}\right]
$$
\n(7)

where L_{pm} refers to the distance from the point of origin of the disturbance to the entrance to the combustor, u_{pm} refers to the mean convective velocity in the premixer, L_f refers to the distance the perturbation travels from the combustor entrance to the center of mass of the flame, and *u*_{comb} refers to the mean convective velocity in the combustor, which can be expressed as a fraction α of the velocity in the premixer.

While the basic idea is relatively straightforward, understanding combustion instability boundary sensitivities is actually much more complex. The reason for this stems from the fact that combustion instability boundaries exhibit a nonmonotonic dependence upon flame location. In other words, the same change in flame shape can cause combustion instabilities to be adversely impacted, positively impacted, or to have no impact. Quantitatively, this can be shown by noting that instability amplitudes will scale as $\cos(f_{\text{Conv}})$, where the cosine is an <u>oscillatory</u> function. This demonstrates that a change in τ_{conv} (or flame center of mass) is controlled by the instability frequency. Indeed, Santavicca has shown that the same change in fuel composition can increase or decrease instability amplitudes for combustors of different length and, therefore, instability frequency. For example, some measurements from a frame engine showed that a higher frequency, "hot tone" mode amplitude increased with ethane addition, while the lower frequency "cold tone" amplitude decreased. It is also controlled by the baseline convective time delay. This non-monotonic behavior is different from the other operability and emissions trends that will be discussed in this paper – for example, increasing hydrogen composition will always extend blowoff boundaries (although the quantitative effect will depend upon geometry and other conditions), or increasing propane composition will always decrease autoignition margin. No such definitive statements can be made for combustion instability boundaries.

3.4 – Autoignition

Autoignition refers to the ignition of the reactive mixture upstream of the combustion chamber. Similar to flashback, it results in chemical reactions and hot gases in premixing sections, but its physical mechanisms are completely different. Rather than the flame propagating upstream into the premixing section, autoignition involves spontaneous ignition of the mixture in the premixing section. Fuel composition directly affects the chemical kinetics of the mixture and its autoignition characteristics.

Some first insights into fuel composition influences on autoignition can be gained from tabulated "autoignition temperatures"; i.e., the temperature above which the mixture will spontaneously ignite, if given sufficient time. It is important to remember that the results shown in this section assume prevaporized fuel that is homogeneously mixed with air. In reality, condensation of higher hydrocarbons into liquid droplets that then lead to locally elevated concentrations can significantly shift autoignition boundaries. Typical results for T_{ign} of atmospheric pressure *n*-alkane mixtures are shown in [Figure 1](#page-4-0)¹, showing that $500K < T_{ign} < \sim 800K$. Methane (CH₄) has the highest autoignition temperature ($\sim 800K$), followed by ethane (C_2H_6) and then propane (C_3H_8) . This result follows from the fact that the larger molecules decompose into reactive fragments more easily than the smaller ones. Also plotted on the figure is the corresponding pressure ratio, for which an isentropic compression from standard temperature and pressure (STP) would lead to this same ignition temperature. For example, it shows that the methane/air blend would autoignite (given sufficient time) at a pressure ratio greater than 33 and a propane/air blend at a pressure ratio greater than 24.

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¹ It is important to recognize, however, that such results reflect not only fundamental properties of the mixture, but also the device in which the measurements were obtained

Figure 1 - Dependence of autoignition temperature upon carbon chain length for normal alkanes, CNH2N+2, at atmospheric pressure (9). Also plotted on the figure is the corresponding pressure ratio, for which an isentropic compression from standard temperature and pressure (STP) would lead to this same ignition temperature.

As shown by these values, in many cases of interest to the high pressure ratio gas turbines used for mechanical drive applications, the compressor discharge temperature can exceed the ignition temperature. In this case, the key issue is not *whether* the mixture will autoignite, but *how long it will take*. In other words, is the time required for ignition (because the ignition process does not happen instantaneously) greater or less than the premixer residence time. As such, we consider "how long it takes", denoted as the "autoignition time" next.

Typical data illustrating autoignition times are plotted in [Figure 2](#page-5-0) for *n*-alkanes mixtures, showing the exponential decrease in ignition times with increase in temperature for the methane and propane blends. The larger *n*-alkane fuels exhibit a non-monotonic variation of τ_{ign} in the 700-900K "negative-temperature coefficient" (NTC) region. These data also show the much shorter ignition times of propane than methane, as well as the even shorter ignition times of the larger *n*-alkanes, a result that could be anticipated from the earlier discussion – in other words, adding higher hydrocarbons increases autoignition risk. While small fractions of blended higher hydrocarbons will only moderately increase autoignition risk if the mixtures are homogeneous, problems in practice are encountered when the higher hydrocarbons condense in the fuel preparation section and then revaporize, but do not have time to fully mix and thus form a pocket of locally elevated concentrated zone that acts as an autoignition initiation site. Finally, data generally show that τ_{ign} varies with pressure as p^{-1} for these *n*-alkane fuels.

Figure 2 - Compilation of ignition time delay data for *n*-alkane/air mixtures ranging from methane to *n*-tetradecane; reproduced from Lieuwen (9) for pressure of 12 atm, using a pressure correction with $n = 1.38$.

Emissions Issues

This section overviews emissions issues and the effects of fuel composition on emissions. The reader is also referred to Lieuwen's book "Gas Turbine Emissions" for in depth treatment of the details of the different emissions issues for various combustor architectures.

$4.1 - NO_x$

 NO_x refers to emissions of NO and NO₂. NO_x primarily originates from NO produced in the combustor which then reacts in the atmosphere to form these other oxides of nitrogen. NO can originate from two places – fuel bound N_2 , which we will assume is negligible in this report (note we are not assuming that there is negligible N_2 in the fuel, but that the N is not part of the fuel molecular structure), or from the N_2 which is present in the air. NO is formed by several reaction mechanisms both within the flame zone itself and post-flame, often referred to as "flame NO_x " and "thermal NO_x ", respectively. There are several mechanisms through which NO_x is produced in the flame itself – these include the Fenimore (or Prompt) NO_x mechanism, N₂O mechanism, NNH mechanism, etc. "Thermal NO_x", sometimes called "Zeldovich NO_x ", arises from reactions of $N₂$ and $O₂$ at high temperatures. For this reason, it continues to be formed after the flame as long as the product gas temperature is sufficiently high. In contrast, "flame NO_x" occurs through reactions of various fuel and oxidizer intermediates which are only really present in the reaction zone. Following Bowman, an approximate formula for thermal NO production is $_{(10)}$:

$$
[NO] \propto [O][N_2]e^{-38,379/T}\tau_{res}
$$
 (8)

This formula and [Figure 3](#page-6-0) show the strong temperature sensitivity of NO formation rates, as well as their direct proportionality to the residence time that the combustion products remain at high temperatures, before cooling as they expand through the turbine section. This equation shows the three principle "knobs" which effect thermal $NO_x - [O]$ atom concentration, temperature, and residence time. To illustrate, Figure [3](#page-6-0) shows the calculated dependence of NO upon combustor residence time (τ_{res}) at several temperatures.

It shows the sharp rise near $\tau_{res} \sim 0$, which is NO produced by flame NO_x and accelerated thermal NO coming from super-equilibrium [O], followed by the linear rise in NO levels, which is thermal NO_x.

Figure 3 - Dependence of calculated NO emissions upon residence time at different flame temperatures. A typical gas turbine combustor residence time is about 25 ms. Calculated using CHEMKIN with the GRI-Mech 3.0 kinetics model at 15 atm pressure and 635K initial temperature (roughly equating to isentropic compression from STP to 15 atm), taking the time origin at the point of maximum heat release rate.

This figure shows that the NO formed within the flame accounts for a small fraction of the total NO production, except for low flame temperatures and/or low residence time. This is an important point, as the NO formation mechanism post-flame for premixed and non-premixed combustors is the same. However, the radical concentrations and reaction details within the two kinds of flame are quite different and, consequently, we can expect significant differences in flame NO_x formation. In other words, for combustion systems with little thermal NO_x emissions, which would be the case for low NO emitting systems (figure above suggestions NO<~5 ppm), we can expect fuel effects. At higher NO levels, NO is controlled by thermal processes and fuel composition effects will be minimal.

4.2 – Carbon Monoxide (CO) Emissions

CO emissions occur in hydrocarbon flames because not all of the fuel is oxidized to $CO₂$. To illustrate several basic points about CO emissions, a comparable calculation of CO levels through a laminar flame is displayed in [Figure 4.](#page-7-0) As shown in the figure, CO exhibits super-equilibrium concentrations within the flame (during decomposition of hydrocarbon fuels), and is oxidized subsequently in the post-flame zone at rates that depend exponentially on temperature. For these reasons, CO levels lie *above* their equilibrium values at a given product temperature (opposite that of NO). Combustor and transition piece duct sizing is often driven by needs to ensure sufficient time for CO oxidation at partial load, where temperatures are low and relaxation times slow. High CO emissions occur when there is insufficient time for these high CO levels to fully oxidize to $CO₂$.

Figure 4 - Dependence of calculated CO emissions upon residence time at different flame temperatures. A typical gas turbine combustor residence time is about 25 ms. Calculated using CHEMKIN with the GRI-Mech 3.0 kinetics model at 15 atm pressure and 635K initial temperature (roughly equating to isentropic compression from STP to 15 atm), taking the time origin at the point of maximum heat release rate.

Flores *et al.* (11) studied fuel composition effects on natural gas combustors for four fuel blends: 100% natural gas, 85% natural gas/15% ethane, 80% natural gas/20 % propane, and 100% propane. Their tests were conducted at atmospheric pressure for inlet temperatures up to 800 K. For each of the latter three cases, they experienced a reduction in CO production over the pure natural gas case. Unfortunately, they do not present absolute numbers. The second and fourth cases saw a reduction of approximately 45% while the third case only saw a reduction of about 15%. It is worth noting that the flame temperature did rise through these cases and may have contributed to accelerated CO oxidation. As with their NO_x results, the authors did note that the amount of fuel through the pilot fuel circuit did impact CO emissions. By increasing the pilot flow, lean blow off (LBO) was reduced at the expense of significantly higher CO at the lower LBO limits, but for the test conditions of interest the CO emissions were largely unaffected by the amount of fuel through the pilot circuit. In the fully premixed test cases, the addition of higher hydrocarbons significantly reduced CO emissions near LBO, probably by extending blowoff limits. At an adiabatic flame temperature of 1610 K, the natural gas case produced 12ppm CO while the other 3 cases all produced approximately 5 ppm. At higher temperature conditions away from blowoff from $1650 K - 1850 K$ range, all fuel blends produced essentially the same amount of CO. Above 1850 K, the pure propane case first begins to deviate by producing a larger amount of CO, followed by the 80% natural gas/20% propane blend at 1950 K. In their follow-up study (12), the authors noted that their models predicted high CO for the ethane case while their data shows slightly lower CO. The model and data both agreed that CO should increase for the case where propane was added to the fuel. They attribute this difference to experimental error and scatter in the data that used to build their model. They still conclude that higher hydrocarbon content leads to higher CO emissions. This trend would be partially explained by equilibrium effectshigher CO₂ concentrations occur with higher hydrocarbon fuels which partially dissociates to CO. For example, an equilibrium calculation shows equilibrium CO levels rising from about 15 ppm to 17 ppm for pure methane to pure propane fuels².

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 2 Calculated at 33 bar, 815 K inlet temperature, and constant 1900 K temperature.

4.3 – Other Emissions

Particulates/Soot

Lean, premixed flames emit near zero levels of particulates. As such, particulates are not a concern for DLN, regardless of fuel composition. In contrast, soot is produced by non-premixed flames, which could occur in non-premixed pilots of premixed systems, or conventional combustion systems.

Sooting tendencies of a premixed fuel/oxidizer mixture is often expressed in term of the critical equivalence ratio ϕ_c , at which a flame begins to exhibit visual soot. A standard definition for this point is where the tip of the flame becomes yellow due to radiation from the hot soot particles: the higher the ϕ_c the lower the tendency to soot.

In premixed flames at fixed flame temperature, fuels with bigger molecular size and tighter structure generally show increasing soot tendency. A frequent summary used to describe fuels' sooting tendencies for premixed flames is Aromatics > Alkanes > Alkenes > Alkynes (see Street and Thomas (13)). However, this should be considered a simplification of the actual situation (14), since the early results of Street and Thomas were obtained without any control on flame temperature.

Calcote and Manos (14) developed correlations for a wide variety of fuels based on a "threshold soot index", TSI, by which it is possible to compare experimental results obtained with different apparatuses and in different conditions from both diffusion and premixed flames. This index varies between 0 corresponding to ethane (low sooting tendency) and 100 corresponding to naphthalene (high sooting tendency). The TSI for premixed flames is defined as $TSI = a - b\phi_c$ where the apparatus dependent *a* and *b* constants were determined by calibration. The TSI has proven to correlate well the sooting characteristic of different fuels as well as multicomponent fuels in diffusion flames (15) .

Unburned Hydrocarbons

Generally elevated levels of unburned hydrocarbons occur under conditions near lean blowoff. As this is also the conditions where elevated CO levels occur, insight into conditions where elevated unburned hydrocarbons will occur can be deduced from the near-LBO, elevated CO discussions descried in the prior section.

5 – Conclusions

Fuel composition influences gas turbine emissions, operability, and operational range (turndown). These fuel composition sensitivities are not described by a single parameter, such as Wobbe index, but by different parameters depending upon the specific issue. Probably the largest influence of higher hydrocarbons in the fuel is on autoignition risk in high pressure ratio DLN aeroderivatives. Higher hydrocarbons can also influence combustion instability boundaries, but the effects are not large, although an effect will be noticed for engines operating with little combustion instability margin. For fuels with elevated hydrogen levels, the largest influence will be on reduced flashback margin, modified combustion instability boundaries, and reduced blowoff risk. The effect on NO_x emissions somewhat depends upon the nominal NO levels from the engine. For ultra-low NO_x engines (say <5 ppm @15%02), some effects may be noted as higher hydrocarbons and hydrogen in natural gas influence certain flame-generated NO_x mechanisms. For systems operating with "higher" NO_x (say, >15 ppm@15%O₂), NO_x production rates are dominated by temperature and, therefore fuel composition effects are much more limited, assuming the engine operates at constant firing temperature. CO and UHC emissions generally are elevated near blowoff boundaries and, therefore, should follow the blowoff sensitivities noted above.

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