Cool Flames – Perspectives on their Importance in Combustion Systems

Overview: Cool flames are a very unique chemical phenomenon that can occur when many hydrocarbons and related fuels are heated in the presence of air. Cool flames are especially unique in that their chemical reaction rate first increases and then decreases with increasing temperature; this is somewhat counterintuitive and means that these flames get weaker (their heat release decreases), rather than stronger, as temperature increases over a range of temperatures, typically ~700-850K (dependent on the nature of the fuel and local conditions, i.e., pressure). As the temperature increases further, however, these relatively 'weak' flames eventually transition to hot ignition! In effect, cool flames are a precursor to hot ignition. Similarly, if a high temperature flame extinguishes, as the fuel-air mixture cools, it is possible for cool flames to occur and for the mixture to reignite! This has not been observed in terrestrial studies; it was observed for the first time in the NASA CFI (Cool Flame Investigation) and has obvious fire safety implications. The name 'cool flames' refers to the fact that the heat released from these chemical reactions is relatively small. As a result, cool flame product temperatures are relatively low and do not produce large amounts of radical chemical species and ionized species that are responsible for the familiar bright light seen in conventional flames. That is why cool flames are difficult to observe experimentally.

Historically, cool flames were observed in the laboratory for many years yet gained widespread interest when it was recognized that cool flames can lead to knock in spark-ignition (SI) engines. As the piston motion in the cylinder and flame propagation compress the fuel-air mixture in an SI engine, unburned fuel-air mixture temperatures increase and cool flames can spontaneously occur, causing the remaining unburned fuel-air to ignite prematurely, leading to uncontrolled combustion in the cylinder, i.e., "knock", which can damage the engine and limit engine efficiency. As a result, higher Octane Number fuels have been developed, where the Octane Number (ON) of a fuel (e.g., 87) refers to its ability to resist cool flames and engine knock. In diesel, compression ignition (CI) engines, cool flames are also responsible for variations in Cetane Number (CN), which is a measure of how long it takes for the fuel to begin to ignite in a compression engine. Generally speaking, fuels with considerable amounts of cool flame behavior are easier to ignite than fuels with negligible cool flame behavior. In addition to engine applications, including advanced engine development such as Homogeneous Charge Compression Ignition Engines (HCCI), the low temperature heat release from cool flames has recently received attention for application to diesel fuel reforming[1] and fuel reforming for fuel cell applications[2] (Naidja et al., 2003).

Types of Reactor Studies

Continuously Stirred Tank Reactors: Historically, cool flames have been studied in two types of idealized laboratory experiments. The first reaction class consists of continuously stirred tank

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[1] L. Hartmann, K. Lucka and H. Köhne, "Mixture preparation by cool flames for diesel-reforming technologies," J. Power Sources Volume 118, Issues 1–2, 2003

[2] Naidja, A., Krishna, C., Butcher, T., Mahajan, D. (2003) "Cool flame partial oxidation and its role in combustion and reforming of fuels for fuel cell systems," Progress in Energy and Combustion Science 29 155-191.

reactors (CSTR's) where the reaction temperature is held constant within the cool flame region, with heat produced during the cool flames being removed from the reactor via heat transfer to the reactor walls to avoid more violent, rapid ignition characteristic of higher temperatures (i.e., 1000K and higher). In such experiments, fresh, unburned fuel/oxidizer mixtures flow continuously into the reactor and products flow out of the reactor. The temperature within the reactor is held fixed by operating the experiment in an external oven that can heat or cool the reactor via heat transfer. The use of dilute fuel/oxidizer mixtures is also a common practice to maintain a uniform reaction temperature. The overall rate of reaction in this type of reactor varies as the fixed reactor temperature is changed; a typical plot showing the intensity of the reaction as indicated by the amount of fuel consumed vs. temperature is shown in Figure 1, where the fuel is *n*-heptane.

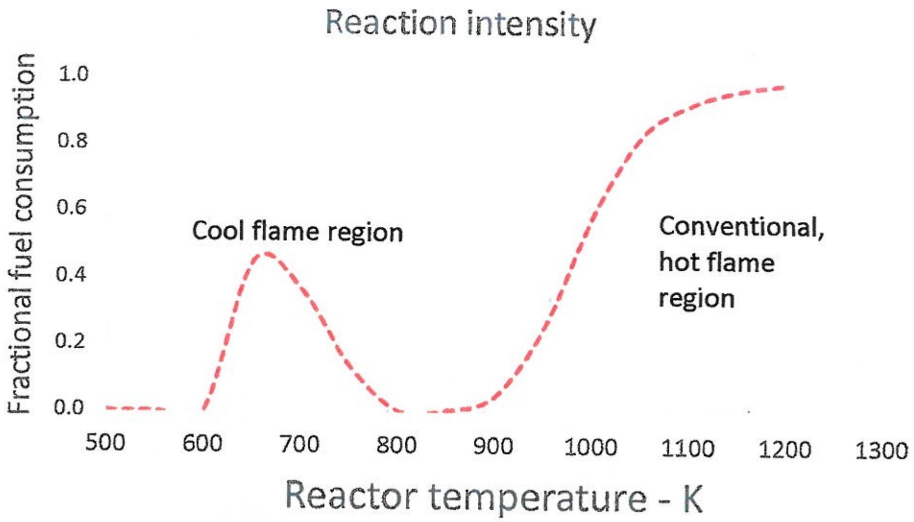

Figure 1: Reactivity of a dilute n-heptane/oxygen mixture over a range of reaction temperatures in a stirred reactor experiment at 13.5 bar pressure. Reactivity is defined as the fraction of fuel consumed in this reactor when the residence time in the stirred reactor is 0.02 seconds.

As shown, the reactivity of this fuel has a local maximum at about 700K and then a second, larger rate of reaction when the temperature reaches or exceeds 1000K. While this is a rather "academic" experiment, as most practical experiments and engines are not operated at constant reactor temperature, it does illustrate the point that cool flames occur at low temperature, for this fuel at about 600K, reach a maximum at about 700K, and then disappear as the temperature reaches about 800K prior to the onset of hot ignition at higher temperatures.

Strictly speaking, cool flames are a result of a very particular family of exothermic reactions that occur in hydrocarbon fuels over a limited range of operating conditions. The decrease in rate of reaction and heat release with increasing temperature (here towards the 800K cool flame extinction temperature) is counterintuitive. These flames weaken as temperatures increase and has led to the term "negative temperature coefficient" (NTC) of the overall reaction over this range of temperatures. The intensity of cool flames generally increases with increasing pressures and fuel/oxidizer ratio.

Rapid Compression Machines and Shock Tubes: The second family of common laboratory cool flame experiments are non-isothermal studies performed in rapid compression machines (RCMs) and low temperature shock tube experiments where the reactive mixture is initially compressed rapidly to temperatures and pressures representative of engine conditions where cool flames occur. After an initial ignition delay period of time, the cool flame occurs, heating the fuel/oxidizer mixture to the point where increasing temperature quenches the cool flame reaction; this is also referred to as 'self-arresting' as the heat release and associated temperature rise from the reaction essentially quenches it. After an often extended second ignition delay period, however, another rapid reaction can occur and transition to full ignition that occurs at high temperatures with complete fuel consumption. This scenario in which cool flames transition to hot ignitions is called "two-stage" ignition. In this case, heat release during the cool flame advances the time of final ignition, relative to the ignition delay of fuels that exhibit little or no cool flame reaction. In this important sense, the cool flame "sensitizes" the fuel/oxidizer mixture by increasing the temperature of the reactive mixture while only consuming a small fraction of the fuel at the lower temperatures.

Figure 2 shows a representative two-stage ignition process for a high pressure (13.5 bar) mixture of *n*-heptane in air, where the temperature of the mixture relative to its initial value of 750K is plotted as a function of time. At first, the mixture reacts very slowly with negligible temperature increase; after a time delay of about 1.0 ms, the first stage ignition (i.e., the cool flame) rapidly raises the gas temperature to about 900K, which represents the end of the cool flame range at this pressure, as shown in Fig. 1. Following the cool flame, the overall rate of reaction again is very slow, rising gradually until the temperature reaches about 1000K, where the rate of reaction rapidly increases again, and all of the remaining fuel is burned as the flame rapidly ignites. In this case, the total ignition delay time is about 2.3 seconds.

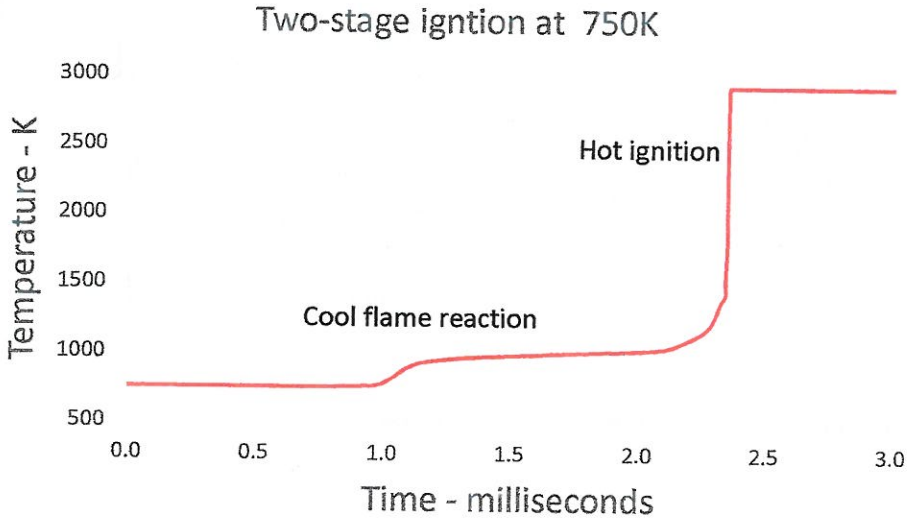

Figure 2. Temperature vs. time for n-heptane/air at 13.5 pressure

There are many intricate interactions made possible by varying the initial temperatures in RCM or low temperature shock tube experiments within the cool flame range shown in Fig. 1. If the compressed gas temperature is at the lower end of the cool flame interval, then substantial reaction and heat release can occur before the temperature reaches the high end of the cool flame temperature range where the cool flame extinguishes. In contrast, if the initial compressed gas temperature is at the high end of the cool flame interval (e.g., 850K), little cool flame heat release occurs before it extinguishes. Regardless of the amount of cool flame heat release, once the temperature has reached the high end of the cool flame range, subsequent slow reaction occurs until the temperature reaches a hot ignition temperature of about 1000K.

The same sequence of reactivity that is seen in RCM and low temperature shock tube experiments occurs in both SI and CI engines, where the reactive fuel/oxidizer mixtures are inducted into the engine combustion chamber at relatively low temperatures and pressures with minimal initial reactivity. Piston motion and flame propagation in SI engines then compress the fuel/air mixtures in these engines, adiabatically heating the unburned fuel/air mixture until it reaches about 600K, where cool flame reactions can begin. Depending on the fuel structure, different fuels then experience different amounts of cool flame oxidation. Some fuels have little or no cool flame reactivity and continue to be heated relatively slowly by adiabatic compression, eventually igniting when the temperature reaches the hot ignition temperature of about 1000K. In contrast, fuels that have substantial cool flame reactivity produce early heat release, and this additional low temperature heat release leads to earlier ignition and combustion in the engine. In SI engines, premature ignition of unburned fuel and air produces engine knock, as noted above, while earlier ignition in Diesel engines is a generally desirable feature. Tendency to knock in SI engines is expressed by its Octane Number (ON), where a high ON indicates better knock resistance with low amounts of cool flame reactivity. In a Diesel engine, the ignition delay time is indicated by the Cetane Number (CN), where a high CN indicates a fuel with a short ignition delay period and large amounts of cool flame reactivity. In fuel safety studies, fuels with more cool flame behavior ignite more easily than fuels with less such reactivity and are therefore more likely to ignite and burn in accident scenarios.

Representative experimental measurements and computed ignition delay times for a variety of fuels is shown in Figure 3. In this plot, the y-axis is time and the x-axis is inverse temperature, such that lower temperatures are towards the right side of the x-axis. The *n*-heptane and *n*-decane have very low ON values (noting that *n*-heptane is the zero-point of the octane scale and the ON for *n*-decane is less than zero) and high CN values (56 and 76, respectively); as such, they both have substantial cool flame behavior. In contrast, *iso*-octane has an ON = 100 and CN = 12 and is used as a reference standard to benchmark the tendency of fuels to resist cool flame behavior. *Iso*-cetane, also named heptamethyl nonane (HMN) has a very low CN = 15 and similar to iso-octane has very little cool flame behavior. These trends can be explained in terms of the dependence of cool flame behavior on the molecular structure of the fuel molecules. As shown in Fig. 3, the high temperature ignition rates of all four fuels are virtually identical at temperatures above 1000K initial temperature, and the considerable differences between the ignition delay times and ON and CN ratings of these fuels are all due to kinetic factors at temperatures below 900K, where the relative propensity of these fuels to produce cool flames are dramatically different.

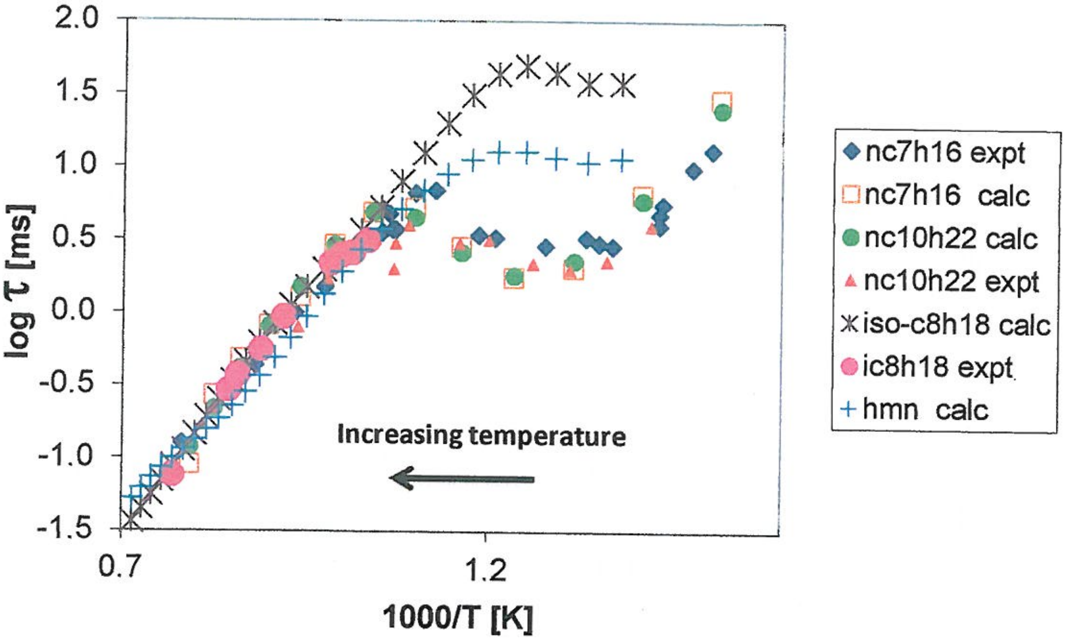

Figure 3. Variations in ignition delay times for n-heptane, n-decane, iso-octane, and iso-cetane. All results are at 13.5 bar pressure and for stoichiometric ratios of fuel/O_2.

Effects of Fuel Structure on Low Temperature Cool Flame Reactivity: As shown in Figure 3, the fuel structure significantly affects the amount of low temperature or cool flame reactivity. This has been understood empirically since the aerial combat days of World War I, in which airplanes with SI engines with low ON fuels performed poorly because they could not be operated at high compression ratios; high engine compression ratios produce greater engine performance and efficiency but also lead to engine knock with lower ON fuels. Fuel research beginning in the 1920s established relative knocking behavior of many types of hydrocarbon fuels and a phenomenological understanding of how fuel structure is related to ON values. In addition, the same research efforts discovered many fuel additives with significant anti-knock capabilities, including tetra-ethyl lead (TEL) and others. However, the fundamental chemistry of engine knock, cool flame behavior, and ON and CN values has been established only in the past 25 years due to the use of computer simulations of complex cool flame chemical kinetics, but many details still remain uncertain. It is however understood that long-chain, saturated hydrocarbon fuels, especially the *n*-alkanes from *n*-heptane to *n*–hexadecane (illustrated in Figure 4), exhibit the greatest amounts of cool flame reactivity, which correlates well with the high CN values and low ON values of these fuels.

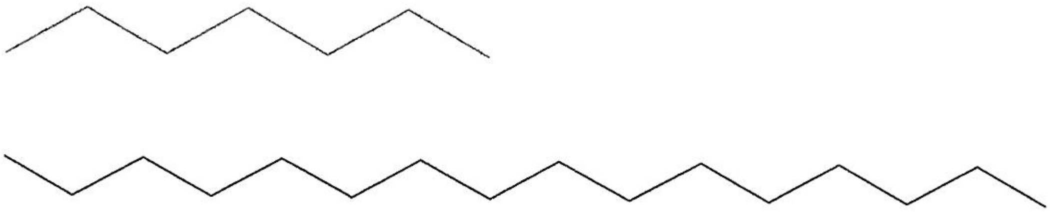

Figure 4. Structures of high CN, low ON straight-chain n-alkane fuels: n-heptane and n-hexadecane.

In contrast, branched alkane fuels with large amounts of side methyl groups such as *iso*-octane, 2,2,4,4,6,8,8-heptamethyl nonane (HMN), and 2,2,4,6,6-pentamethyl heptane, shown in Figure 5, have very little low temperature or cool flame reactivity and therefore have high ON and low CN values.

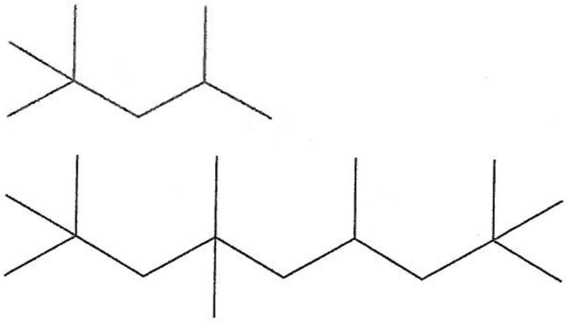

Figure 5. Structures of highly methyl branched iso-alkane fuels: iso-octane and iso-cetane.

<u>Basic Hydrocarbon Oxidation Chemistry</u>: Hydrocarbon oxidation consists of the sequential conversion of the C and H atoms from the original fuel into the final products of CO_2 and H_2O. The fuel is essentially disassembled, one atom at a time, via a sequence of elementary chemical reactions. The elementary chemical reactions that occur can be different as the combustion temperature and pressure change, but the ultimate products are carbon dioxide and water. The difference in chemical potential energy between the fuel and products determines the total heat released by the combustion process, but the actual reaction pathways taken by the chemical reaction determines the overall rate of oxidation and can vary a great deal. *When combustion occurs in the cool flame temperature and pressure regimes, a unique family of reactions dominates the process of fuel oxidation and is responsible for the unusual properties of cool flames.* A knowledge of these cool flame reaction pathways is required to understand cool flame phenomena.

The important fuel oxidation processes begin by removing the first H atom from the fuel species, most often by abstraction of an individual H atom by a radical species such as OH or H. It is conventional to symbolize a fuel molecule by the formula RH (where R is the fuel radical) and a highly reactive radical species as X, so the first H atom abstraction (removal of a hydrogen atom from the fuel molecule) reaction can be written as:

$$RH + X = HX + R \qquad (1)$$

The subsequent fate of the fuel radical 'R' determines whether or not a cool flame is likely. At high temperatures above 1000K, such as in conventional flames or explosions, the radical R decomposes to produce smaller hydrocarbon fragments that quickly react and form final products. However, at relatively low cool flame temperatures, the radical R instead preferentially combines with molecular oxygen O_2 to produce a larger radical species

$$R + O_2 = RO_2 \qquad (2)$$

RO_2, called an "alkylperoxy" radical. Without the RO_2 radical species, cool flames are not possible, but even when RO_2 is formed, there is a long and winding road to travel in order to complete a cool flame.

Firstly, the R radicals are formed preferentially at sites in the fuel where the H atoms are most weakly bonded to the C atom skeleton of the fuel molecule. There are multiple types of C–H bonds in common hydrocarbon fuels, with the "primary" C-H bonds being the strongest and thus most difficult to abstract (break off), "secondary" C-H bonds are rather easily abstracted since they are weaker C-H bonds, and very weak "tertiary" C-H bonds are the easiest to break. In the n-alkanes shown in Fig. 4, all of the C-H bonds in the "backbone" of the molecule consist of rather weakly bonded secondary C-H bonds, except for the 3 C-H bonds at each end of the carbon chain being tightly held in primary bonds. In the branched fuels shown in Fig. 5, there are much higher fractions of "difficult-to-break" primary C-H bonds. This simple difference between the straight-chain n-alkane structure and heavily branched fuels with H atoms that are much more difficult to abstract plays the biggest single role in determining the different rates of cool flame chemistry and differences in resulting ON and CN values for these fuels.

After formation of RO_2 radicals, this radical then preferentially abstracts another H atom, but this time the abstraction is mainly from sites within the RO_2 radical structure. The key issue is the availability of H atoms within the radical that can easily be abstracted from nearby weak secondary and tertiary sites. Lots of available H atoms bound at weak sites produce high rates of internal H atom transfers within the radical species, while few easily abstracted H atoms lead to slower rates of H atom transfer. The products of this internal H atom transfer are called 'QOOH' species.

At this point, cool flames occur when the remaining available reactive site in the QOOH species is filled by addition of another, second molecular O_2 species to make a larger radical O_2QOOH, followed by its decomposition into multiple radical species, including highly reactive OH radicals. These multiple OH radicals then react with more fuel, and each cycle of the chain consists of: (1) abstraction from the fuel, (2) addition to produce RO_2, (3) isomerization of RO_2 to produce QOOH, (4) addition of another O_2 to QOOH, and (5) decomposition of these O_2QOOH species to produce more OH to continue and accelerate the overall rate of fuel consumption and heat release.

As noted above, the cool flame sequence of reactions starts by the addition reaction (2) of O_2 to the fuel radical R, so interruption of the progress of reaction (2) will suppress the cool flame. This interruption is made when temperature increases to the point where the RO_2 begins to decompose back into R and O_2 and the bond energies between R and O_2 are such that these bonds break at temperatures around 800 – 850K, which is why the cool flame regime ends at these same temperatures, as seen in Fig. 1. *The steady increase in decomposition rates of RO_2 radicals as temperature increases over this temperature range is the simple explanation for the NTC behavior that is characteristic of cool flame behavior.*

Unique Opportunity to Study Cool Flames at Microgravity: The CFI droplet combustion studies represent a unique opportunity to study fuel ignition and cool flame combustion under a novel set of conditions that have *never been seen before*. In every class of experiment that has ever been used to study cool flames and NTC behavior, including internal combustion engines, the reacting system enters the cool flame regime from lower temperatures, so the onset of the cool flame and its eventual quenching occurs as temperature increases. The formation of a cool flame by reducing temperature from higher levels is completely unexpected and has never been studied before. In the CFI experiments, the reacting system is cooling as the droplet flame is being quenched due to radiative cooling or fuel consumption, and the system enters the cool flame regime from higher temperatures. The simplest question that should be addressed is whether cool flames resulting from higher temperature conditions behave the same way as cool flames coming from lower temperatures? Many other practical and theoretical questions can also be addressed in the CFI experiments and may lead to completely new hydrocarbon oxidation phenomena.