Topical: Low and Intermediate Temperature Chemistry in Cool and Warm Flames

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Introduction

Low and intermediate temperature combustion, defined by oxidative chemistry occurring at temperatures between approximately 600-800 K (low temperature chemistry, LTC) and 800-1100 K (intermediate temperature chemistry, ITC), respectively, are distinctively different regimes compared to high temperature chemistry (HTC). HTC occurs at over approximately 1100 K and is readily observed in fires, engines, and other combustion events. These different chemistry regimes originate from different chain-branching pathways and produce flames which are characterized as cool flames (LTC), warm flames (ITC), and hot flames (HTC) (Ju et al., 2019; Ju, 2021). Early observations of cool flames were made in the 1800’s when faintly luminescent flames were observed upon the heating of fuel-air mixtures. Since that time, numerous avenues of investigation have been undertaken to characterize and harness LTC and ITC.

Noteworthy differences in fundamental combustion properties have been measured between cool, warm, and hot flames. Among these are ignition reactivity, flame propagation speeds, Markstein length, and products of combustion. Ignition reactivity, which determines the timing and location of auto-ignition in a fuel-oxidizer mixture, differs between LTC and HTC reaction pathways, with cool flames igniting in lean mixtures and stabilizing in rich mixtures, while hot flames ignite and burn near stoichiometric conditions (Borghesi and Mastorakos, 2016). Such dependence of chemical reactivity can substantially affect the subsequent combustion mode evolution in practical stratified mixtures (Tao et al, 2020). Flame propagation speeds, which influence flame spread across combustion chambers and therefore combustion efficiency within combustor cycle times, have been shown to be significantly lower than hot flame propagation speeds for the same fuel-oxidizer mixtures and conditions (Hajilou et al., 2019). The effect of local flow conditions, namely flame stretch, on characteristics such as flame propagation speed differs between cool and hot flames as well (Yang and Zhao, 2021). This different stretch dependence can significantly affect flame dynamics and evolution under practical conditions such as turbulence in engines. The products of LTC, ITC, and HTC and their corresponding flames reflect progressively complete combustion of fuel. Cool flame products include significant amounts of unburned fuel, oxidizer, and quasi-stable species such as formaldehyde, while warm flames generate increasing amounts of oxidized products such as carbon monoxide, carbon dioxide, and water, and hot flames generated from stoichiometric mixtures generate predominantly oxidized products of carbon dioxide and water (Zhang and Ju, 2020). The generation of elevated temperatures and incomplete combustion products of LTC and ITC therefore have ample potential to lead to HTC via regime transition and induce combustion chemistry in unreacted mixtures. As one example, LTC has been shown to lead to first-stage ignition and precede second-stage, high-temperature combustion in fuel sprays under engine relevant conditions (Skeen et al., 2015). The products of first-stage ignition, while far lower in temperature than those of second-stage ignition, are sufficiently elevated and reactive in composition to reduce the ignition delay time of subsequent fuel injections.

Detailed studies of stable cool flames in multi-phase configurations, such as sprays, similar to those that have been extensively carried out for hot flames have been largely limited due to the difficulties in creating cool flames in easily interpreted experimental configurations. The difficulties are exacerbated by the low levels of heat release associated with the partial oxidation that occurs under cool flame burning, as well as flame instabilities and the propensity of cool flame burning to transition to hot flames. These effects severely limit the study of cool flame burning in multi-phase configurations. A major distinction of combustion in microgravity versus combustion in terrestrial environments is that buoyancy and natural convection are suppressed in microgravity
whereas buoyancy flows in terrestrial laboratories can be on the order of 1 m/s for even a candle-sized flame. These flows destabilize weak or low-stretch flames and prevent attainment of very low stretch or weak flames in relevant terrestrial environments. In the absence of buoyancy-induced effects, the reactive-diffusive structures of premixed and non-premixed flames can be studied under more simply modeled conditions, and cool flames can be sustained. This has afforded a number of novel and insightful observations into cool flames and LTC. These observations have included the production of auto-ignited, spherically-symmetrically expanding premixed cool flames, leading to measurements of cool flame propagation speeds (Foster and Pearlman, 2007). Additionally, sustained non-premixed cool flames have been observed in experiments aboard the International Space Station (ISS) upon extinction of hot flames burning around fuel droplets (Nayagam et al., 2012). In fact, cool flame-supported droplet combustion, in which hot flame extinction leads to sustained cool flame burning which, in turn, sustains droplet combustion, has only been shown to be possible in microgravity. Such long-duration (e.g., tens of seconds) cool flame experiments in multiphase configurations allow for understanding of the role of key phenomena which are difficult or impossible to isolate and assess at terrestrial conditions, such as the impact of preferential vaporization on cool flame dynamics for multicomponent fuels.

Overview of Research Needs

Identified research needs include extensive future investigations into LTC and ITC under microgravity conditions for insights into these combustion regimes that will have importance and impacts in both space and terrestrial systems. Specific recommended avenues of investigation include:

- Near-limit cool flames, where competition between LTC and thermal pyrolysis chemistry exist, should be investigated. At a lower limit of ignition propensity, similar to those existing in the upstream regions of engines and other combustors, sufficient energy input may still exist for fuel decomposition or pyrolysis. The generation of fuel fragments and their accumulation under microgravity conditions may then promote cool flame ignition. This lower bound behavior is important for a wide range of fuels which may exist in space habitats as well as terrestrial combustors. Detailed investigations into the interactions between LTC, thermal pyrolysis, and aerodynamic effects, such as flame stretch, will lead to deeper understanding of cool and warm flame dynamics and kinetics in general reacting flow conditions.

- Once the near-limit behavior is understood, control of this near-limit behavior, whether targeting promotion or suppression of ignition, should be investigated. Promotion of ignition is critical for enablement of progressively leaner burning engines while increasing combustion efficiency. In contrast, suppression of ignition will be critical for maintaining personnel safety aboard spacecraft. The development of suitable fire suppressants, as well as appropriate fuel load and environmental conditions, will rely on an understanding of LTC ignition.

- Measurements of ignition timing, flammability limits, heat release rates, emissions, and flame propagation rates should be made in microgravity environments for pure and practical, blended fuel components. Microgravity allows long duration LTC, providing the opportunity for detailed diagnostics, analysis and interpretation. LTC is known to have a significant role in these combustion phenomena, yet LTC and cool flames are challenging to stabilize for detailed study in terrestrial environments, particularly at conditions of
relevance to engines and other combustors. Chemical kinetics are poorly understood at those conditions, which include lean fuel-air ratios and high pressures. Experimental data are needed to validate and improve chemical kinetics mechanisms, and data generated under microgravity conditions are particularly well-suited to such validation and refinement efforts because of the avoidance of buoyancy-induced complexities.

- Deployment of expanded diagnostics, beyond what has been available for ISS experimentation so far, should be explored. Given the relatively recent discovery of cool flames aboard the ISS, there has not been a chance to deploy the types of diagnostic tools for targeted LTC and ITC experimentation that could offer valuable new insights into cool and warm flame burning aboard the ISS. Among the types of as-yet unavailable diagnostics which could be considered in a next period of research opportunities are a variety of laser diagnostic tools for the detection of LTC products, such as formaldehyde, and combustion intermediates and radicals.

- Extensive terrestrial experimentation and computational modeling efforts have been dedicated to the evaluation of LTC enhancement strategies. One such strategy is plasma enhancement via generation of relatively long-lived, plasma-produced species such as ozone (Sun et al., 2019). Significant LTC kinetic enhancement effects have been observed in terrestrial experiments and modeling studies (Brown and Belmont, 2021a; Brown and Belmont, 2021b). The opportunity to test derived kinetics models in the spherically-symmetric geometry of cool flame-sustained droplet burning would aid in validating the conclusions of those terrestrial studies and providing new insights into LTC enhancement strategies.

- Expand the range of ambient conditions, such as pressure, of LTC and ITC research in microgravity. The droplet combustion experiments in the ISS were limited to a range of ambient pressures between 0.5 to 5.0 atm. Even in this limited range, the flames exhibited a wide range of lower temperature burning behavior such as three-stage burning (Dietrich et al., 2017; Farouk et al., 2019), in which HTC transitioned to ITC and ITC transitioned to LTC, and hot flame re-ignition (Farouk et al., 2015; Farouk et al., 2019), where HTC transitioned to LTC/ITC and then periodically transitioned back to HTC. This pressure range, however, is nowhere near the operating regions of real engines.

**Importance of Research Needs to Terrestrial and Space Applications**

The research needs outlined above are highly important to several areas of terrestrial and space applications. These include:

- **Next-generation engines:** There is growing emphasis on, and deployment of, electric vehicles for transportation. However, there are major impediments to the permeation of electrification in commercial air, marine, and rail markets. For these applications, there is no viable replacement for combustion-based propulsion for the foreseeable future. Therefore, minimization of climate impacts from these modes of transportation means that vehicle emissions, such as carbon dioxide, must be reduced through combustion engineering. One pathway to this reduction will come from the design of next-generation engines that utilize techniques such as homogeneous charge compression ignition (HCCI), premixed charge compression ignition (PCCI), reactivity-controlled compression ignition (RCCI), lean burn, detonations, and others (Krishnamoorthi et al. 2019). LTC and ITC are critical to the development and sustainment of lean and high-pressure flames, yet the
chemistry and chemical kinetics are poorly understood and quantified at those conditions. Additionally, aerodynamic strain and flame curvature are omnipresent in practical power and propulsion systems, yet these effects are still poorly understood for cool and warm flames. It is therefore of great utility to investigate the local behavior of cool and warm flames manifested by the interaction of chemistry, transport, and such aerodynamics effects.

- **Low carbon fuels:** The advancement of engine designs cannot occur without understanding the combustion chemistry and properties of current and future fuels. Future fuels are likely to include increasing amounts of bio-derived fuels and electrofuels derived from renewable energy and captured resources, such as carbon dioxide. These fuels are intended to be drop-in replacements for petroleum-derived fuels, but current and future fuels will have some differences in chemical compounds and associated combustion properties. The successful deployment of increasing quantities and types of these sustainable fuels will depend on an increased understanding of their LTC and ITC behavior (Ju, 2021). Considering how these fuels are mixed and the fuel injection techniques commonly utilized in most engine technologies, understanding how the dynamics and chemistry of LTC depend on fuel physical properties and distillation characteristics is critical for these multi-phase, multi-component applications. Failure to account for fuel combustion behavior can readily lead to catastrophic engine failure due to the influence of LTC and ITC on pre-ignition and engine knock, which are damaging phenomena resulting from ignition inside a combustion chamber at unintended locations and times (Agarwal et al., 2017).

- **Space safety:** Microgravity conditions do not support buoyancy-induced flows, which lead to convective cooling of surfaces and dispersion of gas phase fuel species. As a result, LTC and ITC may lead to autoignition at lower temperatures than would occur on earth. Additionally, minimum ignition energy has been shown to be lower for cool flames than for hot flames (Yang and Zhao, 2021), and combustion at much lower ambient oxygen levels than support combustion in terrestrial gravity have been demonstrated. These factors contribute to the potential for highly hazardous conditions in microgravity, where LTC may initiate and progress to HTC at conditions which could not be predicted based on terrestrial ignition measurements. Thus, an improved scientific understanding of LTC and associated cool flames under space-relevant conditions is critical to efforts to advance fire safety design and operational criteria that relate to human occupational safety in low gravity environments.

**Likely Impacts of Recommended Research**

Some likely impacts of the recommended research program for low temperature and intermediate temperature chemistry are readily envisioned. Continued improvements in engine efficiency and progress towards lean-burn engines are anticipated as LTC and ITC are better understood and thereby controlled. The thermal efficiency of engines is not practically limited by the Carnot cycle nor the Otto cycle efficiency. Rather, engine thermal efficiency is compromised by high temperature combustion and heat transfer from flames to engine walls, as well as enthalpy lost in the exhaust gas. Thus, an improved fundamental understanding of cool and warm flames associated with LTC and ITC will allow for significant increase in engine efficiency for a wide range of applications. Recent engine advancements, such as the release of Mazda’s spark-controlled compression ignition (SPCCI) Skyactiv engine, demonstrate the successful translation
of research related to the recommended research scope to lean-burn, high efficiency engines. The integration of fuel-air premixture and compression ignition, such as in the Skyactiv engine, requires careful control, which an improved understanding of LTC and ITC can offer. Yet, the lack of fundamental understanding of the associated intertwined physicochemical processes related to LTC and ITC continues to limit implementation of combustion techniques based in these regimes for both reciprocating engines and the interpretation of near-limit behaviors, such as lean blow off in gas turbine engines. The recommended research program described in this white paper will offer a clearer understanding of the dependence of the physicochemical processes on pressure, temperature, equivalence ratio, and fuel structure, and will be critical as a technology enabler. The result will be the advancement of engines with higher thermal efficiency and reduced emissions that require less complex after-treatment than existing best options for relatively high thermal efficiency, such as diesel engines. This outcome is necessary to meeting current and future emissions reduction and elimination needs.

In addition to harnessing combustion for society’s power and propulsion needs while simultaneously reducing negative impacts of emissions from these systems, the study of LTC and ITC is also likely to lead to improved safety during space travel. The demonstrated potential for sustained cool flames in microgravity environments, discovered in ISS experiments, highlights the importance of studying these combustion regimes to better ensure fire safety in those environments. It is likely that new materials, fuel handling, and fire suppression standards and practices will result from the research program proposed herein.

Beyond these foreseeable likely outcomes, there remains untapped potential to tailor and harness chemical conversion of materials and fuels to meet societal needs. Cool and warm flames are chemical kinetics-controlled phenomena, unlike the commonly encountered hot flames where equilibrium thermodynamics plays a significant role. Better understanding of the relevant chemical kinetics pathways can lead to an entirely new class of flames and chemical conversion processes whose heat release and temperatures can be manipulated using chemical accelerants or retardants, plasma, electric fields, and other methods to create “designer flames” and new processes suited to particular applications. Among the applications which can be readily envisioned are:

- Thermal conversion of waste in space for regenerative manufacturing of fuels and other useful chemicals, as well as waste minimization.
- Understanding and influence of atmospheric chemistry for reduction of atmospheric pollutants through targeted avoidance of problematic species.
- Entirely new, efficient energy conversion technologies are possible once the intricacies of low and intermediate temperature combustion chemistry pathways are understood.

In summary, the understanding that has been gained of LTC and ITC from studies of cool flames and warm flames to-date have already yielded significant advancements in propulsion and safety which have led to new engine designs and an awareness of combustion hazards that has a high likelihood of saving lives in future space travel. Yet, our understanding remains nascent. The relatively recent discovery of sustained cool flames aboard the ISS means that a novel and substantial tool is available in the ISS for additional LTC insights that have not yet been realized. There remains untapped potential that should be explored in the coming decade.
References


