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Kinetic, physical, and thermochemical properties of fuels for recalcitrant transportation sectors

Authors:

Joshua S. Heyne, Ph.D.

Department. of Mechanical and Aerospace Engineering, University of Dayton,

300 College Park, Dayton, Ohio, 45469

jheyne1@udayton.edu

Co-Authors:

Meredith (Med) Colket, Ph. D., Combustion Consulting Services, LLC, med@colket.org
Luke Juneau, SETI Institute Affiliate, lukejuneau5@gmail.com

Uday Hegde, Ph.D., Case Western Reserve University, uday.g.hegde@nasa.gov

Rosa E. Padilla, Ph.D., Universities Space Research Association, rosa.e.padilla@nasa.gov

Abstract

An understanding of fuel properties is critical for the development of new technologies, specifically, across the transportation sector, which may operate from subcritical to supercritical conditions. This paper emphasizes a research campaign based on microgravity ground studies with an extensive experimental capability to characterize novel fuel mixtures for a wide range of operating conditions and advanced diagnostics. Lastly, the utilization of commercial manned and unmanned spacecraft studies to provide a database on the kinetics, transport and thermodynamics of fuel properties.

Background

Decarbonization and the circular carbon economy are the future for aviation, marine, rail, and heavy-duty trucking, where electrification is unlikely. In these applications, electrification or the use of hydrogen and battery technologies is impractical or could lead to worse environmental outcomes, e.g., hydrogen combustion could increase contrail formation. In this space, novel and developing technologies such as supercritical combustion can impact a range of applications (from heavy-duty diesel vehicles to rockets) towards increased efficiencies, sustainable, and a circular carbon economy across a range of applications. For example, in aviation, the range of air and fuel temperatures along with pressures encountered throughout the operational envelope experienced by jet engines includes points varying from sub-critical through super-critical.

While the air pressure exceeds its critical pressure over a relatively small fraction of a typical operating envelope, the air temperature is significantly above its critical temperature and the air density remains essentially gas-like with respect to its dependence on temperature and pressure. In contrast, the fuel temperature, at the moment of injection, is well below its critical temperature, while the fuel pressure is well above fuel critical pressure over much of the operating envelope, and fuel density is essentially liquid-like under these conditions. However, fuel heating from the surface inward, and depressurization, are fast processes which drive interesting fuel density gradients from the center of a fuel sheet, jet, ligament, or drop-out to the freestream of its surrounding air. Within this gradient, at some operating conditions and at certain moments in time, fuel exists as a trans- or super-critical fluid which leads to a poor understanding of how it mixes with air.

Practically, the impact of this phenomenon has been theorized to be the cause of certain observations for which no other explanation could be found. (1) The occurrence of combustible mixtures (and flame) near uncooled hardware structures has been observed to occur at operating pressures that coincide with the critical pressure of jet fuel. (2) Fairly discrete changes to flame shape have also been observed to coincide with operating pressures that are close to the fuel critical pressure. (3) The disappearance of a sharp boundary between a fuel jet and air in crossflow has been observed to occur as fuel temperature approaches its critical temperature, and changes to jet penetration have been hypothesized as the likely cause of unexpected increases in NO_x emissions at similar operating conditions as the jet-in-crossflow experiment.

The future of sustainable transportations fuels is a significant known-unknown. The envelope of potential chemical confirmations, their properties, and their impact on aviation and the environment remains significant. Specifically, the structure of conventional fuel components has evolved to lower heats of formation conformations, while, Sustainable Aviation Fuels (SAFs) have not. As a result, the diversity and range of SAFs can be significant. Already, diverse confirmations not found in high concentrations in conventional jet fuel, such as 2,2,4,6,6-pentamethylheptane and Farnesane, are approved blend components in ASTM D7566.The diversity of these hydrocarbon components and the impact they have on developing aviation hardware remains uncertain, particularly at trans and supercritical conditions.

While the concept of supercritical combustion/oxidation has been known for decades [1], it has recently received increased attention because of its importance in high-efficiency power generation (e.g. Allam cycle [2], where supercritical carbon-dioxide is used as working fluid) and also as a potential process for recovering energy and reclaim water from wet waste streams (e.g. Hydrothermal flames [1], [3], where the combustion/oxidation processes involving flames are induced in aqueous environments at conditions above the critical point of water, $P > 221$ bar and $T > 374°C$). Despite numerous experimental studies of trans- and supercritical reacting and non-reacting flows [4]–[11], the diagnostics mostly remained unsatisfactory at preliminary level of relatively simple visualization of the system with limited CH* and OH* chemiluminescence. Not until recently are experiments being conducted to explore the kinetic processes associated with supercritical conditions [12]. The lack of fundamental understanding of the associated chemical kinetics continues to limit the readily implementation of supercritical combustion. A clearer understanding of the fundamental processes and kinetics on pressure, temperature, equivalence ratio and fuel composition are critical for enabling new technology developments.

Studies on supercritical fluids onboard the International Space Station [13] under a joint collaboration between NASA and CNES (French Space Agency) has further intensified the interest in advancing supercritical combustion specifically related to hydrothermal flame activities. Detailed mechanistic behaviors of supercritical combustion phenomena are not yet fully understood, partly because of 1) the technical challenges associated in ground based and/or flight experiments, 2) the limitations in diagnostic techniques for characterizing supercritical combustion process, and 3) limited insight on the kinetics, transport and thermodynamics parameters required to conduct mathematical simulations.

Existing Methods used to Characterize Fuel Properties

A variety of methods exist [14]–[20] for measuring fuel properties at subcritical conditions, however, becoming challenging as supercritical relevant to rockets and aviation are exceeded. Previous studies have used the pendant or sessile drop, spinning, and the Wilhelmy plate, which are commonly used to measure surface tension for a limited range in pressures and temperature. The studies have reported surface tension and heat vaporization will tend to zero with an increase in the critical pressure and temperature of a fluid, whereas the isothermal compressibility and specific heat increases with an increase in pressure. Methods for measuring specific heat capacity are described as the adiabatic calorimetry, differential scanning calorimetry, and flow calorimetry [20]. In addition, viscosity measurement techniques such as rheometer both for atmospheric and limited studies at high pressure conditions. In addition, correlations for calculating surface tension for pure single component fuels liquids and multicomponent mixtures are also available, such as the Macleod-Sugden and the wide range of versions of the modified Peng-Robinson equations

[14]. However, for complex fuel mixtures, measurements of critical properties are limited at extreme operating conditions across, which are needed for transportation and new technology development.

Experimental Studies- Reactive and Non-Reactive Gases

A fundamental understanding of properties is critical for fuel injection in a system at elevated temperatures and high-pressure conditions. It is extremely critical for the operation of practical applications, such as diesel engines, liquid rocket engines, and industrial processes. Fuel properties will impact the atomization characteristics (drop size, ligaments, breakup formation) in sprays. In liquid fuel injection systems, fuel spray is injected into a chamber at very high pressure (2-11 MPa) and temperature (700-1200 K), relevant to diesel and rocket engine conditions, often exceeding the critical conditions of the injectant. Fuels investigated were single component, n-dodecane, n-hexadecane, n-heptane, to observe atomization characteristics As the ambient temperature and pressure increases there is an opportunity for the fuel-air mixing to transition from the classic two-phase break up paradigm to a more diffusion dominated mixing paradigm without fuel atomization [20]-[24]. Studies have observed fuel properties such as, surface tension diminish). due to a broadening effect at the liquid-vapor interface due to fuel property changes such as density variations across the interface thickness. Fuel properties for n-dodecane, n-hexadecane, n-heptane have been investigated heavily across to observe atomization characteristics. Expanding the capability to adequately represent fluid behavior by the use of fluid properties as they transition from sub-critical to supercritical conditions in a combustion system becomes important for future engine design development.

Several experimental, theoretical, and computational works have demonstrated that fuels injected into supercritical environments do not necessarily undergo purely supercritical mixing but rather so called trans-critical mixing. Fully supercritical mixing requires a combination of sufficiently high fuel temperature, ambient temperature and pressure. Otherwise, the fuel will enter a supercritical environment where the fuel experiences heat transfer effects from the surrounding gaseous environment into promoting evaporation onto the liquid fuel droplet Previous work on isolated droplet investigations have extended to supercritical conditions and have address the experimental challenges to sustain a droplet on a capillary tube or a fiber due to the lack of surface tension [17]. However, to overcome this challenge, the study by Weckenman [16] applied electric fields to study isolated acetone droplets under supercritical pressures (above 6 MPa) and temperatures of up to 530 K in a nitrogen-oxygen mixture.

Ground and Flight Research Recommendations

This paper recommends a research campaign focused on microgravity science program for conducting ground and spaceflight investigations to pursue property characterization in complex fuel mixtures.

Through the expansion of commercial spacecraft launches, the opportunity to test experiments in microgravity will likely increase and extend beyond the International Space Station (ISS). Low-orbit flights and co-manifested payloads will provide extended times for experiments in reduced gravity. Several solvents have high supercritical temperatures and pressures. For instance, water's supercritical temperature is 647K with a critical pressure of 22 MPa and methanol critical properties include 512K at 8.09 MPa. Similar fuel solvents have an above average volatility. The use of unmanned spacecraft with automated experiments can provide a greater safety threshold for riskier experiments. In addition, share rides will cut costs and provide repeated tests.

The TEMPUS electromagnetic levitation facility serves as an example of a platform that could be developed for characterizing fuel properties of interests under transient conditions. The facility has been used for the *Surface Tension Driven Convection* experiments and was operated aboard the United States Microgravity Laboratory (USML 1 & 2) for measuring specific heat, density, electrical conductivity, viscosity, and surface tension as a function of temperature over a wide temperature range, including a variety of metals and alloys. The oscillating-drop-method (ODM) [25] was used for measurements of the viscosity via oscillations damping and surface tension via oscillations frequency, and over a range of temperatures. Heating coils were provided in the facility and could be used to rapidly heat a surrounding gas environment, while introducing a fuel of interest using the ODM approach.

The DECLIC facility on board of the ISS is another example of an experimental platform that provides minimal crew intervention and could potentially be extended to include fuel mixtures of interest across government and industry partners. The existing ground studies for Supercritical Water Oxidation (SCWO) at NASA Glenn Research Center (GRC) provides hardware (reactors and instrumentation) that could be used in both 1-g and 0-g, using GRC’s Zero Gravity Facility (5.2 seconds of 0-g) to serve as a platform for characterizing fuels and in preparation for developing the concepts and hardware that could lead to a flight investigation.

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