Numerical Simulation of Methane-Water Combustion at Transcritical Conditions

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for the degree of

DOCTOR OF PHILOSOPHY

in Mechanical and Aerospace Engineering

by

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ABSTRACT OF THE DISSERTATION

Numerical Simulation of Methane-Water Combustion at Transcritical Conditions

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Combustion at elevated pressure brings advantages in terms of efficiency and emissions. In many different devices a liquid reactant is injected into a high pressure chamber where the reaction occurs. Common applications are diesel, jet, and rocket engines. Frequently, the thermodynamic conditions of the ambient fluid in the combustion chamber are supercritical for both fuel and oxidizer. However, the injected fluid is usually at subcritical temperature. Consequently, two phases exist until the temperature of the liquid rises to its critical value by means of heat transfer. This process is known as transcritical vaporization. Important and challenging problems associated with this scenario have been studied with increasing interest during the past years. The main aspects of study include transcritical single-droplet and spray vaporization, mixing, combustion, phase equilibrium, and transport.

Despite an extensive and growing list of publications, there are still unanswered questions. For example, the presence of sharp gradients in density or composition are not well understood under conditions that one would expect to be supercritical. The possible existence of a heat of vaporization and surface tension in the supercritical regime has been highlighted by some researchers. Understanding the physics governing these phenomena is crucial to control combustion chambers, as well as to provide an opportunity for improving their design.

Other relevant applications for transcritical combustion are the burning of gas hydrates and
direct water injection. It is well known that large quantities of methane are stored in form of
gas hydrates in the ocean at a depth of the order of 1 km. The possibility of burning these
materials locally to extract energy has been suggested. The conditions in which combustion
would occur with so much water in the environment and at high pressure are also not well
understood.

A one-dimensional counterflow diffusion flame model is used in this dissertation together with
real-fluid thermodynamics and laws of phase equilibrium. The presented solutions provide
insights that are relevant to the scenarios posed above.
Chapter 1

Introduction and Literature Review

1.1 Introduction

Combustion under high pressures leads to an increase in both thermodynamic and fuel efficiencies as well as reduced emission of certain pollutants. These advantages are causing the current trend towards burning at high-pressure regimes. For instance, aircraft gas turbine engines now operate at \( \sim 30 \text{ atm} \), a value that has been increasing at a near linear rate for more than 50 years and is expected to continue to do so [1]. Another example is that of diesel engines, which obtain pressures as large as \( \sim 60 \text{ atm} \) after ignition [2–6]. In many rocket engines, one of the reactants is injected in a liquid form at a temperature which is below the critical value but at supercritical pressure. These conditions were named as transcritical [7] and the pressure takes values which are typically of the order of 100 atm but may reach levels as high as 400 atm [8–10].

Ideal-gas approximations are often considered in combustion problems with the argument that at high temperatures and low densities the compressibility factor will be close to unity. At very high pressures, however, this may not necessarily be accurate. It is the responsibility
of any analyst treating these high-pressure flows to justify the ideal-gas approximation. In our study, we present results for a canonical combustion configuration with both ideal and real-gas models for comparison purposes and error estimation.

Another motivation for the present study is combustion at high pressures where the fuel is a mixture of methane and water vapor. This scenario is in relation gas hydrates. These materials are ice-like crystalline solids formed from a network of hydrogen-bonded water molecules that encapsulate guest gas molecules [11]. There is a significant amount of methane naturally stored in the form of methane hydrates, also known as methane ice or methane clathrates. Sediment containing methane hydrates is found within specific pressure-temperature conditions that occur in regions of permafrost and beneath the sea in outer continental margins at depths of the order of a thousand meters [12] where pressure reaches the value of 100 atm. It is not in the scope of this study to determine whether combustion of methane hydrates in their natural environment is practical. Rather, it poses an interesting problem from which conclusions can be extracted for a broader range of applications, including rocket engines, bio-fuels, or exhaust gas re-circulation (EGR) in engines. For a detailed description of methane hydrate combustion, the reader is referred to [13]. Note that mixtures of fuel and water can appear in other situations, e.g., bio-fuels and direct water injection.

The purpose of this project is to provide an accurate framework that describes high-pressure combustion processes where both sub- and super-critical conditions are considered. More specifically, the canonical flame configuration known as counterflow diffusion flame will be coupled with other key elements, such as real-gas thermodynamics and laws of phase equilibrium.

A literature survey on high-pressure combustion and methane hydrates is provided first, in subsequent sections of this Chapter. Then, real-gas thermodynamic relations are introduced in Chapter 2. These will be used throughout the rest of the work. Chapters 3 and 4 provide solutions for the single-phase counterflow diffusion flame at constant and variable
strain rates, respectively. Chapter 5 introduces the laws of phase equilibrium, providing solutions for several systems of interest, such as hydrocarbons with oxygen. These laws are differentiated in Chapter 6 to establish the shifting phase equilibrium formulation. From that, constant pressure vaporization processes and auto-ignition are analyzed. Chapter 7 combines all the previous knowledge to expose and solve the two-phase counterflow diffusion flame model. A summary with concluding remarks and future work recommendations is provided in the final Chapter 8.

1.2 Literature Review: Transcritical Vaporization and Combustion

The presented literature review will summarize the recent findings and progress in the field. Theoretical, numerical, and experimental work will be discussed. Due to the enhanced modern computational capabilities, the community is now able to use the microscopic molecular-dynamics approach to obtain results. This part of the literature will also be examined.

The interest to study vaporization and combustion problems at high pressures emerged from the need to understand the physical phenomena occurring, for example, in liquid-fueled applications such as rocket-engine combustors and diesel engines. The current trend for jet engines is also towards operating at higher compression ratios. Another potential application where high-pressure combustion prevails is the burning of gas hydrates. Vast amounts of these materials exist in nature. They consist of water-ice cages that formed over the years trapping mostly methane gas in their cores. A fraction of them can be found in the permafrost, and another substantial portion exists at the edges of continental shelves in ocean depths of the order of 1 km. There, ambient conditions are characterized by high content of liquid water at a pressure of the order of 100 atm, which is supercritical for the fuel but
subcritical for water. Local burning of methane hydrates has been suggested to extract the energy needed to run equipment for mining this potential source of energy.

A classical two-phase reacting flow problem requires special attention to overcome several obstacles, such as disparity in time scales, highly nonlinear source terms, and inclusion of sub-grid models to resolve length-scales that are too small to be treated numerically in a feasible way. There are diverse extra challenges associated with studying supercritical combustion aside from the already cumbersome issues common in a low-pressure system. The increase in pressure is directly related to an increase in Reynolds number, which implies that the flow becomes more turbulent and thereby, the mixing processes occur in even smaller length scales. Furthermore, departure from the ideal-gas model and transport anomalies appear. Liquid-fuels in a thermodynamic state near their critical point have liquid-like densities, but their diffusivities are typical of a gas, and solubilities are pressure dependent [14]. Surface tension and enthalpy of vaporization go to zero at the critical point, and there is a substantial increase in heat capacities.

Early investigations were limited by the available computational power. Initially, they focused on single-droplet vaporization and combustion under quiescent environments. Placement of a droplet in a subcritical environment produces the classical $d^2$-law for the droplet lifetime. There is a clear interface between the liquid and the surrounding gas which regresses in time as the droplet gasifies. For a droplet in a supercritical environment, heat transfers to the droplet and its surface reaches the critical conditions while keeping a liquid core. The discontinuity between liquid and gas transforms into steep gradients of the physical variables without a clear interface. The boundary of the droplet then becomes the surface that attains critical conditions, which is pressure, temperature, and composition dependent. Comparisons between different models provided error estimates for the burning rates, droplet lifetime, or evolution of flame-to-droplet diameter ratio. Later research analyzed single-droplet vaporization and combustion under convective environments as well as
supercritical sprays. The present literature review will focus on more recent investigations. One very important aspect to study combustion in the transcritical regime is the ability to predict thermo-physical properties accurately. Cubic equations of state have been used extensively. Some of these methods and how they have been applied in recent studies are reviewed in the next section. The novelties presented in new numerical and experimental papers are reviewed after. In relation to the numerical investigations, a section is dedicated to the newest findings using molecular dynamics.

1.2.1 Theoretical and numerical investigations

Supercritical injection has been extensively studied [15] both experimentally and numerically, mainly for systems with liquid oxygen (LOX) injected into gaseous hydrogen which are the classical reactants for rocket engines.

For example, the transient vaporization of a LOX droplet was analyzed under sub- and supercritical conditions by different research groups [7] [16] in a quiescent environment. Phase equilibrium calculations for oxygen-hydrogen mixtures were conducted, revealing that the critical pressure of the mixture could be well above the critical pressure of any of the single components, while the critical temperature of the mixture laid in between. In the supercritical case, the surface of the droplet reached the critical mixing point predicted by phase equilibrium some time after injection.

Another article by the same authors followed two years later, in which the transcritical vaporization of LOX droplet arrays was studied in a convective and reacting environment [17]. Significant differences from the behavior predicted for isolated droplets were revealed. The interactions between heat-release zones of the diverse droplets caused lifetime reductions of at least one order of magnitude. High number of droplets are present in convective environments typical of practical applications.
More modern studies indicated that the presence of neighboring in droplet clouds prevents the surface from reaching the critical mixing state [18]. The effect of stripping was found to be important, while surface tension forces were reduced in the transcritical regime.

Nevertheless, an increased interest in use of methane as fuel has emerged in the last decade. The mixing and combustion of LOX and gaseous methane of a shear coaxial injector operating under supercritical pressures was investigated in [19]. The effects of the momentum-flux ratio of the two propellant streams on the near-injector flow and flame dynamics were examined. Large eddy simulation (LES) was employed together with analytical and empirical models for the resolution of subgrid-scale motions. Thermodynamic properties were obtained using the SRK equation of state, and transport properties were computed using the ECS theory. The chemistry was modeled using a one-step global reaction involving the two reactants and water and carbon dioxide as combustion products.

Several conclusions were extracted from their results. An increase in the momentum flux of the methane stream increased the intensity of the vortices generated in the shear layer between oxygen and methane, enhancing the mixing. Hot products recirculating right after the oxygen post provide the energy to quickly ignite the incoming reactants into the long trailing diffusion-controlled flame. The dominant frequencies of vortex shedding matched those for a rear-facing step flow, a phenomenon that was attributed to the strong inertia of the LOX stream and lighter density of gaseous methane.

As mentioned in the Introduction section, isolated droplets in both quiescent and convective environments have been studied under supercritical burning conditions. Droplet-interaction studies, however, are more limited in the literature. A recent study focused precisely on this problem, where the interaction and vaporization of two liquid oxygen droplets in tandem (see Figure 1.1) in a supercritical hydrogen stream were examined systematically [20]. The droplet temperature is initially uniform at a subcritical value, but the pressure and temperature of
the ambient hydrogen are in the supercritical regime, for both oxygen and hydrogen.

Solutions of the flow field were obtained by solving the conservation equations for a single-phase supercritical flow field. The argument is that once the two droplets are injected into the hydrogen environment, their surface warms up and reaches the critical point of the local mixture almost immediately, due to the cryogenic fluid properties of oxygen and efficient energy transfer from the ambient fluid. Although the droplet core remains at liquid state with a subcritical temperature, the whole flowfield, including both oxygen droplets and surrounding hydrogen, becomes a continuous medium without well-defined interface between phases. Even at the considered pressures in the range of 100-400 atm, freestream velocities from 2.5 to 20 m/s, and spacing ratios of $H/R = 4 – 12$, the Reynolds number was low and the flow treated as laminar. The SRK and corresponding-states theory were also employed as mentioned for previous studies.

A forward bag-type break-up of the leading droplet was observed when the two droplets were initially placed close together at an $H/R$ ratio of 4 and an ambient pressure of 100 atm. As the droplet spacing was increased, the interaction weakened. The leading droplet, which was confronted with the strong incoming stream and influenced by the trailing droplet, mainly deformed perpendicular to the flow direction, while the trailing droplet deformed primarily in the streamwise direction.

Figures 1.2 and 1.3 show the vaporization rates and lifetimes of the droplets for the different
Figure 1.2: Vaporization rates of the leading and trailing droplets: (a) ambient pressure of 100 atm and incoming velocity of 20 m/s, and (b) ambient pressure of 400 atm and incoming velocity of 5 m/s. From literature [20].

Figure 1.3: Droplet lifetime ratios of the leading and trailing droplets: (a) ambient pressure of 100 atm, and (b) ambient pressure of 400 atm. From literature [20].
studied conditions. The trailing droplet produced only minor effects on the vaporization lifetime and moving dynamics of the leading droplet. In contrast, with the presence of the leading droplet, the lifetime of the trailing droplet was substantially prolonged and its moving trajectory is strongly altered. Increasing ambient pressure weakened droplet interaction.

We talked this far about situations in which liquid oxygen is introduced into a supercritical ambient fuel. There have also been studies analyzing the injection of a liquid fuel into a supercritical oxidizer environment. Such situations exist for example for diesel engines, where higher combustion chamber pressures result in higher energy output as well as engine efficiency. A numerical scheme for the simulation of such real fluids mixing at supercritical and transcritical conditions was presented in a recent study [21]. The authors demonstrated its capability to deal with complex thermodynamics while maintaining robustness and high-order accuracy. In this case, the model entailed the multi-component non-reacting Navier-Stokes equations in fully conservative form together with the PR equation of state.

Their numerical scheme is based on a double-flux model, which for pure substances works fine, but presents conservation issues for the multicomponent case. The concerns originate from the coupling between total energy and pressure. When conservation is not satisfied, spurious pressure oscillations arise. The ratio between specific heats $\gamma$ is a parameter in such coupling, and it is constant for the single-component case, but it is a non-linear function of gas composition in the multicomponent scenario. Thus, the authors propose a simple effective specific-heat ratio defined as:

$$\overline{\gamma} = 1 + \frac{p}{\rho e}$$

(1.1)

Through this definition of $\gamma$, the double-flux model can be used without any pressure-equilibrium related problems. The performance of the scheme is showed for two different
two-dimensional test cases. The first one considers a cryogenic nitrogen jet (126.9 K) injected into a high temperature (300 K) nitrogen vessel at 4 MPa. The second case considers the injection of n-dodecane at 500 K into a vessel of nitrogen at 900 K and 6 MPa. The results for this second case are shown in Figure 1.4. The simulations were performed satisfactorily without generation of spurious pressure oscillations.

After reviewing the investigations presented above, one important question remains unanswered. It is well known that for a mixture, the critical temperature lays between the critical temperatures of the individual components, but the critical pressure of the mixture can exceed the individual critical pressures by an order of magnitude. Therefore, when species diffuse into each other in the shear layer, the question of whether there is a supercritical single-phase fluid or a subcritical one arises. The flamelet approach model was used in [22] to study the general structure of cryogenic H2-LOX diffusion flames at supercritical pressure.
and address the question as to whether subcritical mixture states are attained in a H2-LOX coaxial injection problem for given engine operating conditions.

Under the flamelet assumption, an actual diffusion flame profile can be represented by a 1D-counterflow diffusion flame, with only the boundary conditions as parameters together with the strain rate, which depends on the distance between the inflowing streams. Solutions were obtained using this model equipped with the PR equation of state. A high-pressure chemical kinetic mechanism was used for the H2/O2 combustion accounting for 8 species and 27 reactions. The entire regime of burning scenarios was studied, from stable flame until quenching was achieved. It was found that the injected oxygen experiences three different phases, as shown in Figure 1.5: first the oxygen is injected in a supercritical liquid-like state and transitions to a gas-like vapor state (pseudoboiling); second, the supercritical gas-like vapor transitions to an ideal gas; third, as an ideal gas, oxygen mixes and reacts in the hot flame. The main conclusion was that mixing in an attached LOX/GH2 flame occurs essentially under ideal gas conditions. The effect of real fluid mixing rules on flame structure solutions can thus be expected to be small.

A theoretical description of the interface dynamics at supercritical injection conditions was given in two recent papers [23] [24]. The authors used a 32-term BWR equation of state in conjunction with corresponding states theory to compute the thermodynamic behavior of multicomponent mixtures. This framework was combined with non-equilibrium mean-field thermodynamics of two-phase interfaces. For supercritical conditions, it was shown that the
interface zone enters the Knudsen number domain $Kn < 0.1$ in which interfacial forces depart from the classical vapor-liquid equilibrium. They concluded that the interface transitions from the phase-equilibrium scenario to a single-phase dense fluid mixing-layer setting. Three phenomenological factors to the transition from atomization to diffusion-dominated mixing were identified: broadening interface thickness, reduction in mean free path and diminishing surface tension forces. The presence of substantial interfacial free-energy forces and statistical fluctuations during that transition time complicates the accurate computation of transport properties. Without them, the transition time scales cannot be predicted.

1.2.2 Molecular-dynamics simulations

Following the last study reviewed in the previous section, the same research group conducted molecular-dynamics (MD) simulations [25] to gain more insight about the true thermodynamic regimes experienced in transcritical applications.

The authors chose argon as the modeling fluid because it minimizes modeling influences while still resembles nitrogen and oxygen. A system with 25,600 atoms was studied at different pressures and temperatures. The system was first brought to equilibrium and then the properties were averages over 62.5 ps. Simulations were conducted at 0.7, 1.4, 3.0 and 9.4 times the critical pressure and temperatures ranging from 75 K to 235 K.

Considering this context, seven questions were posed, for which seven main conclusions were extracted. The first one is that the supercritical regime is not only one homogeneous fluid, but rather, is a space divided into distinct liquid and gaseous parts. This is due to the large gradients in density within the supercritical regime, where density approaches the ideal-gas values at high temperatures, while it is large like the liquid at cold temperatures. Sound dispersion, a uniquely-liquid property, was measured at supercritical pressures, while it is not observed in gas.
The second conclusion is extracted from Figure 1.6, and it tells us that there is really no difference in the molecular structure of a dense fluid at subcritical conditions (liquid) and the same at subcritical temperature but supercritical pressure (transcritical fluid). There is no reason to distinguish them.

The third conclusion they sought is analogous to the second one but for the gas-side of the thermodynamic diagram. The comparison shown in Figure 1.7 represents an ideal gas (a) which slowly increases its density as pressure is increased at constant temperature. Liquid-like interactions were identified for subfigures (b) and above. However, further analysis of the compressibility factor yielded the conclusion that a supercritical fluid may well be characterized as an ideal gas for $T > 2T_{cr}$ and $p < 3p_{cr}$.

Furthermore, the sensitivity of fluid properties were confirmed for small variations in temper-
ature or pressure under the supercritical regime. For instance, changes in density of about 200 kg/m$^3$ were identified when the temperature was varied by $\pm 2.5$ K.

It was shown that a supercritical fluid requires heat addition (analogous to the subcritical latent heat) to transition from the dense to the gaseous state. More specifically, the same amount of energy is required to heat a fluid from a given liquid temperature to an ideal gas temperature, regardless of pressure, including sub- and supercritical states.

A separate group also published results in a recent article [26] for the transcritical thermodynamic regime using MD. They investigated evaporation of three n-alkane fuels into nitrogen under various temperatures and pressures. A united-atom model for hydrocarbons called SKS [27] was used in combination with a two-center Lennard-Jones potential model [28] for nitrogen to simulate the evaporation process. The configuration of the studied domain is shown in Figure 1.8, where the liquid hydrocarbon in the central box is either n-heptane, n-dodecane, or n-hexadecane, surrounded by nitrogen gas on both sides. With a prescribed initial temperature of the liquid fuel, a set of simulations at different temperature and pressure of the nitrogen were conducted to understand their effects on evaporation. Reduced ambient temperature and pressure values ranged from 0.8 to 2.4 and 0.55 to 14.3, respectively.

Examples of their results for n-dodecane are shown in Figures 1.9a and 1.9b at a supercritical
pressure of 20 MPa and supercritical nitrogen temperature of 1052 K. For simulation times below 1.3 ns, the temperature profiles intersect the vapor-liquid-equilibrium experimental lines, indicating the existence of two phases separated by a well-defined interface. The evaporation process during that time is subcritical-like. Surface tension decreases and vaporization rate increases. At a certain characteristic time, the critical mixing point is reached, the interface disappears, surface tension becomes zero and vaporization rate is maximum. From this point on, the evaporation enters a diffusion-controlled mixing process. Vaporization rate decreases because the density gradient between the liquid core and the ambient decreases with time, which means that the rate of mixing depends on the diffusion coefficient, mass fraction gradient, and temperature gradient. The transition time from the subcritical-like to supercritical-like regimes was found to depend strongly on the ambient pressure and temperature, but was independent of the liquid-layer thickness, meaning that the results could be extrapolated to macroscopic systems. With different characteristic transition times, the three studied fuels behaved qualitatively similar.
1.2.3 Experimental investigations

Among the broad literature on experimental supercritical injection and combustion, two recent representative articles have been selected and are reviewed in this section.

The first one provides a microscopic visualization study on the injection of n-dodecane into a pre-burn-type combustion chamber [29]. In this type of vessel, a premixed mixture of combustible gases are ignited to reach the desired thermodynamic conditions at the time of injection. Experiments are performed under pressure and temperature states realistic for diesel engines. High-speed imaging is performed using long-distance microscopy and diffused back-illumination to resolve ligament structures and droplets in the near-nozzle region. These liquid break-up formations are observed at low pressures and also at pressures slightly greater than the critical pressure of the fuel. However, they are not detected at higher pressures. This could either be because they are smaller than the resolution that could be captured with the used experimental apparatus, or because forces that generate such structures, such as surface tension, vanish under substantially elevated ambient pressure conditions. This is illustrated in Figure 1.10, where blue-square data points correspond to supercritical experiments where the classical liquid breakup mechanism was observed. The magneta squares represent experiments at ambient temperatures and pressures above a certain transition region where surface tension effects were not detected. Thus, an approximate boundary was determined between the spray atomization and diffusion-dominated mixing domains.

The second article RP-3 aviation kerosene was injected at sub/super critical temperature and pressure into ambient gas at atmospheric conditions [30]. A high-speed camera was used to capture macroscopic images while high-speed microscopic shadowgraphy was used to record the near-field structure.

Figure 1.11 shows the effect of the injection temperature on the jet angle when the fuel pressure is subcritical, which demonstrates that the spread becomes greater reaching its
Figure 1.10: P-T diagram with supercritical data. Blue squares show a domain with classical liquid breakup; Magenta squares show the experiments where no evidence of surface-tension effects was found. From literature [29].

Figure 1.11: Effect of injection temperature on jet angle at subcritical pressure ($P_r = 0.83$). From literature [30].

Figure 1.12: Effect of injection temperature on jet angle at supercritical pressure ($P_r = 1.25$). From literature [30].
maximum at near critical conditions. Figure 1.12 illustrates the same effect when the fuel pressure is supercritical. For this situation, the jet spread also reaches its maximum at the critical conditions. The jet angle decreases for supercritical temperatures. The complete set of studied cases is summarized in Figure 1.13.

An under-expanded jet exists with high pressure difference between the injected fuel and the ambient pressure, where the flow speed in the injector is sonic, and a mach disk is formed in the vicinity of the nozzle exit. Most studies of under-expanded jets are done under ideal-gas scenarios. Near-field observations exhibited the formation of a bell-shape mach disk also in the given near- and super-critical conditions. Fuel condensation was encountered downstream of the mach disk. The dimensions of the mach disk increased with fuel pressure, but were insensitive to fuel temperature.

1.3 Literature Review: Methane Hydrates

This section provides a compilation of the literature related to methane hydrates, and more specifically, those publications concerning the goal of this study: combustion of methane and methane hydrates at high pressure. With this purpose, general methane hydrates information is presented first. Then, the review is organized in subsections: laboratory burning of
methane hydrates and high-pressure combustion of methane hydrates.

Hydrate research has expanded substantially over the past decade, resulting in more than 4,000 hydrate-related publications. Gas hydrates are ice-like crystalline solids formed from a network of hydrogen-bonded water molecules that encapsulate guest gas molecules [11]. Although other gases, such as ethane, propane and carbon dioxide can also form gas hydrates, methane hydrates appear to be the most common, naturally occurring type of gas hydrate. A hydrate compound, because it may contain many empty cages (i.e. no trapped methane molecules), is a non-stoichiometric substance [31]. In an ideally saturated methane hydrate, the average molar ratio of methane-to-water is nearly 1:5.75, giving a water-to-methane mass ratio slightly greater than six. These ratios are dependent on how many methane molecules ”fit” into the various cage structures of the water lattice. The observed density is around 0.9 g/cm$^3$. So, the commonly cited energy density ratio for methane hydrate is, in average, 168:1, indicating that 168 unit volumes of methane at standard pressure (1 atm) and 0°C will be released from 1 unit volume of methane hydrate. In the subsurface, this 168:1 ratio is largely independent of depth because the gas hydrate is nearly incompressible at the pressures where gas hydrate is stable on Earth [32].

Under suitable pressures, natural gas, which contains mainly methane, can interact with water to form hydrates at temperatures considerably above the freezing point of water (see Figure 1.14). The diagram shows the boundary at which hydrates form for pure water and pure methane. The hydrates coexist with free methane gas. Addition of salt would move the boundary line to the left, while addition of substances such as CO$_2$, H$_2$S, C$_2$H$_6$ or C$_3$N$_8$ raises temperature of hydrate formation shifting the curve to the right.

Publications appeared during the last decades (see the earliest [33] or a more recent [34]) reporting global hydrate-bound gas estimates. First, a “consensus value” of $21 \times 10^{15}$ m$^3$ of methane at STP (or 10,000 Gt of methane carbon) seemed to be generally accepted. However, a more recent publication indicates that previous studies could have overestimated
the amount of hydrates that actually exist. The widely cited and used consensus value of 10,000 Gt of methane carbon may represent a consensus only for the estimates made in the late 1980s to early 1990s [35]. More recently, a predictive method for the occurrence of methane hydrates in the ocean was developed [36]. The model relied on equilibrium thermodynamics, input data such as sediment type, geothermal gradient, and sea floor depth, and a mass-transfer description for hydrate formation. The locations of the greatest amounts of methane in hydrate form are reported to be the Arabian Sea, the western coast of Africa and near Peru, Chile, and Bangladesh. The predicted total volume of methane that exists as sea floor hydrates, expanded to STP, is \(1.2 \times 10^{17} \text{ m}^3\). The predicted global distribution is portrayed in Figure 1.15.

Literature publications related to modeling and combustion of methane and methane hydrates are summarized in the next subsections.
Burning of Methane Hydrates

The first question that one could ask is whether it is possible to burn methane hydrates in a very aqueous environment. A simple analogy may be the classical combustion of methane with air. If we consider a reaction between these two gases at stoichiometric proportions, the mass of the inert nitrogen is more than thirteen times greater than the mass of the methane. If we now consider the fuel being methane plus water, and the oxidizer being oxygen or enriched air, the mass of the inert water would be lower or equal to the nitrogen mass in the classical burn of methane. Furthermore, experiments show that a portion of the water from the hydrate melts and drains, rather than vaporizing, which would require more energy. Thus, combustion of methane hydrates yielding substantial heat release is achievable.

There are several recent publications on burning of solid-phase methane hydrates in the laboratory at atmospheric pressure. A Japanese group investigated the flame propagation over a methane hydrate cake in an air laminar boundary layer [37] [38] [39]. One of the findings was that under flat plate burning conditions the lower layers of the hydrate would heal and stop releasing methane due to the lack of heat melting them. The methane cake was ignited at the downstream side and the flame would propagate upstream against the flowing air. The conclusion was that the propagation velocity is controlled by the dissociation rate.
of the methane hydrate.

Cylindrical 3 cm diameter chunks of methane hydrate were obtained and burned [40]. The entire piece burned in initial stages, while the flame would move to the top of the cylinder after some time and burn similar to a candle. A portion of the water was evaporated while another fraction dripped. This effect is important because greater evaporation would entail lower flame temperatures which would affect the sustainability of the flame. Different molar ratios of water to methane were tested. With increasing ratio, ignition temperature increased while flame temperature decreased until a crossover occurred. Still, ignition was possible for a wide range of the ratio. These tests were in air; so we would expect an even higher range of combustible ratios for oxygen or enriched air. Less than 15% of the available chemical energy was required to melt the ice.

In another experiment burning of methane hydrate powder and spheres was investigated in a free-convection configuration [41]. The goal was to examine the relationships between the burning behavior of hydrates and their size and shape. A compromise between the melted and evaporated water was found in order to have a self-sustained flame. The rate of methane release was found to be a function of methane hydrate shape. The amount of residual ice was found to be about 4 times greater for the spheres than for the powder, probably due to the larger surface area available in the loose powder. Jets of burning fuel were also identified. Obtained flame temperatures were 300 K lower than the adiabatic flame temperatures. The difference was associated mainly to radiative loss.

Water-laden combustion problems other than gas hydrates combustion appear in engineering applications. For example, water addition in combustors such as stationary gas-turbine engines helps reduce product temperatures and accelerates reactions due to the production of hydroxyl radical (OH). One way to add the water is through fuel emulsions [42] [43]. Going back to methane hydrates, in order to simulate the presence of water in the fuel coming off the hydrates, a nonpremixed counterflow configuration was examined, both experimentally and
numerically [44]. The water was incorporated in the fuel stream, while air was the oxidizer coming from the opposed stream. For a fixed strain rate, the maximum flame temperature was shown to decrease with water addition due to the cooling and dilution effects but flames could sustain water beyond molar ratios of 2 (water to methane). The measured extinction limits (in terms of the water to methane molar ratio) were reduced with increasing strain rates, implying that more (less) water vapor can be added at low (high) strain rates [44]. Favorable comparisons with computations were reported; use was made of the CHEMKIN code and the GRI mechanism by Frenklach et al. [45].

A recent numerical study analyzed the transient evaporation and combustion of a spherical symmetric methane hydrate particle [13]. It entailed assumptions such as diffusion controlled process with a quasi-steady gas film. Three phases were considered, and the dripping effect of melted liquid was neglected. Both infinite (thin flame case) and finite one-step chemical kinetics were used. Simulations using the one-step mechanism demonstrated a narrow flame region. So, the thin flame case predicted well the combustion process. A negligible amount of methane was found to dissolve into the liquid water. Several water-to-methane ratios were tested; decreasing the methane content resulted in lower flame temperatures, which in turn, decreased the vaporization and fuel burning rates. Furthermore, the flame location came closer to the surface of the particle.

1.3.2 High-Pressure Combustion of Methane Gas

A comprehensive overview of methane combustion was presented [46]. Shock tube experiments were undertaken to determine the ignition delay times for methane mixed with other hydrocarbons and diluted in argon. General correlations yielded to empirical expressions to predict ignition delay. A chemical kinetics model was also developed. A previous set of experiments reached pressures of 300 atm [47]. In another publication, methane oxidation...
behind reflected shock waves was studied over a wide range of pressures (9-480 atm) and temperatures (1410-2040 K) [48]. Results were compared with computations using a detailed chemical kinetics model (GRI 1.2). Good agreement between the model predictions and the experimental results was found, particularly for ignition delay times. However, they reported a need for improvement at high pressures, for removal pathways of CH$_3$ were altered and reactions involving HO$_2$ became important.

Ignition of methane-oxygen mixtures in heated spherical and cylindrical vessels at pressures in the 50-1000 bar range was examined [49]. The temporal behavior was monitored and ignition temperatures were measured, which helped deduce activation energy values and rate constants. An order of magnitude uncertainty in the rate constants was reported, giving an indication of a stochastic nature to the challenge of prediction based on empirically derived constants and properties.

Soot formation was studied for methane flames at high pressure [50] [51]. The investigations focused on laminar nonpremixed diffusion flames. The soot reached an asymptotic level for pressures greater than the critical pressure of the fuel. With the co-annular configuration and a methane-air flame at pressures between 5 to 40 atm, the soot was totally oxidized. Counterflow configuration setups with methane diffusion flames at high pressure were studied numerically [10], and experimentally [52]. The numerical analysis, which extended the capabilities of Chemkin to include the high pressure, low temperature ranges corresponding to transcritical conditions, treated supercritical methane/transcritical oxygen flames showing very strong density gradient on the oxygen side of the flame. The density of oxygen decreased by two orders of magnitude between the injected stream and the flame region [10]. Situations with both reactants under transcritical conditions were also examined, showing strong density gradients on either side of the flame. The experimental counterflow [10] was carried out to pressures up to 30 atm. The counterflow configuration is reported to be less susceptible to hydrodynamic instability which makes experimentation simpler. In some ex-
periments, nitrogen was replaced with helium, using methane reacting with oxygen-helium mixtures producing lower Reynolds number (more stability) and less soot. Scaling laws for maintaining adiabatic conditions were obtained; no information on reaction rates and mechanisms was reported.

Methane/air laminar flame speeds were studied using the conventional constant-pressure technique, both experimentally and theoretically [53]. The flames propagated outwards in a confined cylindrical chamber in the range of 1 through 20 atm, but only hydrogen/air results were reported for high pressure cases.

Non-premixed combustion situations in which one of the reactants is at subcritical temperature but subcritical pressure, also known as transcritical conditions, were studied for oxygen and hydrogen [7] [17] [9]. In these studies, the ambient hot gas was supercritical but the cold liquid droplet was not supercritical although existing at supercritical pressure. The gaseous mixture of propellants in the film surrounding the droplet could have a higher critical pressure than either component propellant. So, critical pressure could vary significantly both spatially and temporally. For the same nearly uniform pressure and at the same instant, there could be fluid regions at subcritical conditions and other regions that are supercritical. Although hydrogen and oxygen were used, the transcritical concept is general. These situations are expected for the combustion of methane hydrates at deep ocean pressures.

1.4 Conclusions

A survey on recent literature was presented for the important topic of liquid injection under supercritical conditions, which is relevant to many technological applications such as diesel, jet, and rocket engines. Even though these systems work safely in practice, there are still many question regarding the physical phenomena occurring in their combustion chambers.
Findings from novel theoretical, numerical, and experimental investigations were discussed for different scenarios, such as reacting flows where the liquid fuel is injected into ambient oxydizer, reacting flows where liquid oxygen is injected into ambient fuel, and non-reacting flows where a liquid fuel is injected and mixed with some ambient gas. Some researchers directly assume single-phase behavior when a fluid at supercritical temperature is injected into a supercritical atmosphere. Nevertheless, consensus seems to be emerging based on theory, experiments, and molecular-dynamics simulations concluding that two phases can still exist at supercritical conditions. A transition characteristic time is then identified during which the well-defined interface between liquid-like and gas-like fluids progressively disintegrates. The classical liquid breakup atomization applies at supercritical conditions before the transition concludes. After that, diffusion-dominated mixing governs the vaporization process.
Chapter 2

Real-fluid Thermodynamics

2.1 Introduction

The ideal-gas equation of state is not valid when interactions between molecules in a fluid become important. Besides that effect, thermophysical properties exhibit very sensitive behaviors to variations in pressure and temperature in the thermodynamic regime near the critical point. Furthermore, the critical point is composition dependent. Therefore, it is crucial to use an equation of state that is not only able to accurately model the whole thermodynamic regime, from compressed liquid to superheated gas, but is also equipped with a set of mixing rules that estimate the critical point correctly. Many different equations of state have been suggested to account for real-gas effects. Some of the most commonly employed ones are the so called cubic equations of state, which have their origin in the Van der Waals model and can be expressed as a cubic polynomial in terms of the specific volume $v$ or compressibility factor $Z$. Other variations are the Peng-Robinson model (PR), or the Soave-Redlich-Kwong model (SRK) [54].

The SRK equation consists of only two parameters, and it is reasonably accurate and easy
Figure 2.1: Relative errors of density predictions by three different equations of state compared to experimental results. From literature [14].

to implement. Thermodynamic properties such as enthalpy or fugacity coefficients can be readily obtained from fundamental thermodynamic formulation in combination with this equation of state. These equations require partial derivatives with respect to temperature, pressure and mole fractions of each of the equations provided above. Cubic equations of state are thus simple enough to allow researchers easy manipulation and yet provide accurate results.

However, more complex equations of state have been proposed, which clearly provide more accurate results when compared with experiments as seen in Figure 2.1. The cost is an increased number of parameters which are not always available in the literature for the extensive amount of substances of interest in combustion applications. An example is the modified Benedict-Webb-Rubin (BWR) equation of state suggested by Jacobsen and Stewart [55]. When data is not available for certain substances, the extended corresponding states (ECS) principle is used to evaluate volumetric and transport properties of a fluid over the entire thermodynamic diagram. It establishes a way to determine the properties of a given fluid from those of a different reference fluid and a conformal mapping. For multicomponent systems, a pseudo-pure substance model is adopted but the method is analogous. The correspondence of temperature and density between the mixture of interest and the reference
fluid can be characterized by the following two scaling factors:

\[ f_m = \frac{T}{T_0} ; \quad \tilde{h}_m = \frac{\rho_0}{\rho} \]  

(2.1)

Under the ECS principle, the density of a mixture can be calculated with

\[ \rho_m(T, p) = \frac{\rho_0(T_0, p_0)}{h_m(T, p)} \]  

(2.2)

where \( T_0, p_0, \) and \( \rho_0 \) represent the corresponding temperature, pressure and density of the reference fluid, respectively. The temperature at the conformal state is calculated using Equation 2.1, therefore the corresponding pressure can be derived from the general compressibility:

\[ p_0 = p \left( \frac{h_m}{f_m} \right) \]  

(2.3)

Then the BWR equation of state is used for the reference state:

\[ p_0(T, \rho) = \sum_{n=1}^{9} a_n(T) \rho^n + \sum_{n=10}^{15} a_n(T) \rho^{2n-17} e^{-\gamma \rho^2} \]  

(2.4)

where \( \gamma = 0.04 \) and the temperature coefficients \( a_n \) depend on the selected reference fluid for which data is available. The ECS principle can be applied in a similar fashion to determine transport properties such as viscosity and thermal conductivity.

The methods suggested above require solving the equation of state in each iteration of the main flow solver. A more recent approach suggests that, for a coaxial liquid injector the use of a precomputed library with fluid data is a more efficient method instead of evaluating the equation of state during runtime [56]. Their proposed methodology is based on three main assumptions: (1) mixing occurs in the hot reaction zone; (2) intermediate reaction species only occur in this zone and can hence be assumed to behave as perfect gases; 3) the
cryogenic LOX core does not see other species. Under these assumptions, only one component (oxygen) is treated as a real gas while the rest are essentially ideal gases. Then, mass, species, momentum and energy conservation equations together with a turbulence model are solved to provide the internal energy and partial densities of each species. This information is then passed to a thermodynamic model which computes the primitive variables $p, T$, which are finally fed into the chemistry model that goes back to the conservation equations.

The authors also suggest a different approach in the evaluation of the equation of state for a mixture. Instead of using mixing rules for the computation of parameters $a$ and $b$ for a new pseudo-pure substance, they suggest computing the equation of state for each individual species and apply mixing rules afterwards. Since the equation of state data is now tabulated and does not need to be computed during runtime, the use of the BWR version is affordable and provides more accurate results.

### 2.2 Soave-Redlich-Kwong Equation of State

The Soave-Redlich-Kwong equation of state (SRK EoS) is selected because of its reasonable accuracy for a wide range of fluid states [54].

\[
p = \frac{R_u T}{v - b} - \frac{a}{v(v + b)} \tag{2.5}
\]

This empirical equation, which may be rearranged to a cubic form with regards to the molar volume $v$, has two parameters $a$ and $b$, which are constants for single-component fluids, but become composition, pressure, and temperature dependent in the multicomponent version. The cubic form in terms of the compressibility factor $Z$ is

\[
Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \tag{2.6}
\]
where

\[
    Z \equiv \frac{pv}{R_uT} ; \quad A \equiv \frac{ap}{(R_uT)^2} ; \quad B \equiv \frac{bp}{R_uT}.
\]  

(2.7)

The parameter mixing rules of the SRK EoS are employed [57]:

\[
    a = \sum_{i=1}^{K} \sum_{j=1}^{K} X_iX_j(a_i a_j)^{0.5}(1 - k_{ij}) \quad ; \quad b = \sum_{i=1}^{K} X_i b_i
\]  

(2.8)

The pure species attractive and repulsive parameters \(a_i\) and \(b_i\) may be obtained from the species critical points as

\[
    a_i = a_{ci}\alpha_i \quad ; \quad a_{ci} = 0.42748\left(\frac{R_uT_{ci}}{P_{ci}}\right)^2 \quad ; \quad \alpha_i^{0.5} = 1 + S_i(1 - T_{ri}^{0.5})
\]

\[
    S_i = 0.48508 + 1.5517\omega_i - 0.15613\omega_i^2 \quad ; \quad b_i = 0.08664\left(\frac{R_uT_{ci}}{P_{ci}}\right)
\]  

(2.9)

where \(T_{ci}\) and \(P_{ci}\) are the critical temperature and critical pressure of mixture component \(i\), \(k_{ij}\) is the characteristic binary interaction constant and \(\omega_i\) are the acentric factors. These values are taken from the literature [58]. Sub-index \(r\) stands for “reduced” and equals the property temperature or pressure divided by its critical value. All the attractive and repulsive parameters of chemically stable species such as \(\text{H}_2\), \(\text{O}_2\), \(\text{N}_2\), \(\text{H}_2\text{O}\), or metastable species like \(\text{H}_2\text{O}_2\), may be determined from critical states conditions. However, chemically unstable species such as radicals do not have associated critical states, thus not allowing straightforward calculation of their attractive and repulsive terms. Assuming that the \(i\)th species is a Lennard-Jones gas, for instance, it is possible to estimate the critical volume \(v_{c,i}\) and the critical temperature \(T_{c,i}\) [59] and to obtain that

\[
    a_i = (5.55 \pm 0.12)n\epsilon_i\sigma_i^3 \quad ; \quad b_i = (0.855 \pm 0.018)n\sigma_i^3
\]  

(2.10)

where \(n\) is the Avogadro number, \(\sigma_i\) and \(\epsilon_i\) are the molecular diameter and Lennard-Jones
potential well depth of the $i$th species, respectively.

The specific enthalpy departure function is given by

$$h - h^* = \frac{1}{W} \left\{ R_u T (Z - 1) + \int_{\infty}^{V} \left[ T \left( \frac{dP}{dT} \right)_v - P \right] dv \right\},$$  

(2.11)

where $h^*$ is the enthalpy for an ideal gas at the given temperature and with the same composition. This departure function can be determined using the EoS [60]:

$$h - h^* = \frac{1}{W} \left[ R_u T (Z - 1) + \frac{T}{b} \frac{da}{dT} - a \ln \frac{Z + B}{Z} \right]$$  

(2.12)

The species specific enthalpy $h_k$ is also evaluated using Equation 2.12, where the mixture parameters are replaced by those corresponding to the individual species.

From basic thermodynamic relations, the fugacity coefficient can be expressed in terms of temperature and volume (or temperature and pressure). For the SRK EoS case, the fugacity coefficient of species $i$ is

$$\ln[\Phi_i] = \frac{b_i}{b}(Z - 1) - \ln[Z - B] - \frac{A}{B}(2\left(\frac{a_i}{a}\right)^{0.5} - \frac{b_i}{b}) \ln[1 + \frac{B}{Z}]$$  

(2.13)

### 2.3 Determination of Thermodynamic Relations

We shall proceed by considering constant pressure processes. The partial derivatives of $\Phi$ can be obtained from Equation (2.13). The following relations can be applied to either the
liquid or gas.

\[
\frac{\partial \Phi_i}{\partial T}_{p,T} = \Phi_i((1 - \frac{b_i}{b}) \frac{1}{T} - \frac{A}{B} \left[ \frac{1}{T} - \frac{\partial a}{\partial T} \right] [2(\frac{a_i}{a})^{0.5} - \frac{b_i}{b}] \ln(1 + \frac{B}{Z}) \\
+ \frac{Aa_i^{0.5}}{Ba^{0.5}} \left[ \frac{1}{a \partial T} - \frac{1}{a_i \partial T} \right] \ln(1 + \frac{B}{Z}) + \left[ \frac{b_i}{b} - \frac{1}{Z - B} \right] \frac{Z}{v \partial T} \bigg|_{p,X_i} \bigg) \\
+ \frac{A}{B + Z} \left[ 2 \left( \frac{a_i}{a} \right)^{0.5} - \frac{b_i}{b} \right] \frac{1}{v \partial T} \bigg|_{p,X_i} ;
\]

(2.14)

\[
\frac{\partial \Phi_i}{\partial X_j}_{p,X_i} = \Phi_i \left( \frac{B}{Z - B} \frac{b_i}{b} + \frac{A}{Z + B} \frac{b_i b_j}{b^2} - \frac{2A}{Z + B} \left( \frac{a_i}{a} \right)^{0.5} \frac{b_i}{b} - \frac{b_j}{b^2}(Z - 1) \\
\right) \\
\left[ \frac{b_i}{b} \left( Z - \frac{A}{Z + B} \right) - \frac{Z}{Z - B} + \frac{2A}{Z + B} \left( \frac{a_i}{a} \right)^{0.5} \right] \frac{1}{v \partial X_j}_{p,T} \\
+ \frac{2A}{B} \left[ \left( \frac{a_i}{a} \right)^{0.5} - \frac{b_i}{b} \right] \left[ \frac{b_j}{b} - \sum_{i=1}^{\tilde{N}} X_i \frac{(a_i a_j)^{0.5}(1 - k_{ij})}{a} \right] \ln \frac{Z + B}{Z} \bigg|_{p,t} ;
\]

(2.15)

\[ i = 1, ..., \tilde{N} ; \quad j = 1, ..., \tilde{N} \]

From differentiation of Equation (6.4), one obtains

\[
\frac{\partial h^*}{\partial T}_{p,T} = c_p|_{\text{ideal gas}} ;
\]

\[
\frac{\partial h^*}{\partial X_i}_{p,T} = \int_{T_{\text{ref}}}^{T} c_{p,i}|_{\text{ideal gas}} dT' \\
\frac{\partial (h - h^*)}{\partial T}_{p,X_i} = \frac{1}{W} \left( \frac{T}{b} \frac{\partial^2 a}{\partial T^2} \ln \frac{Z + B}{Z} - R_a \right) + \frac{1}{W} \left( p - a - T(\partial a/\partial T) \frac{B}{Z + B} \frac{1}{v \partial T} \right) \bigg|_{p,X_i} ;
\]

(2.16)

\[
\frac{\partial (h - h^*)}{\partial X_i}_{p,T,X_j, j \neq i} = \frac{1}{W} \left( \frac{T}{b} \frac{\partial a}{\partial T} - a \frac{B}{Z + B} \frac{b_j}{b} \right) + \frac{1}{W} \left( \frac{b_j a - T(\partial a/\partial T)}{b} \right) \\
+ \frac{T \partial^2 a/\partial T \partial X_j - \partial a/\partial X_j}{b} \ln \frac{Z + B}{Z} \\
+ \frac{1}{W} \left( p - \frac{T(\partial a/\partial T) - a}{b} \frac{B}{Z + B} \frac{1}{v \partial T} \right) \frac{1}{\partial X_i} \bigg|_{p,T,X_j, j \neq i} - (h - h^*) \frac{W_j}{W} ;
\]

\[ i = 1, ..., \tilde{N} \]
where the derivatives for \( a \) for a mixture are given by

\[
\frac{\partial a}{\partial T} \bigg|_{X_i} = \frac{1}{2} \sum_{i=1}^{\tilde{N}} \sum_{j=1}^{\tilde{N}} X_i X_j \left[ \left( \frac{a_i}{a_j} \right)^{0.5} \frac{da_j}{dT} + \left( \frac{a_j}{a_i} \right)^{0.5} \frac{da_i}{dT} \right] (1 - k_{ij})
\]

\[
\frac{\partial a}{\partial X_j} \bigg|_T = 2 \sum_{i=1}^{\tilde{N}} X_i (a_i a_j)^{0.5} (1 - k_{ij})
\]

\[
\frac{\partial^2 a}{\partial T^2} \bigg|_{X_i} = \frac{1}{2} \sum_{i=1}^{\tilde{N}} \sum_{j=1}^{\tilde{N}} X_i X_j \left[ \left( \frac{1}{a_i a_j} \right)^{0.5} \frac{d^2 a_j}{dT^2} + \left( \frac{1}{a_i a_j} \right)^{0.5} \frac{d^2 a_i}{dT^2} \right] (1 - k_{ij})
\]

\[
+ \frac{1}{2} \sum_{i=1}^{\tilde{N}} \sum_{j=1}^{\tilde{N}} X_i X_j \left[ \left( \frac{a_i}{a_j} \right)^{0.5} \frac{da_j}{dT} \frac{da_i}{dT} - \left( \frac{a_j}{a_i} \right)^{0.5} \frac{1}{a_i} \left( \frac{da_i}{dT} \right)^2 \right] (1 - k_{ij})
\]

\[
\frac{\partial^2 a}{\partial T \partial X_j} = \sum_{i=1}^{\tilde{N}} X_i \left[ \left( \frac{a_i}{a_j} \right)^{0.5} \frac{da_j}{dT} + \left( \frac{a_j}{a_i} \right)^{0.5} \frac{da_i}{dT} \right] (1 - k_{ij})
\]

The differential of Equation (2.6) can be obtained as

\[
\]

Changes in \( A \) and \( B \) are forced by changes in \( T \) and \( X_i \) for our constant pressure situations. These will in turn cause changes in \( Z \). A change in \( Z \) at constant pressure implies a change in temperature and / or the mole fractions. The above differential equation and the following equations can be applied to either phase. Use of Equations (2.7-2.9) allows the following determinations:

\[
dZ = \frac{\partial Z}{\partial T} \bigg|_{p, X_i} dT + \sum_{i=1}^{\tilde{N}} \frac{\partial Z}{\partial X_i} dX_i = \left( - \frac{Z}{T} + \frac{Z}{v} \frac{\partial v}{\partial T} \right) dT + \frac{Z}{v} \sum_{i=1}^{\tilde{N}} \frac{\partial v}{\partial X_i} \bigg|_{p, X_j, j \neq i} dX_i,
\]

\[
dA = \frac{\partial A}{\partial T} \bigg|_{p, X_i} dT + \sum_{j=1}^{\tilde{N}} \frac{\partial A}{\partial X_i} \bigg|_{p, X_j, j \neq i} dX_i = \left( - \frac{2A}{T} + \frac{A}{a} \frac{da}{dT} \right) dT + \frac{2A}{a} \sum_{i=1}^{\tilde{N}} \left[ \sum_{j=1}^{\tilde{N}} X_j (a_i a_j)^{0.5} (1 - k_{ij}) \right] dX_i.
\]

\[
\frac{dB}{\partial T} \bigg|_{p, X_i} dT + \sum_{j=1}^{\tilde{N}} \frac{dB}{\partial X_i} \bigg|_{p, X_j, j \neq i} dX_i = -\frac{B}{T} dT + \frac{B}{b} \sum_{i=1}^{\tilde{N}} b_i dX_i
\]
From Equations (2.18) and (2.19), the $\tilde{N} + 1$ partial derivatives of $v$ can be determined. In particular, we obtain

$$\frac{\partial v}{\partial T} \bigg|_{p,X_i} = \frac{R_u T}{p} \left( \frac{Z}{T} + \frac{(B - Z)((A/a)(\partial a/\partial T) - 2A/T) - (B/T)(Z + 2BZ + A)}{3Z^2 - 2Z + A - B - B^2} \right);$$

$$\frac{\partial v}{\partial X_i} \bigg|_{p,TX_j,j\neq i} = \frac{R_u T}{p} \left( \frac{2(B - Z)(A/a)\sum_{j=1}^{\tilde{N}}[X_j(a_i a_j)^{0.5}(1 - k_{ij})] + (Z + 2BZ + A)Bb_i/b}{3Z^2 - 2Z + A - B - B^2} \right);$$

$$i = 1, \ldots, \tilde{N}$$

(2.20)

These relations for the partial derivatives can be used in the differential relation for enthalpy.
Chapter 3

Single-Phase Counterflow Diffusion Flame

3.1 Introduction

This Chapter will give similar solutions that provide reliable conclusions about the laminar steady axisymmetric counterflow diffusion flame structure and location at very high pressures. An application of these solutions is found, for example, in the flamelet model for turbulent flames.

The literature on counterflow diffusion flame problems is broad and continues to expand. It includes analytical, experimental and numerical approaches [61, 62]. Such flames are of fundamental interest because they approximate a one-dimensional character and because residence times within the flame zone can be easily varied [63]. This laminar flame has also been proposed as a key element in the complex structure of turbulent nonpremixed flames [64].
Even though most of the literature deals with situations at atmospheric pressure and ideal-gas conditions, some recent papers used numerical methods to examine flame characteristics entailing real-gas formulations to account for the high-pressure effects. Also, most specific examples are for oxygen/hydrogen systems, with less attention being given to hydrocarbons. For instance, an O$_2$/H$_2$ system was explored to find a correlation between the flame thickness and heat-release rate with the pressure-weighted strain rate [65]. Flame instabilities were studied in [66] using a flamelet model. Detailed investigation of the extinction strain rates appeared later for counterflow diffusion flames at subcritical and supercritical conditions for oxygen/hydrogen mixtures [67] and for oxygen/n-alkane hydrocarbons [68]. These papers identified general similarities in the mixture-fraction space in terms of flame temperature, species concentrations, flame thickness, and heat-release rate, suggesting that the flame behaviors at high pressure can be evaluated by their counterpart at low pressure. With regard to the n-alkane family of fuels, similarities indicated that flame properties of a given hydrocarbon can be predicted from those of another hydrocarbon at the same flow conditions.

Counterflow diffusion flame experimental studies at atmospheric pressure are common. For instance, results of an axisymmetric configuration with methane and enriched air were compared to computational solutions obtained from both one-dimensional and two-dimensional mathematical models [69]. The comparison between the experimental and computational data yielded excellent agreement for all measured quantities. Studies of the same kind at elevated pressures are unconventional, but some exist. See, for example, [70–72] for pressures up to 2.5 MPa.

The literature also includes studies with regard to the presence of water premixed with the fuel stream at atmospheric pressure. An experiment [73] was conducted under microgravity conditions to study the influence of water mists on premixed flames propagating in a cylindrical tube. Results showed that the flame speed initially increases due to the thermal expansion of combustion gases with higher water content, while a later decrease in flame
speed is caused by heat removal, mixture dilution, and radical recombination. A numerical counterflow analysis was presented, where air was introduced on one side and a preheated mixture of water vapor/methane entered on the other side [74]. Extinction limits were explored and compared with experimental results. Agreement was found for suitable fuel and oxidizer flow rates. Extinction occurred with lower water content compared to experiments when simulations were performed at higher flow rates, revealing the influence of strain rate. In another study, the dilution extinction limits of $\text{H}_2-\text{O}_2$ diffusion flames were assessed by mixing water with the fuel, where $\text{H}_2\text{O}$ modeled combustion products [75]. Other reasons for water injection into the combustion chamber include decreasing exhaust temperature and associated NOx emissions, flame extinguishment, or studying combustion efficiency [76–79].

In comparison with the reviewed literature, results presented in this Chapter contribute in several significant new aspects: (1) a real-gas model that entails fewer simplifying assumptions than previous studies (a more complete energy equation with the associated enthalpy correction for mixtures is presented and evaluated); (2) evaluation of the effects of various high-pressure corrections and determination of their relative importance; (3) evaluation of the correct use of fugacities as opposed to partial pressures in chemical-equilibrium calculations; (4) quantification of the radiative heat losses at high pressure; (5) evaluation of the Soret effect at high pressure; (6) analysis of turbulent kinetic energy generation due to shear in the stagnation plane; (7) extension of scaling rules to higher pressures; and (8) analysis of the effects of introducing water vapor in the fuel stream at high pressure. To the best of the authors’ knowledge, points 1 through 7 have not been done before. Point 8 has been done for a $\text{H}_2-\text{O}_2$ flame [75], but not for methane and air at high pressures in relation to the methane hydrates and other applications.

In Section 3.2, we review the mathematical model that we use in our study. The method of solution, validation, and results are presented in Sections 3.3, 3.4, and 3.5, respectively. Supporting information on chemical equilibrium is presented in 3.5.5.
3.2 Model

Figure 3.1 shows a sketch that represents the axisymmetric flow between two circular opposed jets and the flame that is generated. Pure methane or a mixture of methane with water vapor flows from the left nozzle while air flows from the right nozzle. Under the boundary-layer approximation, the two-dimensional problem may be simplified to a system of ODEs with the independent variable that is the x-coordinate normal to the stagnation plane [80, 81]. Slightly different formulations are available, depending on which parameter is chosen to alter the strain. Prescribing the momentum fluxes at the exit of the nozzles fixes the radial pressure gradient and the strain rate of the problem, or vice versa. The approach described in [81] is followed with modifications in the energy equation and the equation of state.

![Diagram of non-premixed counterflow axisymmetric configuration](image)

Figure 3.1: Non-premixed counterflow axisymmetric configuration.

The governing equations are summarized below, starting with the steady-state continuity equation in cylindrical coordinates.

\[
\frac{\partial (r\rho u)}{\partial x} + \frac{\partial (r\rho v)}{\partial r} = 0 \tag{3.1}
\]

The stream function is introduced as \( \Psi(x, r) \equiv r^2 F(x) \), which satisfies the steady-state
continuity equation exactly if

$$\frac{\partial \Psi}{\partial r} = r \rho u = 2r F \quad \text{and} \quad -\frac{\partial \Psi}{\partial x} = r \rho v = -r^2 \frac{dF}{dx}. \quad (3.2)$$

Then, the axial velocity $u$ depends only on $x$ and the radial velocity $v$ varies linearly in $r$. The temperature $T$ and species mass fractions $Y_k$ are also functions of $x$ only. Using the small Mach number approximation, the thermodynamic pressure $p$ is assumed to be constant in the equation of state but pressure-gradient terms are allowed in the momentum equations, where the term $d(r \tau_{rr})/dr$ associated with the stress in the radial direction is neglected from the boundary-layer analysis. The pressure gradient in the axial direction is zero at the stagnation point, even without taking any boundary-layer approximation. Furthermore, the Navier-Stokes equations are satisfied exactly at that point. This is a classic result for stagnation-point flow. Away from the stagnation point, but still in the central streamline, the pressure gradient is of the order of Mach number squared ($M^2$). Also, we have that $M << 1$, given that the flow speed will be at most 1 m/s, and the speed of sound will be around 340 m/s in the worst case scenario. Therefore, the pressure gradient in the axial direction is negligible, and the stagnation pressure, which will be the same on either side of the stagnation plane, will also be essentially the same at the boundaries.

With these considerations and neglect of body forces, the momentum equations reduce to third-order ordinary differential equations. From these equations, an eigenvalue independent of $x$ appears: $H = r^{-1} dp/dr$.

Define the function $G(x) = dF/dx$. Then, the radial momentum equation becomes a 2nd-order ODE rather than one of 3rd order,

$$H - 2 \frac{d}{dx} \left( \frac{FG}{\rho} \right) + \frac{3}{\rho} G^2 + \frac{d}{dx} \left[ \mu \frac{d}{dx} \left( \frac{G}{\rho} \right) \right] = 0 \quad (3.3)$$
where \( \mu \) is the viscosity.

The species continuity equation is

\[
2F \frac{dY_k}{dx} + \frac{d}{dx}(\rho Y_k V_k) - W_k \dot{\omega}_k = 0 \quad k = 1, 2, \ldots, K
\]  

(3.4)

where the index \( k \) identifies each species and \( K \) is the total number of species.

The energy equation for non-ideal gases is

\[
2F \left( \left( \frac{dh}{dx} - \sum_{k=1}^{K} h_k \frac{dY_k}{dx} \right) - \frac{d}{dx} \left( \lambda \frac{dT}{dx} \right) + \rho \sum_{k=1}^{K} Y_k V_k \frac{dh_k}{dx} + \sum_{k=1}^{K} W_k h_k \dot{\omega}_k \right) = 0.
\]  

(3.5)

where \( \lambda \) is the thermal conductivity, \( h \) is the mixture specific enthalpy, \( h_k \) is the species specific enthalpy, \( W_k \) are the species molecular weights and \( \dot{\omega}_k \) is the rate of consumption. Both \( h \) and \( h_k \) are computed from fundamental thermodynamic theories as the summation of the ideal-gas enthalpy plus a departure function that accounts for dense fluid effects (see Section 2.2). It includes both the heat of formation and the sensible enthalpy. Heat losses due to radiation are neglected. Below, we confirm their minor importance compared to the energy conversion rate and heat conduction rate. (See section 3.4.) For ideal gases, Eq. 3.5 reduces to

\[
2F c_p \frac{dT}{dx} - \frac{d}{dx} \left( \lambda \frac{dT}{dx} \right) + \rho \sum_{k=1}^{K} c_{p_k} Y_k V_k + \sum_{k=1}^{K} W_k h_k \dot{\omega}_k = 0
\]  

(3.6)

where \( c_p \) is the specific heat at constant pressure. The viscosity \( \mu \) and thermal conductivity \( \lambda \) are to be evaluated both with ideal gases and with empirically correlated functions that were developed to extend kinetic gas theory to include dense fluids [82].

\( V_k \) is the diffusion velocity and it is evaluated using the multicomponent formulation [63], in
which pressure effect has been neglected.

\[
V_k = \frac{1}{X_k \bar{W}} \sum_{j=1}^{K} D_{kj} W_j \frac{dX_j}{dx} - \frac{D^T_k}{\rho Y_k T} \frac{dT}{dx} \quad \text{(3.7)}
\]

\(X_k\) are the species mole fractions, \(\bar{W}\) is the mean molecular weight, \(D_{kj}\) are the ordinary multicomponent diffusion coefficients, and \(D^T_k\) are the thermal-diffusion coefficients. Ideal gas thermodynamic and transport properties, as well as the reaction rates are obtained from the CHEMKIN [83] library of subroutines. The second term on the right hand side of Equation 3.7, also known as Soret effect, is in general neglected. However, for comparison purposes, we perform a check including this effect for one of our cases at 100 atm (see the discussion in Section 3.5.3 and Figure 3.11).

A simplified version of Eq. 3.5 results from the approximation that the enthalpy of the mixture \(h = \sum_k Y_k h_k\) in the convective term.

\[
2F \sum_{k=1}^{K} Y_k \frac{dh_k}{dx} - \frac{d}{dx} \left( \lambda \frac{dT}{dx} \right) + \rho \sum_{k=1}^{K} Y_k V_k \frac{dh_k}{dx} + \sum_{k=1}^{K} W_k h_k \omega_k = 0. \quad \text{(3.8)}
\]

Eq. 3.8 has been used in the literature as a real-gas model [10, 65, 67, 68]. However, the underlying assumption is that \(h = \sum_k Y_k h_k\), which is not necessarily satisfied when dealing with real gases.

The three forms of the energy equation (Eq. 3.5, Eq. 3.6, and Eq. 3.8) are employed in this study for comparison purposes.

The eigenvalue \(H = \text{constant},\) the equation \(G = dF/dx,\) Eq. 3.3 and 3.4, together with the energy equation and the SRK EoS (see Chapter 2, Section 2.2), form a well-posed boundary-value problem, where the unknowns are \(H, F = \rho u/2, G = -\rho v/r, Y_k, T\) and \(\rho.\) For the given chemical mechanism involving \(K\) species, the total number of differential equations is \(K + 3\) and the number of difference equations is \(N(K + 3)\), where \(N\) is the number of grid
points. Plug-flow boundary conditions are specified at the exit of the nozzles. As described in [84], these conditions can be reproduced accurately in laboratory experiments. In the following, $F$ and $O$ stand for fuel and oxidizer, respectively. At $x = 0$:

$$F = \frac{\rho_F u_F}{2}, \quad G = 0, \quad T = T_F, \quad Y_k = (Y_k)_F$$

(3.9)

At $x = L$:

$$F = \frac{\rho_O u_O}{2} = -\frac{\rho_F u_F}{2}, \quad G = 0, \quad T = T_O, \quad Y_k = (Y_k)_O$$

(3.10)

We prescribe $u_F = 1$ m/s. The mass flux at $x = L$ is set to be equal in magnitude to the mass flux at $x = 0$ with opposite sign. Thus, $u_O$ is also prescribed. Previous articles such as [67, 68] match the momentum fluxes instead of mass fluxes. The choice is arbitrary and the consequences are mild as shown in 3.5.6. In our study, the Reynolds Number in the vicinity of the stagnation plane layer is, at most, of the order of $10^4$. Later, we explain how turbulence can be avoided. (See section 3.4.)

With regard to chemical kinetics, the detailed reaction mechanism GRI 3.0 [85] is selected, which consists of $K = 53$ species and 325 elementary reactions. Available reaction mechanisms were developed at relatively low pressures. These mechanisms bring the species into chemical equilibrium, which in the classical form is based on partial pressures. At elevated pressures, however, chemical equilibrium is based on fugacities. We perform a check in 3.5.5 and validate that the differences are small. An unresolved concern arises with the use of existing chemical kinetic mechanisms (pathways) at very high pressures, since there is a lack of experimental validation.
3.3 Solution Method

A new simulator program has been written, which contains the mathematical model and boundary conditions. The differential equations are discretized using conventional finite-differencing techniques for nonuniform mesh spacing. Central differences are used for diffusive terms, with truncation error that is second-order. For better convergence, convective terms are discretized with upwind differencing, using the sign of the velocity to choose in which direction the spatial difference should go. For such terms, the truncation error is of first-order, leading to what is often called “artificial diffusion”, but this form avoids unwanted oscillations during the solution on a coarse mesh. The simulator program calls the boundary-value problem solver TWOPNT [86] to determine the steady-state solution. In the counterflow-diffusion-flame problem, the cost of forming and factoring the Jacobian matrix can be very expensive. For this reason, TWOPNT is based on a modified Newton’s iteration method in which the Jacobian matrix is retained through several steps and re-evaluated only periodically. The iteration process begins from a solution guess with a coarse mesh. When a steady-state solution is found for a particular mesh, TWOPNT constructs a succession of finer grids with more points located where the solution changes abruptly until mesh independence is achieved. The criterion that determines grid independence (defined in Appendix A) is based on two tolerance values chosen by the user. We used 0.5 for both. If the steady-state search fails, TWOPNT undertakes a transient evolution solely to replace the starting guess by a better estimate. The evolution here is a pseudo-transient process, valuable only for producing the steady asymptote. The following time-dependent terms are added to the left side of the momentum, energy and species equations, respectively:

\[
\begin{align*}
\text{Momentum:} & \quad \frac{dG}{dt}, \\
\text{Species:} & \quad \rho \frac{dY_k}{dt}, \\
\text{Energy:} & \quad \rho \frac{dh}{dt} - \sum_k \rho h_k \frac{dY_k}{dt}.
\end{align*}
\]  

(3.11)
The transient term used with the simplified forms of the energy equation (Eq. 3.6 and Eq. 3.8) is $\rho c_p \frac{dT}{dt}$.

Note that the true transient equations would have a time derivative in the continuity equation, thereby disallowing the creation of a stream function until a steady-state is reached. However, these pseudo-transient equations still give asymptotically the steady state while allowing a stream function to be created during the transient period.

Simulations at higher pressures can present convergence difficulties. So, when the pressure is increased, the solution of a previous case at a lower pressure is employed as the initial guess.

### 3.4 Verification and Validation

In order to validate our code, temperature profiles have been compared against experimental data at the highest possible pressure values. Temperature profiles are taken from [70] at 0.2, 0.4 and 0.8 MPa. We ran simulations with the same boundary conditions and domain size, entailing our most complete set of high-pressure corrections. As shown in Figure 3.2, there is good agreement between our computations and the experimental results.

Validation at 100 atm is also presented against numerical results from [68] for a methane-oxygen system where the strain rate is 1000 1/s. Figure 3.2b highlights a small difference in peak temperature. The source of this deviation could be due to the use of different chemical kinetics schemes or the different sub-models. To answer this question, we obtained a solution with our model and a reduced chemical kinetic mechanism that entails 19-species and 15 steps[87]. The curves belonging to our detailed and reduced chemistry sets are practically superimposed. The peak temperature resulting from the use of reduced chemistry is only 4 K hotter than for detailed chemistry, while the peak temperature in [68] is 60 K hotter than our detailed kinetics result. Thus, the deviation from [68] cannot be explained by the use of
different chemical kinetic schemes and is primarily diffusion controlled. Consequently, our additional correction makes a modest difference at the given strain rate.

As mentioned in the Model section, a check on the importance of radiative effects was performed. To this effect, we estimated the radiative heat rate and compared it with the energy conversion rate and the conductive heat rate. The calculations on radiation are based on a method published elsewhere [88]. The radiative heat loss is computed as $q_{rad} = \sum_{k=1}^{K} p_k \kappa_k \sigma (T^4 - T_b^4)$, where $p_k$ is the partial pressure, $\kappa_k$ is the Planck mean absorption coefficient for species $k$, $\sigma$ is the Stefan-Boltzmann constant, and $T_b$ represents the temperature of the background environment (300 K). The Planck mean absorption coefficients depend on the species and temperature. They are taken from 5th degree Gaussian curve fittings reported in [88]. Four species (CO$_2$, H$_2$O, CO, NO) are used. The results are illustrated in Figure 3.3, which shows a blow up of the heating zone from Case 6 (real-gas model without water, see section 3.5) at a pressure of 100 atm.

Figure 3.3a shows temperature and three black curves that represent conductive heat rate (solid), radiative heat rate (dotted), and energy conversion rate (dashed). The energy con-
Figure 3.3: Comparison of radiation, conduction, and energy conversion rates at 100 atm for Case 6 in Sub-figures a and b, and Case 8c in Subfigures c and d.
version rate and heat rate by conduction are practically matched. The radiation curve is on the zero line. Figure 3.3b highlights the small magnitude of the radiative rate compared to conduction and conversion. Sub-figures 3.3c and 3.3d display the same quantities for Case 8c (real-gas model with the highest studied water content, see section 3.5), also at a pressure of 100 atm. The radiative heat rate is now greater than it was for Case 6, but its value is still two orders of magnitude below the other two energy rates. Thus, we conclude that radiation can be neglected.

Let us discuss how the flow can remain laminar even at the high Reynolds number at high pressures. We identify four potential sources of turbulence: (i) turbulence coming from the interior of the two burner ducts; (ii) buoyancy instability; (iii) turbulence being generated in the shear layer of the gas jet; and (iv) turbulence being generated in the shear layer near the stagnation plane region. See the sketch presented in Figure 3.4a where these four regions have been highlighted. Below we review each one of these turbulence sources.

(i) We can assume that the nozzles are equipped with suitable porous materials or very fine grids such that any eddies entering from the nozzles would decay in a very short distance
after entering the studied domain.

(ii) A discussion on the appearance of instabilities due to buoyancy is presented in [84]. The authors report that special care is needed to produce turbulence when it is needed. They also note that laminar flow has been obtained at 25 atm and laminar behavior at higher pressures can be expected if the layer with density variation has its thickness decreasing as $p^{-2/3}$ or faster. See Figure 3.4b, which shows the variation of flame thickness for Case 6 in this study (solid), the variation with $p^{-1/2}$ (dotted, from the literature), and the variation with $p^{-2/3}$ (dashed). There is no significant difference between the three curves in terms of order of magnitude. Hence, we can also assume very little instability will appear from source (ii).

(iii) Turbulence generated in the outer shear layer of the jet may be avoided with the use of a co-flow, which in fact is a common practice in actual experiments.

(iv) To justify our neglect of turbulence from this fourth source, we include an order of magnitude analysis using a well-established equation for the calculation of the advective flux, diffusion, generation, and dissipation of turbulent kinetic energy in a shear-layer. The equation is taken from [89]:

$$
\rho \frac{Dk}{Dt} = -\frac{\partial}{\partial y} (\rho v' k + k' \nu') - \rho u' \frac{\partial k}{\partial y} - \sum \left( \frac{\partial u'_i}{\partial x_j} \right)^2.
$$

The three terms on the right hand side represent diffusion, production, and dissipation, respectively. We identified that the production term is dominant with respect to dissipation. So, we look at the worst case scenario where only production plays a role. We have that $(u' \nu') = \mathcal{O}(k)$ which arbitrarily maximizes production rate by assuming that both velocity components have comparable magnitudes and the fluctuation velocity components are well
correlated. $\partial u / \partial y$ in our coordinate system is $\partial v / \partial x$. We obtain the order of magnitude of this quantity from the solution of Case 6 at 100 atm. Taking the order of magnitude of the radial direction as $\mathcal{O}(r) = 10^{-2}$ m, we get from Figure 3.5 that $\mathcal{O}(\partial v / \partial x) = 10^5 \mathcal{O}(r) = 10^3$ 1/s.

![Figure 3.5: Derivative in the axial direction of $v/r$.](image)

Therefore, a rough but conservative estimate neglecting any decrease in $k$ due to diffusion or dissipation yields

$$\frac{1}{k} \frac{\Delta k}{\Delta t} = \mathcal{O}(10^3 \frac{1}{s}).$$  \hspace{1cm} (3.13)

We obtain the characteristic flow time in the radial direction by dividing the radii of 1 cm by the characteristic velocity of 1 m/s. Hence, $\Delta t = \mathcal{O}(10^{-2}$ s). With this, we get the order of magnitude in the change of turbulent kinetic energy along the radial direction near the stagnation plane:

$$\frac{\Delta k}{k} = \mathcal{O}(10).$$  \hspace{1cm} (3.14)
The maximum mean velocity in the radial direction is of the order of 1 m/s, but it is much smaller near the stagnation point, which is the starting region for this class of turbulence. We take for this region the magnitude $\bar{v} = O(0.1 \text{ m/s})$. The velocity fluctuation for fully developed turbulent flow is of the order of 5 to 10% of the mean velocity. However, near the stagnation point, turbulence only will start being generated. So, we could estimate that the velocity fluctuation $v' = O(10^{-3} \text{ m/s})$ or less in that region near the flow axis. That is, we take the velocity fluctuation in that stagnation region to be an order of magnitude less than the local value for fully developed turbulence. Thus, the turbulent kinetic energy near the stagnation point is $k = O(10^{-6} \text{ m}^2/\text{s}^2)$. At $r=1$ cm, our previous estimate yields $k = O(10 \times 10^{-6}) = O(10^{-5} \text{ m}^2/\text{s}^2)$. $k$ increases tenfold, therefore, the velocity fluctuation increases about threefold. At $r=1$ cm: $v' = O(3 \times 10^{-3} \text{ m/s})$ and $\bar{v} = 1 \text{ m/s}$.

This analysis shows that the velocity fluctuation in the radial direction is two-to-three orders of magnitude below the mean velocity, even when dissipation and diffusion away from the production region are not considered. For our problem, we deem the laminar flow assumption valid because turbulence is essentially not being generated to any meaningful extent.

### 3.5 Results

Eight cases are studied as defined in Table 3.1, each with varied pressure from 1 to 100 atm. The distance between the two nozzles is $L = 2$ cm, similar to what is used in typical experiments. Pure methane flows against air in Cases 1 through 7, where the temperature at both boundaries is 300 K, and the fuel inflow velocity equals to 1 m/s. The air nozzle flow speed is calculated according to the $F$ boundary condition (see Equation 3.10). As mentioned in the Introduction section, one of our goals is to determine the relative importance associated with high-pressure rectifications. Differences across Cases 1-7 reflect three real-gas corrections: (I) replacement of the ideal-gas law by the cubic equation of state; (II) use of the real-gas
Table 3.1: Studied Cases

<table>
<thead>
<tr>
<th>Case</th>
<th>Correction I: EoS</th>
<th>Correction II: Energy equation</th>
<th>Correction III: $\mu$ and $\lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ideal</td>
<td>Ideal (Eq. 3.6)</td>
<td>Ideal</td>
</tr>
<tr>
<td>2</td>
<td>Ideal</td>
<td>Ideal (Eq. 3.6)</td>
<td>Corrected</td>
</tr>
<tr>
<td>3</td>
<td>Cubic</td>
<td>Ideal (Eq. 3.6)</td>
<td>Ideal</td>
</tr>
<tr>
<td>4</td>
<td>Ideal</td>
<td>Corrected (Eq. 3.5)</td>
<td>Ideal</td>
</tr>
<tr>
<td>5</td>
<td>Cubic</td>
<td>Corrected (Eq. 3.5)</td>
<td>Ideal</td>
</tr>
<tr>
<td>6</td>
<td>Cubic</td>
<td>Corrected (Eq. 3.5)</td>
<td>Corrected</td>
</tr>
<tr>
<td>7</td>
<td>Cubic</td>
<td>As in literature (Eq. 3.8)</td>
<td>Corrected</td>
</tr>
<tr>
<td>8a</td>
<td>Equivalent to Case 6 - Fuel inlet contains 10% water vapor.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8b</td>
<td>Equivalent to Case 6 - Fuel inlet contains 20% water vapor.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8c</td>
<td>Equivalent to Case 6 - Fuel inlet contains 40% water vapor.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

No corrections are used in Case 1. Only the transport properties are corrected in Case 2. Case 3 is equipped with the cubic EoS and no other corrections. Case 4 entails the real-gas energy equation (Eq. 3.5), ideal-gas law, and no transport modification. A combination of corrections (I) and (II) are used in Case 5, while Case 6 presents all three corrections. Case 7 is used to study the error introduced by assuming that the enthalpy of the mixture equals the summation of the enthalpy of each component times its mass fraction in the energy equation. Namely, it uses a more simplified version of the energy equation (Eq. 3.8 as presented in previous studies [10, 65, 67, 68] instead of the Eq. 3.5).

In addition, Case 8 is used to study the effect of water vapor content premixed with the methane in the fuel stream. All high-pressure corrections are enabled in this case. The temperature at the exit of the fuel stream is raised to 600 K, a value that is above the saturation temperature of water at 100 atm. See Table 3.1 for a summary of these cases.

The comparative study between cases 1-6 is shown in sub-section 3.5.1. The effects of the new enthalpy approach in the energy equation are discussed in sub-section 3.5.2. Results and discussion of the cases entailing the most complete physical model with and without premixed water vapor (Cases 6 and 8) are shown in sub-sections 3.5.3 and 3.5.4.
3.5.1 Comparing Cases 1-6

To better assess the effects of the three corrections, solutions for Cases 1 through 6 at 100 atm are plotted together in Figures 3.6 and 3.7. For a given pressure, temperature, composition, and fuel-inlet velocity, the most accurate mass flow rates at the boundaries are given by the real-gas model. Use of simplified models such as the ideal-gas law, yield a less accurate density value at the boundaries which of course affects the mass flow rates. The choice here is arbitrary: (i) either keep the fuel-inlet velocity, temperature, pressure, and composition fixed at the boundaries and only change the model; or (ii), if we wanted to keep the mass flow rates the same when comparing between ideal and real models, we would have to modify the temperature, pressure, or composition such that the density at the boundaries matched between real and ideal models. (Or we must change the inlet velocity which would affect the strain rate.) We chose the former approach (i) because they present as the given parameters the more easily measurable quantities. As mentioned above, we prescribe the velocity at the exit of the fuel nozzle and match the mass flow rates of the two nozzles. Note that under the latter approach (ii), we would be studying two different problems.

Sub-figures 3.6a, b, and d show two groups of almost overlapped curves, one containing Cases 1, 2, 4 and the other including Cases 3, 5 and 6. These figures show the whole domain. A narrower domain is shown in the rest of the figures to gain resolution. A closer look to the velocity profiles shows that the correction in transport properties has a very small effect on the solutions. In contrast, application of the cubic equation of state introduces a substantial difference, which moves the flame and stagnation coordinate closer to the center plane. Correction of the energy equation causes more change than transport correction, but is less significant than replacing the equation of state. Furthermore, it moves the stagnation plane away from the center of the domain.

Sub-figure 3.6d shows the function $G$, which is related to the radial velocity $v$. The curves
exhibit an almost linear behavior for most of the domain except for a thin layer around the
flame. We can see a substantial change in the slope of the linear part of the curves for the
cases entailing the cubic equation of state.

Analysis of sub-figures 3.6e and 3.6f shows that substantial changes in density occur due
to the variation in compressibility factor with respect to unity, specially on the fuel side.
Indeed, when we look at sub-figure 3.6f, we see that methane density is significantly higher
for cases with the cubic equation of state (3, 5 and 6), which means that more momentum
flux comes from the left side of the domain. Hence, the difference on the left boundary
of sub-figure 3.6a. Also, an increase of density on the left side combined with almost no
change in density on the right side means that the velocity at the exit of the right nozzle
must increase in magnitude (again due to the used boundary condition for $F$, see Equation
3.10). Since the momentum flux equals to $\rho u^2$, the increase in velocity magnitude on the
right causes the right momentum flux to rise more than the left flux. The final result is that
the stagnation plane in Case 3 gets displaced to the left with respect to Case 1, but it still
sits on the right side of the symmetry plane.

Let us turn our attention to the effects caused by the use of the real-gas energy equation
(Equation 2.3) instead of the ideal version, together with the enthalpy departure function
correction. Sub-figure 3.7a shows temperature profiles for the different cases. As opposed
to the correction in the equation of state, the main effect of mending the energy equation
is shifting the flame towards the air nozzle. The flame structure, however, remains almost
unaltered, except for a slight decrease in flame temperature for the cases with corrected
energy equation, which can be explained if we look at the enthalpy.

Sub-figure 3.7b portrays the enthalpy departure function and it’s percentage difference com-
pared to the sensible enthalpy of the mixture. The correction is more important in the
cold regions and in the heating zones. The correction becomes less important in the hot
region. Overall, the percentage difference between departure function and sensible enthalpy

54
is below at most 4%. The corrections in enthalpy departure and compressibility factor are very similar among the cases where they apply, with shifts in the $x$-direction due to the flame location. Their effect diminishes at the location where the flame peaks, confirming the tendency towards ideal-gas behavior in the flame core.

In terms of reactants (Figure 3.7c), the different corrections only change the location where the mass fractions drop according to the flame position for each case. Sub-figure 3.7d shows that the $x$-coordinate where CO$_2$ is generated also changes accordingly.

Sub-figures 3.7e and 3.7f show the percentage difference between ideal and corrected transport properties for the cases in which they are mended. The difference is about 3% in average in the flame regions, while it becomes 20% or more in the cold regions. The absolute value of transport properties at cold temperatures is much smaller compared to their counterparts at hot temperatures, which brings the percentage difference up even though the absolute difference is not so vast. Thus, great differences with respect to Case 1 were not expected.

### 3.5.2 New enthalpy approach: Case 6 vs. Case 7

As discussed in Section 3.2, our most complete model differs from previous studies because we do not assume $h = \sum_k Y_k h_k$ in the convective term of the energy equation. To assess the consequences of such simplification, enthalpy and temperature profiles are contrasted between the two approaches in this section.

We study the behavior of the mixture enthalpy versus temperature at fixed composition in Figure 3.8. The composition is prescribed, taken from Case 7 at the $x$-coordinate where the flame temperature peaks. Sub-figure 3.8a portrays the enthalpy departure function of the mixture from Equation 2.11 (dotted lines) versus the same property but computed from the summation of the individual components times the mass fractions (dashed lines). The
Figure 3.6: Comparison of variables between Cases 1-6 at 100 atm.
Figure 3.7: Comparison of variables between Cases 1-6 at 100 atm.
departure function is very close to 0 for both cases at atmospheric pressure, consistent with ideal-gas behavior. As pressure is increased, the departure becomes more important. At very high temperature, the departure is closer to zero than at cold temperatures, but it does not behave exactly as in the ideal situation. The enthalpy mixture calculation yields a positive departure above 700 K, while the summation approach always yields negative values. The absolute values of differences between the mixture and the summation approaches are noticeable. Sub-figure 3.8b shows the percentage difference between the mean enthalpy computed from the mixing rules and the mean enthalpy computed from the summation of components. The differences are bounded above by 1% below 10 atm. They become more important at 100 atm, with differences reaching about 6% relative difference at the highest temperature. With this information, we would like to see what the effect of such differences is on the flame.

If we introduce the composition dependence that exists in the counterflow domain, for example for Case 7, we see in Figure 3.9a that the relative difference between computing the enthalpy directly from mixing rules or from the summation approach is below 2%. With this information in mind, we now compare counterflow diffusion flame solutions between Cases 6 and 7 at various pressures. Sub-figure 3.9b shows temperature percentage differences below 3%, while flame location and structure are practically unaltered.

### 3.5.3 Case 6: Complete Model

The goal of this section is to analyze Case 6 (which entails our most complete model) in order to obtain conclusions about the pressure effect on the flame and check if the flame structure complies with previously reported correlations with the pressure-weighted strain rate.

Solutions are presented in Figure 3.12. Sub-figure 3.12a shows velocity and temperature
Figure 3.8: Enthalpy curves versus $T$. (Composition from Case 7 at flame peak location.)

Figure 3.9: Differences in enthalpy and temperature profiles between Case 6 and Case 7.
profiles. As expected from the momentum-flux ratio, the stagnation plane is to the right of the symmetry point \((x = L/2)\). The stagnation plane would lie on the center of the domain if the momentum fluxes \(\rho u^2\) at the two nozzles were balanced. However, given the fixed density values of methane and air at the nozzles, the boundary condition \(F(x=L)\) (see Eq. 3.10) implies that the momentum flux of the methane stream is greater than that of the air stream. Thus, stagnation occurs closer to the air nozzle. See Section 3.5.6 for a more detailed comparison between the two boundary conditions. The increase in pressure increases flame temperature and narrows flame width. The first increment in pressure causes the most substantial temperature rise, while further escalation in pressure does not imply such a high relative temperature increase. Higher pressure suppresses species dissociation which tends to bring the temperature down, and higher temperature favors dissociation. At higher pressures the kinetics are faster. So, the balance between the pressure and temperature effects on dissociation is determining. However, there is only so much energy that can be extracted from the reaction, so one can not expect a linear flame temperature increase with pressure, but an asymptotic behavior. The flame temperature at 1 atm equals 1,987 K, while its value at 100 atm is 2,255 K. The x-coordinate where the maximum flame temperature occurs moves closer to the stagnation plane as pressure rises, but it always sits to its right, on the oxidizer side.

Previous publications such as [68] reported correlations between flame temperature and pressure \(T_m \sim p^{0.0474}\), and flame thickness with pressure-weighted strain rate \(\delta \sim 1/\sqrt{p\alpha}\). \(\alpha\) is the strain rate defined as the maximum absolute velocity gradient in the flow field. The flame-thickness scaling obtained in this study was shown in Section 3.4, Figure 3.4, showing close agreement with the \(\delta \sim 1/\sqrt{p\alpha}\) correlation. Another correlation for the heat-release rate was obtained in [67]. There, the authors present an analysis using average transport and thermodynamic properties in the flame zone and assume Lewis number of unity, yielding \(\dot{q} \sim p^{0.534}\sqrt{\alpha}\). As displayed in Figure 3.10a, our result shows that the heat-release rate correlates more accurately with the square root of \(p\).
Figure 3.10: Heat-release rate and non-dimensional temperature scalings for Case 6 at 100 atm.

[52] provides experimental results for laminar counterflow diffusion flames at pressures below 3 MPa. A scaling for the flame temperature is identified, which we repeated in this paper for comparison purposes. The result is shown in Figure 3.10, where the normalized temperature and x-coordinate are $\hat{T} = (T - T_o)/(T_{MAX} - T_o)$ and $\hat{x} = x/\delta_{diff}$, respectively. $\delta_{diff} = \sqrt{\frac{\alpha_o p_o}{a \ p}}$, where $\alpha_o$ is a thermal diffusivity evaluated at a mean temperature of 1000 K and at 1 atm for the oxidizer stream, and $a$ is the strain rate. As the plot highlights, the curves at different pressures collapse to a single curve, as suggested in the provided reference. The curve at the highest pressure (100 atm) shows the greater departure, suggesting that this correlation might only be valid up to a certain pressure threshold. Real-gas transport properties might explain the departure at high pressures.

As anticipated in Section 3.4, a check has been performed on the effect of including the thermophoretic contribution to the diffusion velocity. At very high pressures, the flame thickness is very narrow and the temperature gradient is at its highest magnitude. Hence, one could argue that the Soret effect may play an important role. On the contrary, the result displayed in Figure 3.11 shows that the differences between including and neglecting the Soret effect are very small. Inclusion of this effect tends to increase the flame temperature
slightly. The local velocity peak in the reaction zone also increases modestly.

![Graph showing temperature and velocity profiles](image.png)

Figure 3.11: Soret effect on Case 6 at 100 atm.

Sub-figure 3.12c shows the mass fractions of methane and oxygen. The curves become much steeper at high pressures due to the smaller flame thickness. The following may be difficult to see by eye inspection and observations; they were made with a closer computational view. At 1 atm, there is coexistence of both reactants near the region of maximum temperature, although mass fraction values are small (i.e. < 0.005). Methane that diffuses into the oxygen decays quickly, while oxygen diffuses a much longer distance into the methane side and past the stagnation plane. In contrast, at 100 almost no overlapping exists. For example, at \( x = 11.54 \text{ mm} \), the mass fraction of both reactants is < 0.0005 and it decays very quickly moving in either direction. Sub-figure 3.12d represents carbon dioxide mass fractions. This combustion product is generated along a broader region at low pressure, and its presence narrows as pressure raises. CO\(_2\) mass fraction peak value also increases with pressure. Similarly to the flame temperature behavior, the most substantial increment in CO\(_2\) mass fraction occurs when pressure is raised from 1 to 20 atm. In comparison, further increments do not seem to yield such a strong effect. The reasoning behind this is the same as for the temperature profiles.
Figure 3.12: Set of variables for Case 6 at various pressures.
3.5.4 Case 8: Methane and Water Vapor

Consider now Case 8, in which water vapor flows into the domain premixed with the methane. Three sub-cases are studied with increasing amounts of water vapor: 10%, 20% and 40%. For brevity, only a few representative plots are reported for the last case in figure 3.13. The trends with increasing water content are discussed below.

At 10% water vapor, temperature profiles highlight that raising pressure yields identical effects as for previous cases: it increases flame temperature, it narrows flame width, and the temperature peak moves closer to the stagnation plane. Flame temperature at 1 atm is 2,029 K while it equals 2,305 K at 100 atm. These values are 42 K and 49 K hotter than for Case 6, respectively. Note that the temperature boundary condition on the left side has been increased by 300 K with respect to all the previous cases. Thus, a new simulation of Case 6 where the left temperature boundary condition matches the 600 K of Case 8a is performed. The resulting flame temperature at 1 atm is 2,043 K. Now, Case 8a at 1 atm is 14 K colder compared to this new result. Therefore, addition of 10% of water acts as an energy sink. Nevertheless, 14 K is not a very substantial temperature difference. For enthalpy departure, the cold region of the air stream is unchanged with respect to Case 6. The curves on the cold region of the fuel stream, however, are closer to each other, highlighting more sensitivity to the temperature boundary condition increment than to pressure.

Density is generally lower on the fuel side compared to Case 6. The presence of water, which is heavier than methane, tends to increase the density. However, having a higher temperature on the left boundary is a dominant effect. Regarding the compressibility factor, the trend is inverted on the fuel side with respect to Case 6. Here \((1 - Z)\) is becoming more negative with increasing pressure, which also contributes to reduce the density.

Water product is generated in the flame region, where its mass fraction becomes greater than at the boundary for all pressures. The peak value increases with pressure. The previous
trends on CO\textsubscript{2} production do not seem to be altered with the presence of extra water. The hotter gas coming from the left enhances both $\mu$ and $\lambda$ on the fuel side, comparing with Case 6. The properties are not altered in the rest of the domain.

The water content in the fuel mixture is elevated to 20\% in Case 8b. The flame temperature is 21 K colder at 1 atm and 31 K colder at 100 atm compared to Case 8a. These flame temperatures are also lower than the case with no water. Again, the energy sink effect of water is dominant, and the consequence is even lower flame temperatures when more water is added. Density remains practically unaltered with respect to Case 8a. The presence of more water content on the left side of the domain affects the compressibility factor where all the $1 - Z$ curves are moved in the positive direction, tending to increase the density of the mixture. Comparison against Case 8a indicates that the presence of extra water on the left stream increases the magnitude of the enthalpy departure function keeping the same sign in the cold zone on the fuel side. In the heat-release zone, the enthalpy departure behaves as in Case 8a.

Mass fraction of water features a local peak in the flame region, where more water is generated as a combustion product, but its magnitude now is lower than the 0.2 value coming from the left boundary. No changes occur in the CO\textsubscript{2} mass fraction. Transport properties are also not altered.

Figure 3.13 contains the solutions for Case 8c in which the water content in the fuel stream is 40\%. Similarly to all previous cases, the stagnation plane lies to the right of the symmetry plane. Peak temperature at 1 atm is 56 K colder comparing with Case 8b, and it is 90 K colder at 100 atm. Density is shown in sub-figure 3.13b, portraying a slight increase with respect to Case 8b on the cold fuel stream region. The $1 - Z$ trend discussed for Case 8b is even more obvious here as shown in sub-figure 3.13c, where all the curves are now positive at the left boundary.
Figure 3.13: Set of variables for Case 8c with 40% water vapor in the fuel stream.
Methane, oxygen, and water mass fractions are represented in Figure 3.13d. The water mass fraction flowing from the left is now too high compared to the water generated as a combustion product. This translates into a smooth decrease of the mass fraction gradient in the flame zone, which becomes steep again for greater $x$. The local peak that was identified in Cases 8a and 8b no longer exists. The enthalpy departure function becomes more significant along the cold region of the fuel side, while it is diminished within the flame zone. Transport properties remain unaffected.

The water content in the fuel stream has been increased above 40% with the goal of finding the burning limit. The greatest percentage of $\text{H}_2\text{O}$ resulting in a flame solution is of 67% at 1 atm, with a flame temperature of 1,607 K. Further study of this limit is required, including results at high pressure.

### 3.5.5 Chemical Equilibrium

Reaction mechanisms provide data to compute the forward rates of each reaction that is part of the mechanism. Reverse rates are usually computed from forward rates and the principle of chemical equilibrium. This principle is embedded in most commercial codes, usually based on the classical partial pressures. At high pressure, however, fugacities should be used instead of partial pressures for better accuracy in chemical-equilibrium calculation. The theory for chemical kinetics of non-ideal gases is not well established. So, we are forced to use the same kinetics developed for ideal gases. The goal of this section is to assess the differences that arise when we calculate the product species composition in equilibrium of a hydrocarbon reaction, both using the classical ideal formulation and the non-ideal counterpart.

In the following, the index $i$ corresponds to a particular reaction while the index $k$ indicates species. $\nu_{ki}$ represents the stoichiometric coefficient of species $k$ in the reaction $i$. $X^{\text{classic}}$ and $X$ are the mole fractions of the product species in chemical equilibrium for the classical
case and for the non-ideal case, respectively.

The equilibrium constant is determined from thermodynamics:

\[ K_{p_i}(T) = \exp \left( -\frac{\Delta G^o_i}{R_u T} \right) = \exp \left( \frac{\Delta S^o_i}{R_u} - \frac{\Delta H^o_i}{R_u T} \right) \] (3.15)

where \( \Delta G^o_i \), \( \Delta H^o_i \), and \( \Delta S^o_i \) are the Gibbs function, enthalpy, and entropy changes that occur in passing completely from reactants to products in the \( i \)th reaction.

In the classical case, the equilibrium constant for a mixture of ideal gases is based on partial pressures:

\[ K_{p_i} = \frac{\prod_k (P_k / P_o)^{\nu_{ki}^{products}}}{\prod_k (P_k / P_o)^{\nu_{ki}^{reactants}}} = \frac{\prod_k (X_k^{classical})^{\nu_{ki}^{products}}}{\prod_k (X_k^{classical})^{\nu_{ki}^{reactants}}} \left( \frac{P}{P_o} \right)^{\Delta \nu_i} \] (3.16)

where \( P_o \) is the standard state pressure of 1 atm, and \( \Delta \nu_i = \sum_k \nu_{ki}^{products} - \sum_k \nu_{ki}^{reactants} \).

For non-ideal systems, fugacities must be employed [90]:

\[ K_{p_i} = \frac{\prod_k (f_k / P_o)^{\nu_{ki}^{products}}}{\prod_k (f_k / P_o)^{\nu_{ki}^{reactants}}} = \frac{\prod_k (\phi_k X_k)^{\nu_{ki}^{products}}}{\prod_k (\phi_k X_k)^{\nu_{ki}^{reactants}}} \left( \frac{P}{P_o} \right)^{\Delta \nu_i} \] (3.17)

where \( f_k \) is the fugacity of species \( k \) and \( \phi_k = f_k / (X_k P) \) is the fugacity coefficient. These expressions for both classical and non-ideal cases will be used in the laws of mass action below.

A generic reaction between a hydrocarbon and air is

\[ n_F \left[ C_n H_m + \frac{n + m/4}{\Phi} (O_2 + 3.76N_2) \right] \rightarrow X_1 O_2 + X_2 CO_2 + X_3 H_2 O + X_4 CO + X_5 OH \]

\[ + X_6 H + X_7 H_2 + X_8 O + X_9 N + X_{10} N_2 + X_{11} NO \] (3.18)
where \( n_F \) is the number of moles that gives one mole of products, \( X_1 \) through \( X_{11} \) are the mole fractions of the considered product species, and \( \Phi \) is the fuel-to-air equivalence ratio.

To determine the mass fractions \( X_k \) \((k = 1, \ldots, 11)\) and \( n_F \) at equilibrium, we use four mass balance equations, seven laws of mass action associated with elementary reactions, and the fact that the summation of all mass fractions must equal one. In the following, \( r = \frac{n + m/4}{\Phi} \).

\[
\begin{align*}
n n_F &= X_2 + X_4 \\
m n_F &= 2X_3 + X_5 + X_6 + 2X_7 \\
2 r n_F &= 2X_1 + 2X_2 + X_3 + X_4 + X_5 + X_8 + X_{11} \\
7.52 r n_F &= X_9 + 2X_{10} + X_{11}
\end{align*}
\]

The elementary reactions and their corresponding laws of mass action (based on partial pressures) are

\[
\begin{align*}
\frac{1}{2} O_2 &\rightleftharpoons O, \quad K_{p1} = \frac{X_8}{X_4^{1/2}} \left( \frac{P}{P_0} \right)^{1/2} \\
\frac{1}{2} H_2 &\rightleftharpoons H, \quad K_{p2} = \frac{X_6}{X_7^{1/2}} \left( \frac{P}{P_0} \right)^{1/2} \\
\frac{1}{2} N_2 &\rightleftharpoons N, \quad K_{p3} = \frac{X_9}{X_{10}^{1/2}} \left( \frac{P}{P_0} \right)^{1/2} \\
\frac{1}{2} O_2 + \frac{1}{2} N_2 &\rightleftharpoons NO, \quad K_{p4} = \frac{X_{11}}{X_4^{1/2}X_{10}^{1/2}} \\
CO + \frac{1}{2} O_2 &\rightleftharpoons CO_2, \quad K_{p5} = \frac{X_3}{X_4X_1^{1/2}} \left( \frac{P}{P_0} \right)^{-1/2} \\
H_2 + \frac{1}{2} O_2 &\rightleftharpoons H_2O, \quad K_{p6} = \frac{X_3}{X_7X_1^{1/2}} \left( \frac{P}{P_0} \right)^{-1/2} \\
\frac{1}{2} H_2 + \frac{1}{2} O_2 &\rightleftharpoons OH, \quad K_{p7} = \frac{X_3}{X_7^{1/2}X_1^{1/2}}
\end{align*}
\]

These laws of mass action are readily modified for the non-ideal case by multiplying each mass fraction by its fugacity coefficient, in agreement with Equation 3.17. The fugacity
Table 3.2: $X_{k}^{\text{classic}}/X_{k}$, Stoichiometric: $\Phi = 1.0$

<table>
<thead>
<tr>
<th>T(K)</th>
<th>$O_2$</th>
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<td>0.99994</td>
<td>1.00260</td>
<td>1.00141</td>
<td>1.00012</td>
<td>1.00626</td>
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coefficients are obtained according to our choice of EoS, from the following expression [54]:

$$
\ln(\phi_k) = \frac{b_k}{b}(Z - 1) - \ln(Z - B) - \frac{A}{B} \left(2\frac{a_k^{0.5}}{a^{0.5}} - \frac{b_k}{b}\right) \ln \left(1 + \frac{B}{Z}\right)
$$

(3.21)

Equations 3.19 and 3.20, together with $\sum_{k=1}^{11}X_k = 1$, form a system of non-linear algebraic equations. We use the Matlab solver “fsolve”, together with the “trust-region-dogleg” algorithm. The pressure is prescribed at 100 atm, and the temperature is varied from 2300 K to 3000 K. The product composition is obtained for three different equivalence ratios ($\Phi = 1, 0.8, \text{and } 1.1$). Ratios between the mole fractions for the classical case and those for the non-ideal case are formed and presented in Tables 3.2, 3.3, and 3.4.

We can see from the results that the differences are very small, always below 1% for the stoichiometric and fuel-lean cases. Only the fuel-rich case shows ratios slightly above 1%, but it only exceeds this value by a few decimals. These results make the use of the classical chemical equilibrium more comfortable at elevated pressures for combustion problems. However, one must keep in mind that differences in chemical pathways may still exist, and therefore the uncertainty on reaction rates also remains.
Table 3.3: $X_k^{classic}/X_k$, Fuel-lean: $\Phi = 0.8$

<table>
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<th>T(K)</th>
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<th>$H_2O$</th>
<th>CO</th>
<th>OH</th>
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Table 3.4: $X_k^{classic}/X_k$, Fuel-rich: $\Phi = 1.1$

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3.5.6 Mass Flux vs Momentum Flux

The differences between the boundary conditions for $F$ introduced by Equation 3.10 (matching the mass fluxes of both nozzles), versus matching the momentum fluxes are highlighted in Figure 3.14. It includes velocity, temperature, density, and mass fraction curves for Case 6 at various pressures. We observe that the main difference between the two boundary conditions is a shift in the x-coordinate of the flame and the stagnation plane. Finding the stagnation plane in the center of the domain is expected when balancing the momentum fluxes. This clearly occurs at elevated pressures. At atmospheric pressure, however, the heat release zone is wide enough to perturb the velocity field and cause stagnation to occur closer to the fuel side.
Figure 3.14: Comparison between matching mass fluxes versus matching momentum fluxes for Case 6.
3.6 Conclusion

Analysis of combustion at high pressure with the presence of dense fluids requires relaxation of certain assumptions that are commonly taken. The use of ideal-gas approximations in these scenarios requires justification. This Chapter presents solutions for a steady laminar counterflow diffusion flame using a real-gas model. The relative effect of different relaxations is analyzed by solving a one-dimensional system of differential equations equipped with detailed chemistry and detailed transport. The considered reactants are methane and air. A path for error estimates is identified in this canonical configuration. It can serve as a template for other researchers. In particular, three different corrections have been examined: (I) replacement of the ideal-gas law by a suitable non-ideal cubic equation of state; (II) consideration of the energy equation for real gases equipped with properly corrected thermodynamic properties such as enthalpy; (III) modification of transport properties such as dynamic viscosity and thermal conductivity. Solutions are presented for several cases in which each of the corrections are applied individually or combined. Results show that the largest correction is the replacement of the ideal-gas law, followed by the amendment of the energy equation, while rectification of transport properties is less significant. Substantial differences appear mainly in terms of flame location. Correction of the equation of state moves the flame towards the stagnation plane, closer to the fuel stream, whereas the correction of the energy equation has the opposite effect. The main differences in flame location are due to the fact that the real-gas equation of state provides more accurate values of the flow properties in the cold regions. This conclusion should be kept in mind during the design process of high-pressure combustors.

Even with the new corrections, heat-release rate, flame temperature, and thickness still follow well previously published correlations with pressure and pressure-weighed strain rate, respectively. Radiative heat losses and the Soret effect are shown to be negligible, even at the highest pressure.
An analysis has been developed on the existence of turbulence. Specifically, four plausible causes of turbulence in the counterflow have been identified, and based on established practice, we demonstrated that the first three mechanisms can essentially be eliminated. We showed, using an extremely conservative analysis (i.e., with elimination of turbulent kinetic energy diffusion and dissipation and with maximizing of the production term), that the fourth mechanism will not generate any significant turbulence for the applicable length scale.

The presented form of the energy equation is more general compared to the version commonly found in the literature, which assumes in the convective term that $h = \sum_k Y_k h_k$. Comparison of the two shows discrepancies in terms of flame temperature and enthalpy that are below 3%.

The difference between matching mass fluxes versus momentum fluxes between the two nozzles affects only the flame location and does not impact any of our major findings.

Furthermore, computations are made for a case equipped with the most complete model and including water vapor premixed with the methane. Solutions are discussed for percentages of water vapor equal to 10%, 20% and 40% by mass. Presence of water not being generated as a combustion product acts as an energy sink, therefore flame temperatures decrease with increasing water content. Escalation of pressure produces similar effects on the flame for the problem with extra water and without it. These effects include increase of flame temperature, narrowing the flame region, and displacement of the flame position closer to the stagnation plane. This plane is located to the right of the symmetry line, closer to the air nozzle, for all the studied cases. The greatest percentage of premixed water content at which a flame solution has been obtained equals 67% at 1 atm. This limit requires further exploration, specially at higher pressures.
Commercial software packages use chemical kinetic laws established for lower pressure range. Chemical equilibrium laws at very high pressure require the use of fugacity rather than partial pressure. Comparative calculations have been presented for a range of prescribed temperatures and at 100 atm. Results indicate differences below 1%. Thus, application of these kinetic laws at the higher pressures with regard to the ability to predict accurately equilibrium and rates becomes more comfortable. However, chemical pathways may still be different at high pressures.
Chapter 4

Single-Phase Counterflow Diffusion

Flame Extinction Analysis

4.1 Introduction

Chapter 3 provided comprehensive methane/air counterflow diffusion flame results comparing ideal with real-gas solutions, and also with cases entailing a combination of a real-gas model with certain ideal-gas approximations, all at constant strain rate. With the given context, the previous analysis is extended in the present Chapter for a methane-oxygen diffusion flame. Here, the most complete model, presented in Section 3.2, is used to analyze three important aspects: (i) comparison between the use of detailed kinetics and reduced kinetics; (ii) flame extinction analysis where the fuel is pure methane and where it is a mixture of methane and 40% water vapor. Comparisons are made among real-gas model with detailed kinetics, real-gas model with reduced kinetics, real-gas results from the literature, and ideal-gas model; and (iii) effect of varying the mass-flow-rate ratio of the two counterflow streams. Results are presented in Section 3.5 with a summary of conclusions given in Section 4.3.
The velocities at the exit of the nozzles are prescribed using the equations below. These are useful to analyze the variation of mass-flow rate ratio between the two nozzles at constant strain rate, and also the opposite case, where strain rate is varied and the mass-flow rate ratio is constant. We express the inflow velocities as a function of strain rate and mass-flow rate ratio. Given that for stoichiometric conditions with oxygen and methane ($\dot{m}_O/\dot{m}_F)_s = 4$, we define the oxygen-to-fuel mass-flow rate equivalence ratio as

$$\Phi = \frac{(\dot{m}_O/\dot{m}_F)}{(\dot{m}_O/\dot{m}_F)_s} = 4 \left( \frac{\rho_O}{\rho_F} \right) \left( \frac{u_O}{u_F} \right)$$ (4.1)

where the subscript $s$ denotes stoichiometric ratio. The density ratio will be prescribed for any case in which pressure, temperature and mass fractions are prescribed at the boundaries.

Define the global strain rate as

$$s_r = \frac{(u_F - u_O)}{L} = \frac{\hat{s}_r}{L}$$ (4.2)

If we prescribe both $\Phi$ and $\hat{s}_r$, then $u_F$ and $u_O$ are determined:

$$u_O = \frac{-1}{1 + \frac{1}{4\Phi} \left( \frac{\rho_F}{\rho_O} \right)}$$,  \quad u_F = \hat{s}_r + u_O$$ (4.3)

4.2 Results and discussion

The results are organized in three subsections. First, solutions obtained using detailed kinetics (GRI 3.0) are compared to results using reduced kinetics. Extinction properties are studied in the next sub-section, where strain rate is increased while keeping a constant stoichiometric mass-flow rate ratio $\Phi = 1$. Finally, the mass-flow-rate ratio variation at constant strain rate is presented. Pressure ranges between 1 to 100 atm.
4.2.1 Reduced kinetics

The goal of this subsection is to compare the results obtained using detailed kinetics (GRI 3.0) with those obtained using reduced kinetics. A 19-species and 15-step reduced mechanism for methane and oxygen is selected [87].

First, at a low strain rate that is far from extinction, we compare the results obtained using both detailed and reduced kinetics for different pressures. See in Figure 4.1a that the curves are almost perfectly superimposed.

At high strain rate, the differences are still small but more noticeable. Sub-figures 4.1b and 4.1c show the velocity and temperature when \( p = 100 \text{ atm}, \Phi = 1, \) and the strain rate is the maximum possible before extinction occurs. We can see in Sub-figure 4.1b that the local velocity peaks are slightly higher for the reduced kinetics case. This is caused by the greater flame temperature that we also obtain with the reduced kinetics, as shown in Sub-figure 4.1c. The difference in peak temperature is 37.3 K (1.22 \%) and the difference in flame location is 18.5 nano meters, which represents a 0.2\% of \( L \) for this case.

4.2.2 Extinction

Flame extinction is examined in this Subsection. Extinction occurs when the flow time scale becomes sufficiently lower than the chemical time scale. The inverse of the global strain rate is a good measure of the characteristic time scale. Thus, the counterflow diffusion flame extinguishes when the strain rate is increased until it reaches a certain value known as the extinction strain rate. Previous studies by [65], [67], and [68] used the so-called arc-continuation method to obtain the whole “S” curve of burning regimes. In the 1D counterflow flame, this method consists of increasing the strain rate by forcing a temperature decrease in two arbitrary internal nodes within the flame zone. There, the temperature is decreased
Figure 4.1: (a) Detailed vs reduced kinetics at $\Phi = 1$ and various pressures; (b) and (c) Detailed vs reduced kinetics at high strain rate, $p = 100$ atm, and $\Phi = 1$. (b) Velocity profile; (c) Temperature profile.
with respect to the initial guess, which is a solution at a lower strain rate. After the iterative process converges, the new solution yields a narrower flame, the velocity at the nozzles is larger, and consequently, the strain rate increases. This method requires the replacement of the two boundary conditions for $F$ with two internal conditions for temperature. It does not allow control over the velocity at the exit of the nozzles or the mass-flow rate ratio. Also, the velocity at the exit of the nozzles becomes very large, comparable to the speed of sound, for strain rates near the extinction limit.

For these reasons, our approach to increase the strain rate is mainly based on reducing the distance between the two nozzles. This is combined with slight increases in velocity at the exit of the nozzles to help achieve convergence. However, these velocities are kept below 10 m/s. Only the stable-burning regime is studied. Figure 4.2 shows our results for extinction strain rate and extinction temperature as a function of pressure. Four curves are presented. The first three are for the cases with pure methane and oxygen, and they correspond to solutions with the real-gas model with detailed kinetics, real-gas model with reduced kinetics, and ideal-gas model with detailed kinetics. The fourth curve corresponds to the case where the fuel stream is a mixture composed of methane with 40% water vapor by mass.

For the cases without inflowing water vapor, the three presented curves are compared against the data from [68], where a different detailed kinetic mechanism was employed for methane and oxygen as reactants. Furthermore, the model in that publication involves the simplification that the enthalpy of the mixture equals the summation of the partial enthalpies times the mass fractions of the species. Several points are extracted from Figure 4.2a. Good agreement for extinction strain rate is found between the four curves at pressures up to 20 atm. Relative differences between the ideal-gas and real-gas models increase with pressure, starting at 4.5% at 20 atm and growing to 15% at 100 atm. Differences between detailed and reduced kinetics with the real-gas model are lower for all pressures, maxing at almost 8%. 
The extinction strain rate is linear with pressure up to 50 atm for all the detailed-kinetics models, and up to 20 atm for the reduced-kinetics model. At higher pressure values, the gradient of extinction strain rate with respect to pressure decreases. The ideal-gas solution implies higher extinction strain rates for pressures above 20 atm compared to our real-gas results, both with detailed and reduced kinetics. This is consistent with the fact that higher flame temperatures are obtained with the ideal-gas model, as reported in [91], which results in flames that are harder to extinguish. The ideal-gas result is closest with that from [68].

The extinction temperature is displayed in Figure 4.2b. Results in the present study generally give lower temperatures than in [68]. The discrepancies are associated with a combination of factors, such as the use of a different reaction mechanism, as well as the simplification in calculating the mixture enthalpy. Near extinction, higher strain rates imply lower flame temperatures. Very good agreement is found between our real and ideal-gas cases with detailed kinetics for pressures up to 70 atm. The major discrepancies appear at 80 and 90 atm, and there is good agreement at 100 atm. At a given strain rate, the use of reduced kinetics results in higher flame temperatures, as shown in the previous subsection. Thus, it is not surprising that the extinction flame temperature for the reduced kinetics is above the temperature corresponding to our detailed-kinetics computations for all strain rates above 5 atm. Another interesting feature is that extinction flame temperature above 50 atm was reported to increase moderately and linearly with pressure [68]. However, only two data points were reported, at 50 and 100 atm. Several intermediate pressure values are studied herein, and a local decrease in extinction temperature is found between 70 and 90 atm. This occurs in all of our cases, both with detailed and reduced kinetics. The effect also appears in our ideal-gas solutions, although more modestly. It is conceivable that the model in [68] would also predict a similar local decrease in extinction temperature for the mentioned pressure range, but this was not addressed.

The local minimum in extinction temperature shown in Figure 4.2b can be explained. At
fixed composition and enthalpy for a real gas, the temperature decreases almost linearly with increasing pressure while, for an ideal gas, it remains constant. This is represented in Figure 4.3a, where the real-gas adiabatic flame temperature calculations are for a stoichiometric global one-step reaction of methane and oxygen becoming water vapor and carbon dioxide, and the initial temperature of the reactants is prescribed to 298.15 K. The enthalpy for an adiabatic flame without dissociation is totally determined by initial conditions and heats of formation; for the diffusion flame, these are also dominant factors. Now, in Figure 4.2b, composition is not fixed; rather, as shown for the ideal gas, the reduced dissociation with increasing pressure causes a superlinear variation of temperature at high pressures. The combination of the superlinear increase with the linear decrease for the real gas is the likely cause of the temperature minimum which previous investigators did not capture.

Temperature variations at constant pressure have substantial effects on dissociation. The local minimum in extinction temperature described above has a direct effect on mass fractions of species such as hydrogen and carbon dioxide. These variables are displayed in Figure 4.4. CO₂ mass fraction increases from 50 to 70 atm, both for real and ideal gas cases with detailed kinetics. This is consistent with the increase in extinction temperature. From 70 to 90 atm, the mass fraction decreases, and then increases again from 90 to 100 atm. This inflection is also consistent with the extinction temperature trend. Similarly, for the reduced kinetics case, CO₂ mass fraction decreases from 50 to 90 atm, and then increases from 90 to 100 atm, also following the extinction temperature tendency.

All three cases show a reduction in H₂ mass fraction from 50 to 90 atm followed by an increase in mass fraction from 90 to 100 atm. Thus, this trend does not correlate as well with the extinction temperature as for CO₂.

At the extinction strain rate, the trends in compressibility factor and enthalpy departure function do not change as pressure is increased, as shown in Figure 4.5. Comparison is made for these two variables between the cases with detailed and reduced kinetics, resulting in
Figure 4.2: (a) Extinction strain rate and (b) extinction temperature as a function of pressure ($\Phi = 1$).

good agreement.

The case where the fuel stream is a mixture with 60% methane and 40% water vapor mass fractions is now discussed. Extinction strain rate and temperature are also presented in Figure 4.2. Extinction strain rate occurs at a much lower magnitude for all pressures above 1 atm compared with the case with no water. In other words, it is much easier to blow off the flame given all the extra water vapor. Strain rate increases with pressure and is bounded above at 70 atm. Higher pressures decrease it by 1 to 2% for each 10 atm until 100 atm.

Extinction temperature behavior is very different from the previous case. Now, it increases between 1 and 20 atm and it decreases almost linearly for higher pressures up to 100 atm. The reduced dissociation with increasing pressure is a dominating factor for this initial pressure range. However, other factors play an important role for higher pressures. For example, a plot in Figure 4.3b of adiabatic flame temperature versus pressure for a real gas considering the presence of extra water reveals a stronger pressure effect compared to the case with no inflowing water. The difference in adiabatic flame temperature is around 20 K for the case with no water, while it is about 132 K for the case with water. This element alone does not explain the much greater drop in extinction temperature shown in Figure 4.2b, which is
$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$

$T_{\text{initial}} = 298.15 \text{ K}$

Figure 4.3: Adiabatic flame temperature for a real gas and complete combustion of methane and oxygen with initial temperature of 298.15 K. (a) 0% water vapor; (b) 40% water vapor.

Figure 4.4: (a) CO$_2$ mass fraction and (b) H$_2$ mass fraction at extinction strain rate ($\Phi = 1$). Solid line is for real gas with detailed kinetics; dotted line is for real gas with reduced kinetics; dashed line is for ideal gas with detailed kinetics.
To further analyze this temperature difference, the mass-fraction values of the major species are given in Table 4.1 at the peak-temperature coordinate. Carbon dioxide mass fraction first increases from 1 to 20 atm and then decreases until 100 atm. Carbon monoxide mass fraction also decreases with pressure. The carbon reduction is explained by looking at methane mass fraction, which has the opposite behavior, first decreasing from 1 to 20 atm and then increasing until 100 atm. Thus, less methane is burnt in the hottest flame region with increasing pressure above 20 atm, which contributes to lower flame temperatures. Note that the summation of the major species shown in Table 4.1 account for 97% or more of the total mass.

Figure 4.6 shows the mass-diffusion fluxes for carbon dioxide and water vapor at different pressures in the flame region. The location of the maximum flame temperature is marked with vertical dashed lines at the different pressures of interest. The ratio between the max-
Table 4.1: Major-species mass fractions at peak-temperature coordinate and various pressures.

<table>
<thead>
<tr>
<th>$p$ [atm]</th>
<th>$Y_{CH_4}$</th>
<th>$Y_{O_2}$</th>
<th>$Y_{H_2O}$</th>
<th>$Y_{CO_2}$</th>
<th>$Y_{CO}$</th>
<th>$Y_{H_2}$</th>
<th>$\sum Y_{major}$</th>
<th>$T_{max}$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0088</td>
<td>0.3699</td>
<td>0.3177</td>
<td>0.1173</td>
<td>0.1527</td>
<td>0.0032</td>
<td>0.9696</td>
<td>2275.10</td>
</tr>
<tr>
<td>20</td>
<td>0.0046</td>
<td>0.407</td>
<td>0.3086</td>
<td>0.1427</td>
<td>0.1163</td>
<td>0.0016</td>
<td>0.9808</td>
<td>2438.30</td>
</tr>
<tr>
<td>50</td>
<td>0.009</td>
<td>0.4217</td>
<td>0.3078</td>
<td>0.1259</td>
<td>0.1183</td>
<td>0.0014</td>
<td>0.9841</td>
<td>2337.10</td>
</tr>
<tr>
<td>100</td>
<td>0.0162</td>
<td>0.4552</td>
<td>0.293</td>
<td>0.1038</td>
<td>0.1115</td>
<td>0.0011</td>
<td>0.9808</td>
<td>2141.30</td>
</tr>
</tbody>
</table>

Table 4.1: Major-species mass fractions at peak-temperature coordinate and various pressures.

Figure 4.6: Diffusion fluxes in the flame region at various pressures. (a) CO$_2$ (b) H$_2$O.

The maximum diffusion fluxes of CO$_2$ to H$_2$O decrease with pressure from 0.54 at 20 atm to 0.47 at 100 atm. With the given mass fractions from Table 4.1, the computed ratio of mass-diffusion velocities for the same two species increases from 1.16 at 20 atm to 1.32 at 100 atm. Carbon dioxide is therefore diffusing away faster than water vapor and the difference increases with pressure, indicating that there is more water-content build-up, which in turn lowers the flame temperature.
4.2.3 Mass-flow rate ratio

The effects on the flame position and structure are studied in this Subsection when $\Phi$ has its value ranging from 0.5 to 2.5. Figure 4.7 shows velocity profiles and temperature profiles as a function of pressure and $\Phi$. Increasing the oxygen-to-fuel ratio translates into a higher oxygen mass-flow rate, and it pushes the flame towards the fuel nozzle. Contrarily, decreasing $\Phi$ displaces the flame towards the oxygen nozzle. When $\Phi = 1$, the oxygen mass-flow rate is four times greater than the methane mass-flow rate. Therefore, the flame seats closer to the fuel nozzle. Increasing pressure has the same effects on the maximum flame temperature and thickness, regardless of the value of $\Phi$. This analysis differs from [91]. There, the boundary conditions were varied to match the momentum fluxes or to match mass-flow-rate fluxes between the two nozzles. Nevertheless, the consequences on the flame were the same as those demonstrated in this section for different mixture ratios.
4.3 Conclusions

This Chapter presents solutions for the 1D counterflow diffusion flame problem at high pressures using the same real-gas model presented in Chapter 3. Here, strain rate has been varied as opposed to the previous Chapter, where it was constant. Solutions with detailed chemical kinetic schemes are compared against results with reduced kinetics. It is concluded that the differences are negligible at low strain rates, regardless of the pressure. At high strain rates right before extinction occurs, the differences are more noticeable, but still slight (i.e. less than 2% in peak temperature). In particular, flame temperature becomes higher with use of reduced kinetics, which causes a greater local flow speeds near the flame region. This provides the obvious advantage of much faster computations using reduced kinetics with almost no error increment.

The extinction properties are studied in terms of maximum strain rate and flame temperature that allow sustaining a flame in steady state. Strain rate is increased by reducing the distance between the two nozzles instead of increasing the inflowing velocities. The latter, previously used in the literature, implies very high flow velocities approaching the speed of sound. This fact is not compatible with the assumptions made in developing the model. Two cases are studied: one with pure methane flowing against oxygen, and the other with a mixture of methane and 40% water vapor (by mass) also impinging against oxygen.

For the case with no inflowing water, our results indicate that the flame extinguishes at lower strain rates than previously reported, especially when pressure is higher than 20 atm. Differences between the ideal-gas and real-gas models increase with pressure and are as great as 15% at 100 atm. Differences between using detailed and reduced kinetics with the real-gas model are, at most, 8%. Extinction flame temperature is also lower than in previous studies. In prior research by [68], a linear and moderate increase in extinction temperature was assumed when pressure was increased between 50 and 100 atm because no intermediate
calculations were presented. However, a local decrease in extinction temperature is obtained herein for pressures of 70, 80 and 90 atm. This is associated with the combination of two opposite effects of increasing pressure: one is that the real-gas adiabatic flame temperature decreases with pressure for constant enthalpy and composition, and the other is that less dissociation occurs with increasing pressure, which in turn causes higher temperature.

Extinction properties for the case with extra water vapor are substantially different. Extinction strain rate is much lower for all pressures, and even though it increases from 1 to 20 atm, it reaches almost an asymptotic value for higher pressures. Extinction temperature increases substantially from 1 to 20 atm due to the reduced dissociation. However, it decreases almost linearly with increasing pressure until 100 atm. Three factors are emphasized in relation to this trend: (i) the adiabatic flame temperature at constant enthalpy and composition decreases much faster with extra water than without it; (ii) less methane burns in the peak temperature region for pressures between 20 to 100 atm; and (iii) carbon dioxide diffuses faster than water vapor with increasing pressure, implying the accumulation of water, which in turn lowers the flame temperature.

Finally, the effects of varying the mass-flow rate ratio between the two nozzles are also assessed, concluding that it only produces a shift in the flame position without affecting its structure or temperature.
Chapter 5

High-Pressure Phase Equilibrium

5.1 Introduction

Combustion effects under high pressure environments have been analyzed in the two Chapters using a single-phase approach. Whenever water was premixed with the fuel, temperature was high enough to ensure that no liquid existed. The purpose of this Chapter is to establish a suitable theoretical framework that allows investigation of a problem where both a supercritical fluid (single phase) region as well as two-phase domain may exist.

Liquid-vapor phase equilibrium calculations have been used in the past for applications primarily related to the oil and refinery industries. Less attention has been given to situations where liquid-fuel injection is used. Consider an incompressible round liquid jet with a diameter of $O(100) \ \mu m$ injected into a gaseous environment. Previous numerical investigations indicate that three-dimensional hydrodynamic instabilities develop on a time from $O(10)$ to $O(100) \ \mu s$ after injection [92]. A typical velocity would be of $O(100) \ m/s$, which means that the jet penetrates between a millimeter to a centimeter (10-100 diameters) in that time. In one to ten microseconds at pressures of $O(100) \ atm$, mass can diffuse by molecular means a
distance of order of several hundred nanometers to a micron. This diffusion layer thickness is much larger than molecular spacing, which is a few nanometers for a hydrocarbon at about 100 atm. This analysis of length- and time-scales associated to the liquid jet indicates that diffusion of species from the surrounding fluid into the liquid jet occurs much faster than the break-up process of the liquid, and the diffusion layer is much greater than the molecular spacing, even at very high pressures. Thus, continuum theory for the diffusion and thermodynamic laws for the phase equilibrium are valid and must be applied in the analysis. The first approach in the analysis of such situations is the study of vapor-liquid equilibrium at high pressure presented in the next section. Results for binary mixtures and for mixtures with more than two components are presented after.

5.2 Phase-Equilibrium Equations

The formulation for high-pressure phase equilibrium is well known and can be found in several thermodynamic and chemical engineering books (i.e. [93, 94]). Qualitative behavior of mixture critical pressure and temperature was also described in these and other references. The main novelty in our results is in the evaluation of the SRK EOS for particular hydrocarbon-oxygen mixtures as well as the methane-water mixture. The formulation is reviewed below, and results of interest for current combustion mixtures are included.

Thermal, mechanical and chemical potential must be balanced at the interface between liquid and gas phases for a multicomponent mixture to be in equilibrium:

\[ T_l = T_g \quad ; \quad P_l = P_g \quad ; \quad \mu_l = \mu_g \quad \text{(5.1)} \]
The relationship between chemical potential and fugacity is:

\[ \mu_i^\circ - \mu_i = R_u T \ln \frac{f_i}{\tilde{f}_i^\circ} \quad \text{and} \quad \lim_{P \to 0} \left( \frac{f_i}{P_i} \right) \to 1 \]  

(5.2)

The chemical potential equality may be expressed in terms of the fugacity as \( f_{i,l} = f_{i,g} \), whereby, bringing in the fugacity coefficient \( \Phi \) gives

\[ X_{li} \Phi_{li}(p, T, X_{l1}, ..., X_{li}, ..., X_{l\tilde{N}}) = X_{gi} \Phi_{gi}(p, T, X_{g1}, ..., X_{gi}, ..., X_{g\tilde{N}}) ; \ i = 1, ..., \tilde{N} \]  

(5.3)

where

\[ \Sigma_{i=1}^{\tilde{N}} X_{il} = 1 ; \ \Sigma_{i=1}^{\tilde{N}} X_{ig} = 1 \]  

(5.4)

For systems with only two species, the algebraic Equations 5.3 and 5.4 are used to solve for the mole fractions of each species in both liquid and gas phases. For systems with more than two species, ratios must be defined between pairs of mole fractions. One ratio value is needed for every extra species. Let us generalize to \( \tilde{N} \) species with \( 2\tilde{N} \) unknowns, which are the mole fractions in each phase for all species. Consider that \( K \) species are predominantly liquid \((K < N)\), and \((N - K)\) species are predominantly gaseous. We have \( \tilde{N} \) chemical potential equations, \((K - 1)\) mole ratios for the predominantly liquid species, \((\tilde{N} - K - 1)\) ratios for the predominantly gaseous species, and two mole fraction summations. Therefore, the number of equations that we have is \([\tilde{N} + (K - 1) + (\tilde{N} - K - 1) + 2] = 2\tilde{N}\) and the system is closed.
The fugacity coefficients are obtained for the selected equation of state using the expressions presented in Chapter 2. These coefficients depend on pressure, temperature and composition, and the system to be solved is highly non-linear. Thus, the solution is obtained through an iterative process:

- Pressure and temperature are prescribed (input parameters).
- System 5.3 and 5.4 (plus any necessary mole fraction ratios) is solved using fsolve Matlab function and the “Trust-region Dogleg” algorithm, which is a variant of the Powell Dogleg method described in [95]. The following steps are performed in each iteration:

1. Guess \( X_{i,l} \) and \( X_{i,g} \).
2. Use the presented mixing rules (Chapter 2) to evaluate the coefficients \( a \) and \( b \) in the SRK EoS for both liquid and gas phases.
3. Solve for \( Z \) from the cubic EoS for both phases.
4. Calculate fugacity coefficients for both phases, \( \Phi_{i,l} \) and \( \Phi_{i,g} \).

A dedicated code has been written to obtain solutions. Iterations are performed using the “fsolve” Matlab function until convergence is achieved.

More information can be inferred once the previous system is solved. At high pressure values and a given temperature, the energy required to vaporize one mole of component \( i \) from the liquid solution to the gaseous mixture is substantially different from the latent heat of vaporization. The former is the enthalpy of vaporization of component \( i \) while the latter is defined as the energy required to vaporize one mole of pure liquid \( i \) in its own vapor at a given temperature and the corresponding saturation pressure. The enthalpy of vaporization
as a function of the fugacity coefficient is:

$$\Delta \bar{h}_{v,i} = \bar{h}_{i,g} - \bar{h}_{i,l} = R_u T^2 \frac{\partial}{\partial T} \left[ \ln \frac{\Phi_{i,g}}{\Phi_{i,l}} \right]$$

(5.5)

The surface tension coefficient of the liquid $\sigma_i$ is evaluated using the Parachor parameter for each species $P_i$, which is taken from the literature [96]:

$$\sigma_i = \left( \frac{P_i}{\bar{v}} \right)^4$$

(5.6)

where $\bar{v}$ is the molar specific volume given by the EoS.

### 5.3 Results: Two-Species Systems

Contrary to most of the hydrocarbons, methane has critical pressure and temperature that are much closer to the critical values for oxygen. Thus, the mixture of these two components are described by curves that are sharper, and the range of pressures for which two phases are obtained is narrower. This effect can be seen in Figure 5.1a. For a prescribed temperature, increasing the pressure reduces the liquid mole fraction of methane, implying that there is more oxygen being dissolved into the liquid mixture. The oxygen mole fraction in the liquid decreases when the temperature is increased at a given pressure.

As heavier hydrocarbons are computed, the differences between the critical properties of the hydrocarbon and the oxygen become greater and the mole fractions of liquid and gas phases are more unequal. This effect may be seen in Figure 5.1b. For pressures greater than the critical pressure of the hydrocarbon, increasing temperature at a fixed pressure raises the mole fraction of the hydrocarbon in the liquid. However, as the critical pressure is approached, the mole fraction slightly drops again.
Figure 5.1: Binary Systems of (a) methane and oxygen, (b) decane and oxygen, in phase equilibrium (normalizing pressure corresponds to fuel).

Figure 5.2: Critical properties of hydrocarbon/oxygen mixtures vs. mole fraction.

(a) Critical Temperature
(b) Reduced Pressure

The mixture critical temperature values vary monotonically between the maximum and the minimum critical temperature of the two pure species (see Figure 5.2a). The critical pressure, however, rises higher than the critical pressure of any component species and there can still be two phases (or sub-critical conditions; see Figure 5.2b). In this last plot, the normalizing pressure for each hydrocarbon is the critical pressure of the pure hydrocarbon. At temperatures below 550 K the methane gaseous phase and the water liquid phase are dominant for all pressures equal or above the critical pressure of water. For temperatures above 550 K, gaseous-water mole fraction increases above 50%. Liquid-water mole fraction is still much greater than liquid methane, with more methane dissolving into the liquid.

The variation of the enthalpy of vaporization with temperature and pressure is given in
Figure 5.3: Hydrocarbon Fuel and Oxygen Enthalpy of Vaporization (Normalizing pressure corresponds to Fuel).

Figure 5.3 for methane, or decane, with oxygen. The enthalpy of vaporization decreases with pressure at constant temperature. At constant pressure, however, the enthalpy of vaporization may increase at low temperatures and then decrease monotonically until it reaches 0 at the critical point.

Figure 5.4 shows density and surface tension variations for decane with oxygen. In Figure 5.4a the composition is varied from the liquid/gas phase equilibrium values at prescribed pressure and temperatures. Density increases with increasing decane fraction both for the liquid and for the gas phases. Density increases faster in the liquid than in the gas with increasing fuel fraction. Figure 5.4b shows how surface tension tends to decrease with temperature at constant pressure until it reaches 0 at the critical point. However, surface tension increases with temperature at low temperature ranges and high pressures. At constant temperature, surface tension decreases with increasing pressure.
Analysis of phase-equilibrium for a mixture composed of reactants and products is of interest for applications such as Exhaust Gas Recirculation (EGR). A single-step stoichiometric reaction between decane and oxygen results in mixtures with four major species: $C_{10}H_{22}$, $O_2$, $H_2O$, and $CO_2$. Two mole fraction ratios must be constrained to conduct the phase equilibrium calculation. We will consider $CO_2$ and $H_2O$ predominantly in the gas phase and always in the product stoichiometric molar proportion of 11/10. The other ratio is selected to be between the oxygen and the products, and will be varied as a parameter. See Figure 5.5, which applies at twice the critical pressure of the decane, and every curve belongs to one of the oxygen-to-products ratio. As expected, for the higher proportions of oxygen vs. products, concentrations of the reactants are greater in the liquid phase while concentration of products is lower. As temperature is increased, more decane is dissolved into the liquid and less of the other species. For a pure concentration of decane, we get its critical temperature. For low temperatures, more water is in the liquid phase. As temperature is increased, the fraction of water in either phase decreases. The same occurs for oxygen and carbon dioxide, although these two are predominantly in the gas phase. For pressures greater than the critical pressure of decane, altering the ratio between oxygen and products changes the
critical temperature of the mixture. Ratios with more oxygen weight result in higher critical temperatures. As it happened for the decane-oxygen binary system, decane mole fraction decreases for a pressure increment. Liquid oxygen mole fraction, however, increases. The fraction of oxygen that dissolves into the liquid increases with increasing pressure and also with increasing oxygen-to-product ratio. The same effect occurs with CO₂.

Figure 5.5: Decane, Oxygen and Products Phase Equilibrium ($P_r = P/P_{c_{DECANE}} = 2$).
Chapter 6

Zero-Dimensional Shifting Phase Equilibrium

6.1 Introduction

The phase equilibrium formulation presented in the previous Chapter is very useful to gain insight on how much of each species in a mixture is present in each phase at a given pressure and temperature. The system of equations can be solved directly for systems with two species but require certain constraints, such as ratios between fractions of species, for mixtures with more than two components. Getting solutions for that highly non-linear system can become challenging, especially around the critical point. The purpose of the present Chapter is to apply differential calculus to the phase equilibrium relations. As we will see, convenient definition of new global mass fractions will yield information on how much mass is in each phase. The formulation is also more general since it allows direct application to systems of more than two species.
6.2 Definitions

The use of mole fractions normalized over both phases is convenient. Let \( \xi_g \equiv N_g/N_0; \) \( \xi_l \equiv N_l/N_0 = 1 - \xi_g; \) \( \xi_{gi} \equiv N_{gi}/N_0; \) and \( \xi_{li} \equiv N_{li}/N_0. \) Thus,

\[
\begin{align*}
\xi_{gi} &= X_{gi}N_g/N_0 = X_{gi}\xi_g ;
\xi_{li} &= X_{li}N_l/N_0 = X_{li}\xi_l \\
X_{gi} &= \xi_{gi}/\xi_g ;
X_{li} &= \xi_{li}/\xi_l \\
i &= 1, \ldots, \tilde{N} - 1 \tag{6.1}
\end{align*}
\]

With only phase change and no chemical change, \( N_i \) (the number of moles in species \( i \)) remains fixed at its initial value \( N_{i0}; \) that is \( N_{gi} + N_{li} = N_i = N_{i0} = \) constant. Defining \( N_g = \sum_{j=1}^{\tilde{N}} N_{gj} \) and \( N_l = \sum_{j=1}^{\tilde{N}} N_{lj}, \) we also have \( N_g + N_l = N = N_0 = \) constant. Consequently,

\[
\xi_{gi} + \xi_{li} = \frac{N_{i0}}{N_0} \equiv \xi_i = \xi_{i0} \ ; \ i = 1, \ldots, \tilde{N} \tag{6.2}
\]

We now establish the relations for mass fractions based on both phases. Define \( \psi_{gi}, \psi_{li}, \psi_g, \) and \( \psi_l \) as the overall mass fractions of gaseous species \( i, \) liquid species \( i, \) sum of all gaseous species, and sum of all liquid species, respectively. It follows that

\[
\begin{align*}
\psi_{gi} &= \frac{\xi_{gi}W_i}{\sum_{j=1}^{\tilde{N}}(\xi_{gj} + \xi_{lj})W_j} = \frac{\xi_{gi}W_i}{\sum_{j=1}^{\tilde{N}}\xi_jW_j} ; \\
\psi_{li} &= \frac{\xi_{li}W_i}{\sum_{j=1}^{\tilde{N}}(\xi_{gj} + \xi_{lj})W_j} = \frac{\xi_{li}W_i}{\sum_{j=1}^{\tilde{N}}\xi_jW_j} ; \\
\psi_g &= \frac{\sum_{j=1}^{\tilde{N}}\xi_{gj}W_j}{\sum_{j=1}^{\tilde{N}}(\xi_{gj} + \xi_{lj})W_j} = \frac{\sum_{j=1}^{\tilde{N}}\xi_{gj}W_j}{\sum_{j=1}^{\tilde{N}}\xi_jW_j} = \sum_{j=1}^{\tilde{N}}\psi_{gj} ; \\
\psi_l &= \frac{\sum_{j=1}^{\tilde{N}}\xi_{lj}W_j}{\sum_{j=1}^{\tilde{N}}(\xi_{gj} + \xi_{lj})W_j} = \frac{\sum_{j=1}^{\tilde{N}}\xi_{lj}W_j}{\sum_{j=1}^{\tilde{N}}\xi_jW_j} = \sum_{j=1}^{\tilde{N}}\psi_{lj} = 1 - \psi_g \tag{6.3}
\end{align*}
\]
The specific enthalpy $h$ (or enthalpy per mole $\bar{h} = Wh$) will deviate from the ideal gas specific enthalpy $h^*$ (or $\bar{h}^*$) at the same temperature. For the SRK EoS case, the gas-phase enthalpy $h_g$ and the liquid-phase enthalpy $h_l$ each follow from the enthalpy departure function introduced in Chapter 2:

$$h = \frac{\bar{h}}{W} = h^*(T) + \frac{1}{W}[R_uT(Z - 1) + \frac{T(da/dT) - aZ}{b} ln\frac{Z + B}{Z}]$$  \hspace{1cm} (6.4)

For the non-ideal fluid, the volume is not exactly equal to the sum of weighted volumes of the components: $v \neq \Sigma_{j=1}^{\bar{N}} X_j v_j$. A similar character occurs for the enthalpy: $\bar{h} \neq \Sigma_{j=1}^{\bar{N}} X_j \bar{h}_j$.

The enthalpy for the two-phase mixture is given by

$$h = \psi_g h_g + \psi_l h_l = \psi_g(h_g - h_l) + h_l$$  \hspace{1cm} (6.5)

Since, at the same temperature $T$, a different $Z$ value exists for each phase, Equation (2.13) yields $\bar{N}$ values for each phase while two values of $v$ and two values of $h$ are obtained from Equations (2.6) and (6.4), respectively. We can, at fixed pressure $p$, temperature $T$, and division of moles between phases (i.e., $\xi_g = 1 - \xi_l$), consider Equations (5.3, 5.4, 2.6, 2.13, 6.1, 6.2, 6.3, 6.4) as $8\bar{N} + 4$ equations (counting two equations each for $h$ and $v$) for the $8\bar{N} + 4$ variables: $X_{gi}, X_{li}, \xi_{gi}, \xi_{li}, \psi_{gi}, \psi_{li}, \Phi_{gi}, \Phi_{li}, h_g, h_l, v_g, v_l$.

### 6.3 Shifting Equilibrium

In a phase change without chemical reaction, we have $\Delta N = 0$; $dN_l = -dN_g$; $d\xi_l = -d\xi_g$; $dN_{li} = -dN_{gi}$; and $d\xi_{li} = -d\xi_{gi}$. It follows that, for small changes in composition due
to vaporization or condensation,

\[
\begin{align*}
\frac{dX_{li}}{\xi_l} &= -\frac{1}{\xi_l} d\xi_{li} + \frac{\xi_{li}}{\xi_l} d\xi_l ; \\
\frac{dX_{gi}}{\xi_g} &= -\frac{1}{\xi_g} d\xi_{gi} + \frac{\xi_{gi}}{\xi_g} d\xi_g ; \\
\end{align*}
\]

(6.6)

The derivative of Equation (5.3) considering pressure and temperature changes is

\[
\begin{align*}
\left[ \Phi_{gi} + X_{gi} \frac{\partial \Phi_{gi}}{\partial X_{gi}} \right] dX_{gi} &= \left[ \Phi_{li} + X_{li} \frac{\partial \Phi_{li}}{\partial X_{li}} \right] dX_{li} \\
+ X_{gi} \left( \sum_{j \neq i} \frac{\partial \Phi_{gi}}{\partial X_{gj}} dX_{gj} \right) - X_{li} \left( \sum_{j \neq i} \frac{\partial \Phi_{li}}{\partial X_{lj}} dX_{lj} \right) \\
= & \left[ X_{li} \frac{\partial \Phi_{li}}{\partial p} - X_{gi} \frac{\partial \Phi_{gi}}{\partial p} \right] dp + \left[ X_{li} \frac{\partial \Phi_{li}}{\partial T} - X_{gi} \frac{\partial \Phi_{gi}}{\partial T} \right] dT ; \\
& \quad i = 1, \ldots, \tilde{N} \\
\end{align*}
\]

(6.7)

Substitution from Equation (6.6) yields

\[
\begin{align*}
\beta_{ii} d\xi_{gi} + \sum_{k \neq i} \beta_{ik} d\xi_{gk} &= \delta_i dp + \epsilon_i dT ; \\
& \quad i = 1, \ldots, \tilde{N} \\
\end{align*}
\]

(6.8)

Equation (6.8) presents a linear system of \( \tilde{N} \) equations for the \( \tilde{N} \) values of \( d\xi_g \). It can be
solved to yield the solutions. We define $A_i \equiv [\beta_{ik}]^{-1}[\delta_k]$ and $B_i \equiv [\beta_{ik}]^{-1}[\epsilon_k]$.

$$d\xi_{gi} = -d\xi_{li} = A_idp + B_idT;$$

$$dX_{li} = \left[ \frac{X_i \sum_{j=1}^{\tilde{N}} A_j}{\xi_l} \right] dp + \left[ \frac{X_i \sum_{j=1}^{\tilde{N}} B_j}{\xi_l} \right] dT;$$

$$dX_{gi} = \left[ \frac{A_i - X_{gi} \sum_{j=1}^{\tilde{N}} A_j}{\xi_g} \right] dp + \left[ \frac{B_i - X_{gi} \sum_{j=1}^{\tilde{N}} B_j}{\xi_g} \right] dT; \quad (6.10)$$

$i = 1, ..., \tilde{N}$

Now, consider the addition to the mixture of a small amount of heat $\delta q$. Specifically, it will be assumed that the energy is added at constant pressure. As equilibrium shifts, we have

$$d\psi_g = -d\psi_l;$$

$$d\psi_{gi} = -d\psi_{li} = \frac{W_i A_i}{\sum_{j=1}^{\tilde{N}} \xi_j W_j} d\xi_{gi} = \frac{W_i A_i}{\sum_{j=1}^{\tilde{N}} \xi_j W_j} dp + \frac{W_i B_i}{\sum_{j=1}^{\tilde{N}} \xi_j W_j} dT \quad (6.11)$$

The differentials for the fractional change in gas mass of species $i$ and for the fractional change in total gas mass are given by

$$\frac{1}{\psi_g} d\psi_{gi} = \frac{W_i A_i}{\sum_{j=1}^{\tilde{N}} \xi_{gj} W_j} dp + \frac{W_i B_i}{\sum_{j=1}^{\tilde{N}} \xi_{gj} W_j} dT;$$

$$\frac{1}{\psi_g} d\psi_g = \frac{\sum_{i=1}^{\tilde{N}} W_i A_i}{\sum_{j=1}^{\tilde{N}} \xi_{gj} W_j} dp + \frac{\sum_{i=1}^{\tilde{N}} W_i B_i}{\sum_{j=1}^{\tilde{N}} \xi_{gj} W_j} dT \quad (6.12)$$

When a small amount heat per unit mass $\delta q$ is added to the mixture at constant pressure, the First Law of thermodynamics becomes $dh = \delta q$:

$$dh = \psi_g (dh_g - dh_l) + dh_l + (h_g - h_l) d\psi_g = \delta q \quad (6.13)$$
The differential of the enthalpy per unit mass for a multi-component gas or liquid is given as

\[
dh = \left( \frac{\partial(h - h^*)}{\partial T} \right)_{p,X} \frac{dT}{dt} + \sum_{i=1}^{\tilde{N}} \left( \frac{\partial(h - h^*)}{\partial X_i} \right)_{p,T,X_{j\neq i}} \frac{dX_i}{dt} + \sum_{i=1}^{\tilde{N}} \left( \frac{\partial h^*}{\partial T} \right)_{X_{j\neq i}} dT \tag{6.14}
\]

Through Equations (6.13, 6.14), the added heat \( \delta q \) causes a change \( dT \) in the temperature. The change in temperature causes a shift in \( X_{gi}, X_{li}, \xi_{gi}, \xi_{li}, \psi_{gi}, \) and \( \psi_{li} \) through Equations (6.10, 6.11).

### 6.4 Zero-dimensional Model

In this model, composition and temperature vary with time but remain uniform in space. Pressure is constant and volume is allowed to change accordingly. Initial conditions must be provided. It is necessary that phase equilibrium is enforced in the initial state. Heat must be provided to drive the change of phase; combustion can occur only at higher temperatures where vaporization is completed. In that case, oxygen and fuel must be present in the initial state; they may enter through either phase or both phases. The classical piston-cylinder setup shown in Figure 6.1 is a suitable example for this model.

From Equations (6.10, 6.11, 6.13, 6.14), we may construct a system of ordinary differential equations governing the two-phase behavior as it proceeds through the shifting equilibrium change at constant pressure.

\[
\frac{d\xi_{gi}}{dt} = - \frac{d\xi_{li}}{dt} = B_i \frac{dT}{dt} ;
\]

\[
\frac{dX_{li}}{dt} = \left[ \frac{X_{li} \sum_{j=1}^{\tilde{N}} B_j - B_i}{\xi_l} \right] \frac{dT}{dt} ;
\]

\[
\frac{dX_{gi}}{dt} = \left[ \frac{B_i - X_{gi} \sum_{j=1}^{\tilde{N}} B_j}{\xi_g} \right] \frac{dT}{dt} ; \quad i = 1, \ldots, \tilde{N} \tag{6.15}
\]
The differentials for the fractional change $\dot{r}_i$ in gas mass of species $i$ and for the fractional change $\dot{r}$ in total gas mass are given by

$$
\dot{r}_i \equiv \frac{1}{\psi_g} \frac{d\psi_{gi}}{dt} = \frac{W_i B_i}{\sum_{j=1}^{\tilde{N}} \xi_{gj} W_j} \frac{dT}{dt} ; \quad \dot{r} \equiv \frac{1}{\psi_g} \frac{d\psi_g}{dt} = \frac{\sum_{i=1}^{\tilde{N}} W_i B_i}{\sum_{j=1}^{\tilde{N}} \xi_{gj} W_j} \frac{dT}{dt} ; \quad i = 1, ..., \tilde{N} \quad (6.16)
$$

Clearly, $\dot{r} = \sum_{j=1}^{\tilde{N}} \dot{r}_i$.

Now, the rate of enthalpy change can be related to the rate of heat addition (or subtraction) also to the time derivatives of temperature and mole fractions.

$$
\frac{dh}{dt} = \psi_g \left( \frac{dh_g}{dt} - \frac{dh_l}{dt} \right) + \frac{dh_l}{dt} + (h_g - h_l) \frac{d\psi_g}{dt} = \frac{\delta q}{dt} \equiv \dot{q} \quad (6.17)
$$

or equivalently

$$
\psi_g \left( \frac{dh_g}{dt} - \frac{dh_l}{dt} \right) + \frac{dh_l}{dt} + (h_g - h_l) \psi_{g\dot{r}} = \dot{q} \quad (6.18)
$$

The following relation can be applied for both the gas enthalpy $h_g$ and the liquid enthalpy $h_l$.}

---

**Figure 6.1:** Piston-cylinder for two-phase shifting equilibrium.
\[
\frac{dh}{dt} = \left( \frac{\partial(h - h^*)}{\partial T} \bigg|_{p,X_i} + \frac{\partial h^*}{\partial T} \bigg|_{X_i} \right) \frac{dT}{dt} \\
+ \sum_{i=1}^{\tilde{N}} \left( \frac{\partial(h - h^*)}{\partial X_i} \bigg|_{p,T,X_j,j \neq i} + \frac{\partial h^*}{\partial X_i} \bigg|_{T,X_j,j \neq i} \right) \frac{dX_i}{dt}
\] (6.19)

Substitution of Equation (6.19) into Equation (6.17) for the rates \(dh_g/dt\) and \(dh_l/dt\) yields a governing equation for the temperature derivative \(dT/dt\). These first order ODEs are sufficient together with initial conditions to determine the \(6\tilde{N} + 6\) variables \(X_{gi}, X_{li}, \xi_{gi}, \xi_{li}, \psi_{gi}, \psi_{li}, \psi_{g}, \psi_{l}, h_g, h_l, h,\) and \(T\) as functions of time during the heating and phase change at constant pressure.

Once the vaporization is completed or the mixture critical temperature has been exceeded, most of these equations have lost their usefulness; only Equation (6.19) would still be applicable for \(h_g\). Since the heats of formation are included in \(h_g\), that equation would still apply when gas-phase chemistry begins. It has been assumed however that gas-phase chemistry begins after vaporization is completed or after the mixture critical temperature is exceeded. Once vaporization is completed, \(h = h_g = \text{constant}\) and Equation (6.19) provides a relation between temperature change and composition change. Equations (6.15) and (6.12) no longer are relevant in the post-vaporization period; rather, changes in \(X_{gi}, \xi_{gi},\) and \(\psi_{gi}\) will be driven by chemical kinetic laws (see Section 6.6).

### 6.5 Results

Results are presented in this Section for two cases. One is with two species (methane and water) and the other is for three species (methane, water and oxygen). They will provide relevant information for next Chapter, where the a two-phase mixture of methane and water will issue from one of the opposing jets in the counterflow diffusion flame.
6.5.1 2 species: Methane and Water

The mixture considered herein is has the following molar composition: \( N_{\text{CH}_4} = 1; N_{\text{H}_2\text{O}} = 16/27 \). The absolute molar values are not relevant, but rather the ratio between them. The selected composition is equivalent to 60% methane and 40% water by mass. Results are provided at pressures of 40, 100, 250, and 500 atm in Figures 6.2 - 6.5.

In each of these Figures, subfigures (a) and (b) show the mole fractions of methane and water, respectively, in each phase (for instance, moles of gaseous methane/ number of moles in gas phase). The critical point is identified at the temperature value where the two phases become identical. Once known, it is highlighted in all other plots with a vertical dashed line to serve as a reference. Subfigures (c) and (d) show the global mole fractions in each phase (for example, moles of gaseous methane/ total number of moles). Subfigure (e) plots the total fraction in the liquid and in the gas, accounting for both species. Subfigure (f) displays the mixture enthalpy, accounting for both species and phases. The enthalpy is calculated with two different methods and compared as a check. Hence, two items are shown in the legend: \( h \), which is calculated from Equation 6.5, and \( h + dh \) which is computed by adding the enthalpy differential from Equation 6.19 to the enthalpy value at the previous temperature. We expect the curves to always be superimposed.

As we saw in Chapter 5, when two species have very similar critical temperature and pressure values, such as methane and oxygen, two-phases cannot exist at pressures that are much higher than the critical value for any of the components. In the case under consideration, the opposite effect is true. Critical pressure for water (220.64 bar) is much larger than for methane (46.1 bar). This allows reaching very high pressures, such as 500 atm, and liquid and gas phases still coexist in equilibrium.

By looking at the vertical lines for the critical point, we deduce that critical temperature increases with pressure and then decreases at very high pressures. Only a small percentage
of methane would dissolve in the liquid at very high pressure and high temperature, but the presence of this component in the liquid phase is very minimum for all other cases. Practically all methane is gas throughout the process. The main vaporizing component is water. Vaporization completes at higher temperatures with increasing pressure.

Vaporization is always completed before the critical temperature is reached. For a given starting temperature, the enthalpy decreases with pressure. Thus, more heat is required to vaporize at higher pressures, despite the fact that the enthalpy of vaporization decreases with pressure.
6.5.2 3 species: Methane, Water and Oxygen

The mixture considered herein is has the following molar composition: $N_{\text{CH}_4} = 1; N_{\text{H}_2\text{O}} = 16/27; N_{\text{O}_2} = 2$. The proportions between methane and oxygen are stoichiometric, and between methane and water the same as in the previous section. Results are provided at
Figure 6.3: Methane and water in phase equilibrium at $p = 100$ atm.

pressures of 40, 100, 250, and 500 atm in Figures 6.6 - 6.9. The Sub-figures for this system with three species are organized as they were for the previous system with two species.

The same comments exposed for the previous two-component system apply here. The main vaporizing component is still water, with little methane and oxygen present in the liquid
Figure 6.4: Methane and water in phase equilibrium at $p = 250$ atm.

phase. The mixture under consideration contains both oxidizer and fuel, and it may be ignited after vaporization is completed. This is studied in the next section.
Figure 6.5: Methane and water in phase equilibrium at $p = 500$ atm.

6.6 Ignition Delay

Following completion of the vaporization process studied in the previous section, the reacting mixture contained in the constant-pressure cylinder may continue to warm up if heat is provided until it ignites. Once a certain high temperature value is reached, the heat supply
Figure 6.6: Methane, water and oxygen in phase equilibrium at \( p = 40 \) atm.

could cease and the mixture would then auto-ignite. The auto-ignition process is studied in this section using the classical ODEs provided in any combustion textbook. Then, equations are developed for the real-gas case. Solutions to the initial value problem are sought for the same mixture presented in the previous section (i.e. stoichiometric proportions of oxygen and methane, with different dilution \% of water).
Figure 6.7: Methane, water and oxygen in phase equilibrium at \( p = 100 \text{ atm} \).

An initial temperature value of 1200 K is selected because it is high enough for the temperature run-away to occur quickly. From the 1st Law of thermodynamics for an adiabatic constant-pressure reactor:

\[
\frac{dh}{dt} = 0 \quad (6.20)
\]
Figure 6.8: Methane, water and oxygen in phase equilibrium at $p = 250$ atm.
Figure 6.9: Methane, water and oxygen in phase equilibrium at $p = 500$ atm.

### 6.6.1 Ideal-gas equations

For an ideal gas, Equation 6.20 can be further developed to yield the following ODE governing the temporal change in temperature of the reacting mixture:

$$
\frac{dT}{dt} = \frac{-N \sum_{i=1}^{N} T_i \dot{\omega}_i}{\sum_{i=1}^{N} [X_i] c_{pi}}
$$

(6.21)
where \([X_i]\) are the species molar concentrations, \(\bar{h}_i^*\) is the ideal-gas molar enthalpy of species \(i\), \(\bar{\omega}_i\) is the molar consumption rate of species \(i\), and \(\bar{r}_{pi}\) is the molar specific heat at constant pressure of species \(i\). Equation 6.21 can be integrated directly using an explicit difference scheme. The consumption rates are provided from the CHEMKIN library of subroutines. The time step must be chosen small enough to capture the fast nature of the reactions and avoid numerical divergence. At a pressure of 1 atm, the maximum possible time step was found to be \(10^{-9}\) s. At higher pressure, such as 100 atm, the time step had to be decreased to \(10^{-11}\) s.

The species concentration temporal change can be obtained as a result of both chemical reactions and changing volume:

\[
\frac{d[X_i]}{dt} = \dot{\omega}_i - [X_i] \left[ \frac{\sum_{j=1}^{\bar{N}} \dot{\omega}_j}{\sum_{j=1}^{\bar{N}} [X_j]} + \frac{1}{T} \frac{dT}{dt} \right]
\]  
(6.22)

Once \(dT/dt\) is obtained from Equation 6.21, it can be substituted into Equation 6.22 to solve for the change in concentrations.

### 6.6.2 Real-gas equations

Real-gas equations are developed starting from Equation 6.20. The real-gas molar enthalpy equals the sum of the ideal-gas molar enthalpy plus the departure function: \(\bar{h} = \bar{h}^* + (\bar{h} - \bar{h}^*)\). Its differential becomes:

\[
d\bar{h} = \left[ \frac{\partial \bar{h}^*}{\partial T} + \frac{\partial (\bar{h} - \bar{h}^*)}{\partial T} \right] dT + \sum_{i=1}^{\bar{N}} \left[ \frac{\partial \bar{h}^*}{\partial X_i} + \frac{\partial (\bar{h} - \bar{h}^*)}{\partial X_i} \right] dX_i
\]  
(6.23)
Dividing by the time differential and using Equation 6.20, one can solve for \( \frac{dT}{dt} \):

\[
\frac{dT}{dt} = -\sum_{i=1}^{\hat{N}} \left[ \frac{\partial \tau_i}{\partial X_i} + \frac{\partial (\pi - \pi^*)}{\partial X_i} \right] \frac{dX_i}{dt}
\]

(6.24)

The time derivative of the mole fractions of species \( i \) is needed to solve Equation 6.24. To get it, first we invoke the definition of molar consumption rates:

\[
\hat{\omega}_i = \frac{1}{V} \frac{dN_i}{dt} = \frac{1}{\bar{v}} \frac{dX_i}{dt} + X_i \sum_{j=1}^{\hat{N}} \hat{\omega}_j
\]

(6.25)

The temporal variation of the number of moles of species \( i \) is obtained from differentiating its definition:

\[
N_i = X_i N_{TOTAL} = X_i \sum_{j=1}^{\hat{N}} N_j;
\]

\[
\frac{dN_i}{dt} = \frac{dX_i}{dt} N_{TOTAL} + X_i \sum_{j=1}^{\hat{N}} \frac{dN_j}{dt} = \frac{dX_i}{dt} N_{TOTAL} + X_i V \sum_{j=1}^{\hat{N}} \hat{\omega}_j
\]

(6.26)

Combining Equations 6.25 and 6.26, \( \frac{dX_i}{dt} \) becomes:

\[
\frac{dX_i}{dt} = \left( \hat{\omega}_i - X_i \sum_{j=1}^{\hat{N}} \hat{\omega}_j \right) \bar{v}
\]

(6.27)

The rate of change of the molar concentrations is:

\[
\frac{d[X_i]}{dt} = \frac{d(X_i/\bar{v})}{dt} = -\frac{X_i}{\bar{v}^2} \frac{d\bar{v}}{dt} + \frac{1}{\bar{v}} \frac{dX_i}{dt}
\]

(6.28)

where

\[
\frac{d\bar{v}}{dt} = \frac{\partial \bar{v}}{\partial T} \frac{dT}{dt} + \sum_{i=1}^{\hat{N}} \frac{\partial \bar{v}}{\partial X_i} \frac{dX_i}{dt}
\]

(6.29)
Combination of the previous two Equations yields:

\[
\frac{d[X_i]}{dt} = \frac{1}{\bar{v}} \frac{dX_i}{dt} - X_i \left( \frac{\partial \bar{v}}{\partial T} \frac{dT}{dt} + \sum_{j=1}^{\tilde{N}} \frac{\partial \bar{v}}{\partial X_j} \frac{dX_j}{dt} \right)
\]  

(6.30)

Thermodynamic relations presented in Chapter 2 are used in Equations 6.24 and 6.30.

### 6.6.3 Results

Temperature curves are plotted as a function of time in Figure 6.10. Simulations are stopped shortly after auto-ignition occurs, so only the run-away phenomena is captured. Initial temperature is prescribed a 1200 K. The starting composition is a stoichiometric mixture of methane and oxygen. Two cases are presented: one without premixed water vapor and the other with 40% water by mass. Sub-figures (a), (b), and (c) show the comparison between these cases both for the ideal and for the real-gas formulations presented above. The pressures are 1, 40, and 100 atm, respectively.

Premixed water vapor causes ignition to be delayed by 41% at 1 atm, by 14.4% at 40 atm, and by 15.2% at 100 atm.

Real-gas effects are negligible at 1 atm and they become greater with pressure. However, a maximum ignition delay difference of 2% exists between the ideal and real gas models at 100 atm.
Figure 6.10: Temperature as a function of time.
Chapter 7

Two-Phase Counterflow Diffusion Flame

7.1 Introduction

The material exposed this far is combined in the present Chapter to generate a novel model approach to the counterflow diffusion flame where the inflowing streams allow both liquid and gas phases. In the particular problem under consideration, the fuel stream is composed of a two-phase mixture of methane and water, while only oxygen flows from the opposing jet. A sketch is shown in Figure 7.1. The liquid flowing from the fuel nozzle is heated by the flame as it travels downstream and vaporizes according to the shifting equilibrium laws. Similarly to what is done in Chapters 3, the goal now is to describe the problem with a set of one-dimensional ODEs valid in the central streamline of the axisymmetric domain. There are two distinct regions: one extends from the exit of the fuel nozzle to the x-coordinate where vaporization is completed, and the other includes just the single-phase domain. The model presented in Chapter 3 applies for the second region. The description of the two-phase
domain is presented in the next sections.

7.2 Model

One important aspect of the shifting phase equilibrium formulation presented in previous Chapters is that the total composition remains fixed. This is not necessarily true for our two-phase region in the counterflow problem, since combustion products may enter the two-phase domain by means of mass diffusion transport. For a mixture composed of 60% methane and 40% water (by mass), the temperature at which vaporization is completed is known from the solutions provided on Chapter 6 as a function of pressure. The gaseous composition at the location where this temperature occurs is checked using solutions from Chapters 3 and 4. The analysis indicates that small traces of combustion products diffuse into the region where temperature is below the completed-vaporization value. However, the error is less than 1% if we proceed with the assumption composition is constant in the two-phase domain. Thus, only methane and water are considered in the two-phase domain. Since this conclusion is based on solutions for the single-phase problem, the error must be re-examined after obtaining solutions for the two-phase problem. Other assumptions include kinematic equilibrium (i.e. the velocity of liquid and gas are identical), and transport occurs only through the continuous phase, which for our case is gas. We are interested in solving for the steady state. However, the transient terms of the conservation equations will be kept since
they are helpful in the solution method.

For the analysis of flowing mixtures, it is convenient to use mass fractions \( Y_{gi} \) and \( Y_{li} \) for the species in the two phases and the volume fraction of the liquid phase \( \phi = V_l/V \) rather than mole fractions. It is readily established that

\[
Y_{gi} = \frac{X_{gi}W_i}{\sum_{j=1}^{\tilde{N}} X_{gj}W_j}; \quad Y_{li} = \frac{X_{li}W_i}{\sum_{j=1}^{\tilde{N}} X_{lj}W_j};
\]

\[
X_{gi} = \frac{Y_{gi}/W_i}{\sum_{j=1}^{\tilde{N}} Y_{gj}/W_j}; \quad X_{li} = \frac{Y_{li}/W_i}{\sum_{j=1}^{\tilde{N}} Y_{lj}/W_j}
\]

(7.1)

For the given two-component system, \( \tilde{N} = 2 \), \( \psi_1 = \psi_{\text{CH}_4} = 0.6 \) = constant, and \( \psi_2 = \psi_{\text{H}_2\text{O}} = 0.4 \) = constant. It follows that

\[
\psi_1 = \psi_{g,1} + \psi_{l,1} = Y_{g,1}\psi_g + Y_{l,1}\psi_l = Y_{g,1}\psi_g + Y_{l,1}(1 - \psi_g)
\]

(7.2)

Then, the mass fraction of gas and liquid are

\[
\psi_g = \frac{\psi_1 - Y_{l,1}}{Y_{g,1} - Y_{l,1}}; \quad \psi_l = 1 - \psi_g
\]

(7.3)

The gas density \( \rho_g \), liquid density \( \rho_l \), and mixture density \( \rho \) are given by

\[
\rho_g = \frac{\sum_{j=1}^{\tilde{N}} X_{gj}W_j}{v_g}; \quad \rho_l = \frac{\sum_{j=1}^{\tilde{N}} X_{lj}W_j}{v_l}; \quad \rho = \frac{\psi_2}{\rho_l} + \frac{\psi_1}{\rho_g}
\]

(7.4)

where \( v_g \) and \( v_l \) are the volume per mole for gas and liquid, respectively; they are determined using the equation of state (Equation 2.6). The liquid phase volume fraction \( \phi \) becomes

\[
\phi = \psi_l \frac{\rho_l}{\rho_l}
\]

(7.5)

As in Chapters 3 and 4, the following equation derived from the stream function can still be
used instead of solving the continuity equation directly:

\[ G(x) = \frac{dF}{dx} ; \text{ where } F'(x) = \frac{\rho u}{2} \text{ and } G(x) = -\frac{\rho v}{r} \]  

(7.6)

As mentioned before, transport is only considered to be important in the continuous phase, which is gaseous. Thus, a modification is required in all the transport terms for each of the conservation equations. Essentially, we would like to represent the gaseous mass per unit of total area in the flux terms. This area is of course normal to the direction of the flow. For example, if the flux under consideration were due to mass diffusion:

\[
\text{Diffusion of gaseous mass} \quad \text{Area} = \text{Diffusion of gaseous mass} \quad \frac{\text{Area Gas}}{\text{Area}}
\]  

(7.7)

The first approximation for the ratio of area ”occupied” by the gas to total area is with the same ratio of volumes:

\[
\frac{\text{Area Gas}}{\text{Area}} \approx \frac{V_g}{V} = 1 - \phi \]  

(7.8)

Even a better approximation, according to the scaling between area and volume is:

\[
\frac{\text{Area Gas}}{\text{Area}} \approx \frac{V_g^{2/3}}{V} = (1 - \phi)^{2/3} \]  

(7.9)

Only the viscous dissipation term is affected in the original radial-direction momentum equation 3.3, which now becomes:

\[
\frac{\partial G}{\partial t} + H - 2 \frac{\partial}{\partial x} \left( \frac{FG}{2} \right) + 3 \frac{G^2}{\rho} + \frac{\partial}{\partial x} \left[ (1 - \phi)\mu_g \frac{\partial}{\partial x} \left( \frac{G}{\rho} \right) \right]
\]  

(7.10)

The momentum equation is needed to calculate variations in pressure \( p \) with \( x \) position. For our low-speed flow with constant cross-sectional area, we consider these pressure gradients to be small. For thermodynamic calculations, pressure may be considered uniform through
the flow. In cases where phase change is rapid and large gradients in mixture density result, this assumption must be re-examined.

The exchange of mass and energy between liquid and gas phases has to be taken into account in the energy and species conservation equations. The fractional gas mass phase-change rate per unit volume of mixture \( \dot{r} \) is used, which was defined in Equation 6.16. The time derivatives associated with the total rate \( \dot{r} \) and the rate for the species \( \dot{r}_i \) can be now viewed as Lagrangian time derivatives:

\[
\begin{align*}
    r_{0,i} &= \frac{W_i B_i}{\sum_{j=1}^{N} \xi_{g,j} W_j} ; \\
    \dot{r}_i &= r_{0,i} \frac{DT}{Dt} = r_{0,i} \left( \frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} \right) \\
    r_0 &= \sum_{i=1}^{N} r_{0,i} ; \\
    \dot{r} &= r_0 \frac{DT}{Dt} = r_0 \left( \frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} \right)
\end{align*}
\]  

(7.11)

The fractional change in mass is set equal to the fractional change in mass flux.

\[
\dot{r} = \frac{\text{Rate of change of gaseous mass/volume}}{\text{Gaseous mass/volume}}
\]

\[
\begin{align*}
    \dot{r} &= \frac{\partial}{\partial t} \left[ \rho_g (1 - \phi) \right] + \frac{\partial}{\partial x} \left[ \rho_g (1 - \phi) u \right] \\
    &= \frac{1}{\psi_g} \left( \frac{\partial \psi_g}{\partial t} + u \frac{\partial \psi_g}{\partial x} \right)
\end{align*}
\]  

(7.12)

In the development of the energy and species conservation equations, the numerator of the left-hand-side of Equation 7.12 will arise. It can then be replaced by the right side of Equation 7.11.

The energy equation for the two-phase mixture includes the effects of heat transport by conduction and by mass transport. Effects of exothermic chemical kinetics are not included in the two-phase domain where temperature is low. They only occur in the single-phase domain after vaporization is completed. If the gas is the continuous phase through which the mass and heat diffusion occur, we have

\[
\begin{align*}
    \frac{\partial}{\partial t} (\rho h) + \frac{\partial}{\partial x} (\rho hu) &= \frac{\partial}{\partial x} \left[ (1 - \phi) \lambda_g \frac{\partial T}{\partial x} \right] - \frac{\partial}{\partial x} \left[ (1 - \phi) \rho_g \sum_{j=1}^{N} \left( Y_{g,j} V_{g,j} h_{g,j} \right) \right]
\end{align*}
\]  

(7.13)
For the enthalpy of the mixture,

$$\rho h = \phi \rho_l h_l + (1 - \phi) \rho_g h_g$$  \hspace{1cm} (7.14)$$

Equation 7.13 can be recast in a form that can be used to calculate more directly temperature $T$.

$$\left[ (h_g - h_l) \rho_g (1 - \phi) r_0 + \phi \rho_l \frac{\partial h_l}{\partial T} + (1 - \phi) \rho_g \frac{\partial h_g}{\partial T} \right] \frac{\partial T}{\partial t}$$

$$- \phi \rho_l \sum_{i=1}^{\tilde{N}} \frac{\partial h_l}{\partial X_{l,i}} \frac{\partial X_{l,i}}{\partial t} - (1 - \phi) \rho_g \sum_{i=1}^{\tilde{N}} \frac{\partial h_g}{\partial X_{g,i}} \frac{\partial X_{g,i}}{\partial t}$$

$$\left[ (h_g - h_l) \rho_g (1 - \phi) r_0 + \phi \rho_l \frac{\partial h_l}{\partial T} + (1 - \phi) \rho_g \frac{\partial h_g}{\partial T} \right] u \frac{\partial T}{\partial x}$$

$$+ \left[ \phi \rho_l \sum_{i=1}^{\tilde{N}} \frac{\partial h_l}{\partial X_{l,i}} \frac{\partial X_{l,i}}{\partial x} + (1 - \phi) \rho_g \sum_{i=1}^{\tilde{N}} \frac{\partial h_g}{\partial X_{g,i}} \frac{\partial X_{g,i}}{\partial x} \right] u$$

$$- \frac{\partial}{\partial x} \left[ (1 - \phi) \lambda_g \frac{\partial T}{\partial x} \right] + \frac{\partial}{\partial x} \left[ (1 - \phi) \rho_g \sum_{i=1}^{\tilde{N}} (V_{g,i} Y_{g,i} h_{g,i}) \right] = 0$$  \hspace{1cm} (7.15)$$

In our steady flow, both total mass and total mass flux are conserved. The fractional changes in mass and mass flux for a given phase are proportioned accordingly. For a given species in the discrete phase, the fractional changes in mass and mass flux are also proportioned. However, for a species in the continuous phase, mass diffusion does not allow that simple relation. The species conservation equations governing mass fractions $Y_{li}$ and $Y_{gi}$ may be written as

$$\frac{\partial}{\partial t} (\rho \psi_i u) + \frac{\partial}{\partial x} (\rho \psi_i u) = - \frac{\partial}{\partial x} \left[ (1 - \phi) \rho_g (V_{gi} Y_{gi}) \right] ; \ i = 1, ..., \tilde{N}$$  \hspace{1cm} (7.16)$$

where

$$\rho \psi_i = \rho_l \phi Y_{li} + \rho_g (1 - \phi) Y_{gi}$$  \hspace{1cm} (7.17)$$
A recast of these equations yields

\[(Y_{g,i} - Y_{l,i}) \rho_g (1 - \phi) r_0 \frac{\partial T}{\partial t} + \rho \phi \frac{\partial Y_{l,i}}{\partial t} + \rho_g (1 - \phi) \frac{\partial Y_{g,i}}{\partial t} \]

\[
\left( \rho \phi \frac{\partial Y_{l,i}}{\partial t} + \rho_g (1 - \phi) \frac{\partial Y_{g,i}}{\partial t} \right) u + (Y_{g,i} - Y_{l,i}) \rho_g (1 - \phi) r_0 u \frac{\partial T}{\partial x} \]

\[+ \frac{\partial}{\partial x} [(1 - \phi) \rho_g V_{g,i} Y_{g,i}] = 0 ; \ i = 1, ..., \tilde{N} \tag{7.18} \]

Additional relations are the species continuity equations for the discrete phase. Since the liquid is the discrete phase with \(Y_{l,i} = \psi_{l,i}/\psi_l\), we have

\[
\frac{DY_{l,i}}{Dt} = \frac{\partial Y_{l,i}}{\partial t} + u \frac{\partial Y_{l,i}}{\partial x} = \frac{1}{\psi_l} \frac{\partial \psi_{l,i}}{\partial t} - \frac{\psi_{l,i} \psi_t \partial T}{\psi_l \partial x} + \frac{u \psi_{l,i} \partial \psi_{l,i}}{\psi_l \partial x} - \frac{w \psi_{l,i} \partial \psi_{l,i}}{\psi_l \partial x} \]

\[+ \frac{\psi_{g,i}}{\psi_l} \dot{\theta}_i + \frac{Y_{l,i} - \psi_{g,i}}{\psi_l} \dot{\theta} ; \ i = 1, ..., \tilde{N} \tag{7.19} \]

Thus,

\[
\frac{\partial Y_{l,i}}{\partial t} + \frac{\psi_{g,i}}{\psi_l} (r_{0,i} - Y_{l,i} r_0) \frac{\partial T}{\partial t} + u \frac{\partial Y_{l,i}}{\partial x} + \frac{\psi_{g,i}}{\psi_l} (r_{0,i} - Y_{l,i} r_0) u \frac{\partial T}{\partial x} = 0 ; \ i = 1, ..., \tilde{N} \tag{7.20} \]

\(\tilde{N}\) species equation are taken. The redundancy with the conditions \(\Sigma_{j=1}^{N} Y_{l,j} = \Sigma_{j=1}^{N} Y_{g,j} = 1\) is used as a check.

We have to solve for \((2\tilde{N} + 4)\) unknowns: \(\tilde{N}\) values of \(Y_{g,i}\), \(\tilde{N}\) values of \(Y_{l,i}\), \(F\), \(G\), \(T\), and \(H\). Continuity (Equation 7.6), radial momentum (Equation 7.10), energy conservation (Equation 7.15), the constant eigenvalue \(dH/dx = \text{constant}\), species continuity equations for the continuous phase (Equations 7.18), and the species continuity equations for the discrete phase (Equations 7.20) provide \(2\tilde{N} + 4\) relations.
7.3 Solution Method

Now, there are a sufficient number of equations to solve the problem, both in the two-phase and in the one-phase domain. We are still dealing with a boundary value problem, so we can impose boundary conditions at the exits of the two nozzles. We prescribe composition, temperature, and axial velocity, plus the condition that the radial velocity is 0 ($G = 0$). The evaluation of residuals, however, cannot be treated as a single domain for the solution using Newton’s method. This was the first solution attempt and it was not successful. The reason was a discontinuity in the gas-phase mass fractions at the $x$-coordinate where vaporization is completed. Essentially, temperature rises quickly near the flame and the gas-phase mass fraction of water vapor increases from almost 0 in the cold region to almost 0.4 (total water-fraction value) at the interface.

The proposed solution method is to treat the two domains as two separate boundary value problems. Solution is first sought on the two-phase domain. A value for the eigenvalue $H$ is picked from a solution from Chapter 3 with similar conditions. Then, velocity, temperature, and composition are imposed at the exit of the fuel nozzle. The temperature at the right boundary of the two-phase domain is known, because it has to match the vaporization temperature for the given mixture at the given pressure (it is taken from Chapter 6). The end coordinate of the two-phase domain is also chosen, with a value that approximates the location of the vaporization temperature form the solutions on Chapter 3. Boundary conditions for $Y_{g,i}$ and $Y_{l,i}$ are taken from the phase equilibrium code (Chapter 5) at the given temperature, pressure, and composition. A condition for the right-boundary $F$ does not need to be provided, since Equation 7.6 is only a 1st order ODE. Thus, the right boundary of $F$ (and therefore of $u$) arises from the solution. With the given considerations, the only remaining condition is for the function $G$ at the right boundary. From the Chapter 3 plots, it is inferred that $G$ is approximate linear in that region. Therefore, a variable boundary condition is imposed by linear extrapolation from the two previous mesh points. If $J^*$ is the
last mesh point in the two-phase domain, where $\phi = 0$, the condition for $G(J^*)$ is

$$G(J^*) = G(J^* - 2) + \frac{[G(J^* - 1) - G(J^* - 2)]}{[x(J^* - 1) - x(J^* - 2)]} [x(J^*) - x(J^* - 2)]$$

(7.21)

Once the solution converges for the two-phase domain, the final values of $F(J^*)$ and $G(J^*)$ are used to prescribe conditions for the first mesh point of the single-phase domain. These ensure continuity in the velocities and mass fluxes. The temperature left-boundary condition for the single-phase domain is the vaporization temperature. The imposed eigenvalue $H$ is the same, since it must be constant throughout both regions. Rather than prescribing composition on the left boundary of the single-phase domain, the total mass flux (convection and diffusion) is prescribed using data from the two-phase domain for methane and water, and setting it to 0 for the rest of the species present in the GRI 3.0 mechanism. This allows diffusion of combustion products and it also allows a way to estimate the error of our initial assumption that the composition in the two-phase domain remains constant in $x$ in that domain. Temperature and composition are prescribed on the right boundary of the single-phase domain. On that side, the value of $F$ arises from the solution, giving the velocity $u$ at the exit of the oxidizer nozzle.

Thus, the exposed method does not allow control over the mass-flow rate coming from the oxidizer nozzle. Instead, the flux there varies throughout the iteration process in such a way that the flame location provides the right temperature at the interface between the two domains as well as the energy needed for vaporization. Solutions are presented in the next section.
7.4 Results

The methodology described in the previous section is followed here to solve for the counter-flow diffusion flame when the fuel stream is a two-phase mixture of 60% methane and 40% water in phase equilibrium. The distance between the two nozzles is kept at $L = 2$ cm as in Chapter 3. We define the interface as the $x$-coordinate where vaporization is completed. It is prescribed at $x = 0.5$ cm. Figure 7.2 shows the converged steady-state solutions at $p = 1$ atm for the two-phase domain, which extends from the left nozzle ($x = 0$) to the interface. All independent variables are initialized as linear functions of $x$ varying between their boundary values. The initial mesh is coarse with 15 grid points.

Subfigure (a) shows the $F$ function and the final grid-point distribution. The mesh is finer near the interface, where gradients become steeper, especially for the gaseous mass fractions of the species, which are shown in Subfigure (g). Subfigure (b) shows the $G$ function, which exhibits the linear behavior near the interface, as dictated by the imposed boundary condition. Temperature is displayed in Subfigure (c), which is characterized by a steep gradient when approaching the interface. Axial velocity is plotted in Subfigure (d). All values are positive, so the stagnation plane falls in the single-phase domain. Similarly to solutions from Chapter 3, the velocity has a local minimum, which is near the interface. Density curves are shown in Subfigure (e). Proper evaluation of the mixture density, accounting both for liquid and gas, yields a density value that is much larger than that used in Chapter 3. As we have seen before, density is determining when it comes to flame location. Subfigure (f) shows the liquid-volume fraction $\phi$, which varies only when temperature rises. Thus, vaporization is occurring as a function of temperature. This can be seen too in Subfigure (i), where the total mass fractions in liquid and gas are plotted. Subfigure (h) indicates no variation in the liquid mass fractions. So, while there is still liquid, it is composed mostly of water with almost no methane diluted in it.
Figure 7.2: Two-phase domain solutions of counterflow flame at $p = 1$ atm.

With the two-phase domain solutions already converged, left-side boundary conditions for the single-phase problem are accessible. The model presented in Chapter 3 is used to get solutions there. Temperature and gas-phase mass fraction profiles have been merged in Figure 7.3, showing solutions for the entire domain. A vertical dashed line represents the interface position. It is observed that continuity in temperature and its gradient arises naturally, so it does in the mass fractions. However, discontinuities are very clear on the gradients of the mass fractions at the interface. This fact is what makes it difficult to solve as a single-domain boundary value problem. When one evaluates the transport terms by mass
diffusion, the derivatives of the mass fractions times the diffusion velocities are singular.

The summation of all mass fractions at the left boundary of the single-phase domain results in 1.00291, which is less than 0.3%. This justifies our initial assumption of constant composition in the two-phase domain.

Figure 7.3: Profiles including two- and single-phase domains at $p = 1$ atm.
Chapter 8

Conclusions and Future Work

A numerical-simulation approach to solving laminar counterflow diffusion flames accurately at high pressure has been provided. The problem is relevant for a broad band of applications, ranging from internal combustion, turbine, and rocket engines. These problems are characterized by flows that transition from sub- to super-critical conditions when the reactants are injected. Additionally, researchers who study turbulent combustion have been using the so-called flamelet model, which is based on retrieving tabulated data from counterflow laminar flames. The counterflow configuration can also be used to model the burning of methane hydrates, where one of the two opposing streams carries fuel plus water, which originate from the hydrate, and the other stream is oxidizer. Other topics where the scenario of burning at high pressure with additional water include bio-fuels, exhaust-gas-recirculation, or direct water injection. This flame configuration has been widely used in experimental studies because of its simple laboratory implementation, making it easy to carry out measurements. However, difficulties arise when these experiments are attempted at very high pressures.

Within this context, the project goal has been to establish a framework where real-fluid thermodynamics and high-pressure phase equilibrium laws are coupled with a counterflow
diffusion flame, entailing detailed transport properties and detailed chemical kinetics. Solutions have long been available for the counterflow problem where only one phase was considered and the common ideal-gas assumption was embraced. However, our analysis on the length- and time-scales characteristic of the liquid breakup of an injected jet indicate that such simplifications are not suitable. For instance, the diffusion layer thickness developed at the liquid-gas interface between the jet and surrounding fluid becomes much larger than the average molecular spacing at pressures of the order of 100 atm. Therefore, one concludes that continuum theory is valid in those regions and it must be applied.

It is then very important to be able to capture accurately the whole thermodynamic regime of interest for the considered applications. This is covered in Chapter 2. The Soave-Redlich-Kwong equation of state has been selected for its reasonable accuracy near the critical point. It is a two-parameter equation, and these parameters are determined through mixing rules. Thermodynamic relations with property derivatives are calculated from the given EoS. They become useful in all subsequent chapters of the dissertation.

A template of ideal-gas error estimates has been provided in Chapter 3 for the single-phase counterflow problem. Solutions have been compared with and without real-gas corrections in the equation of state, transport properties, and energy equation. Replacement of ideal-gas law by the cubic EoS causes the main deviation in the solutions, mainly in the flame location. In this sense, real-gas effects are important in the cold regions of the domain. Thus, if a researcher is interested in capturing reaction-zone locations accurately, the ideal-gas approximation should be relaxed. Comparisons have also been made with cases that included premixed water vapor with the fuel stream. Percentage of water content has been studied up to 40% in the fuel stream. The higher the water dilution, the lower the flame temperature. The reaction zone structure remains almost unaltered. Checks have also been performed on turbulence generation, chemical equilibrium effects using fugacities, radiation, and Soret effects, concluding that they can all be neglected.
Single-phase counterflow flame work has been extended in Chapter 4 by varying the strain rate to study extinction properties. Comparison has been made between real- and ideal-gas models, between use of detailed and reduced chemical kinetics, and also between water and no water vapor in the fuel stream. Good agreement was found between all our cases and those reported in the literature for extinction strain rate at low pressures. The differences were enhanced with pressure, yielding lower strain values at extinction for our real-gas model, both with detailed and reduced kinetics. Extinction strain remained almost constant with pressure when 40% water vapor was added, and its value was significantly lower. Extinction temperature analysis revealed a local minimum between pressures of 50 and 100 atm, a range where the variation was thought to be linear before. These can all be significant effects depending on the problem a researcher is facing. For example, combustion instabilities can be related to local extinction and re-ignition of the reactants.

High pressure phase equilibrium formulation has been presented in Chapter 5, establishing the basis for treating mixtures with liquid and gas. Binary and multicomponent systems including common hydrocarbons have been analyzed, highlighting the fact that liquid and gas phases may coexist at pressures that are several-fold higher than the critical value of any of the components in the mixture. When the critical properties of the present components are similar, this effect is not as significant (i.e. methane and oxygen).

Differential calculus on the phase equilibrium equations has been used in Chapter 6. It establishes the shifting phase equilibrium formulation. First, it has been used for our relevant mixtures of methane and water, or even with premixed oxygen to consider a reacting mixture. The vaporization process has been analyzed concluding that it is always completed before the critical point is reached. Auto-ignition of the subsequent all-gaseous reacting mixture has also been studied, suggesting that the presence of water acts as a delaying factor, with a stronger effect at low pressure compared to high pressure. Real-gas effects have been proven less significant for the auto-ignition problem.
The coupling between all previous pieces of this project has been accomplished in Chapter 7, where formulation for the two-phase domain has been exposed. The problem cannot be solved as a single-domain boundary value problem like has been done for Chapters 3 and 4. A solution method has been proposed and applied successfully at 1 atm, highlighting the vaporization process upstream of the flame. Further cases must be studied, especially at higher pressures. Comparison with the single-phase problem would be interesting to determine the differences in flame properties.
Bibliography


Appendix A

Newton’s Method

A system of coupled algebraic and/or differential equations can be represented in vector form as

\[ f(v) = 0 \]  \hspace{1cm} (A.1)

where \( v \) is an array containing all the unknowns and \( f(v) \) is the vector of all equations. For any arbitrary value for each of the unknowns \( v \), such as an educated initial guess, Equation A.1 will likely not be satisfied. This evaluation yields a vector of residual functions:

\[ f(v) \neq 0 \]  \hspace{1cm} (A.2)

The goal of Newton’s method is to seek for an array of solution values \( v \), such that satisfy A.1 within an acceptable tolerance. The solution approach is based on the Taylor’s series expansion for \( f \) in iteration space \( n \):

\[ f(v_{n+1}) \approx f(v_n) + J(v_{n+1} - v_n) \]  \hspace{1cm} (A.3)
where only the linear terms are kept, and \( J = \partial f / \partial v |_{v_n} \) is the Jacobian matrix, which contains the derivatives of all the residual functions with respect to the \( i \)-th unknown, and is evaluated at \( v_n \). The target of each iteration is to get \( f(v_{n+1}) \approx 0 \). From Equation A.3 one obtains

\[
v_{n+1} = v_n - J^{-1} f(v_n) = v_n + s_n \quad \text{where} \quad s_n = -J^{-1} f(v_n)
\]

Equation A.4 can be successively used from a set of initial guesses until convergence is attained. However, a few modifications are considered to gain numerical advantage. Evaluation of the inverse of the Jacobian matrix is usually one of the most expensive steps in this algorithm. In the modified Newton’s method, the Jacobian matrix is retained through a specified number of iterations before it is reevaluated (20 has been found to be suitable in this project). Another precaution ensures that the estimated solutions \( v_{n+1} \) fall within a desirable range. For that purpose, upper and lower limiting values are defined for each variable. The factor \( \delta_B \), with values between 0 and 1, is chosen as the largest number that keeps \( v_{n+1} \) within bounds. Proofs that Newton’s modified method converges suggest the error \( v_s - v_n \) decreases geometrically, which implies that \( s_n \) also decreases geometrically. So, We would expect the change \( s_n \) to become shorter as the iterative process advances. If that does not occur, a damping factor \( \delta_D \) is imposed. \( \delta_D \) decreases geometrically in each iteration if the maximum magnitude of \( s_{n+1} \) is not less or equal to the maximum magnitude of \( s_n \).

\[
\delta_D = 2^{-0.5}, \ 2^{-1}, \ ..., \ 2^{-2.5}
\]

With the previous considerations, Equation A.4 becomes:

\[
v_{n+1} = v_n + \delta_B \delta_D s_n
\]
Absolute \((ABS)\) and relative \((REL)\) tolerance values are defined to decide whether or not the algorithm has achieved convergence. The precise criteria for stopping at \(v_n\) is:

\[
|s_{i,n}| \leq \begin{cases} 
\text{either } ABS, & \text{or} \\
REL \times |v_{i,n}|
\end{cases}
\]

(A.7)

where the sub-index \(i\) in the notation here refers to the \(i\)-th entry in the vector. Tolerance values used in this project are: \(ABS = 10^{-6}\) and \(REL = 10^{-3}\).

Two ratios are defined to help decide whether a grid is sufficiently fine or it requires refinement. First, the variation over each grid interval should be less than a controlled fraction of the variation over all grid intervals:

\[
RATIO1_{k,p} \equiv \frac{|v_{k,p} - v_{k,p-1}|}{\max_p v_{k,p} - \min_p v_{k,p}} \leq TOLER1
\]

(A.8)

Sub-index \(k\) in the notation here refers to the \(k\)-th unknown, while sub-index \(p\) is the grid point number (i.e. \(p = 1, ..., N\)).

The second feature to be checked is the variation angle of slope at each interior grid point, which should be less than a controlled fraction of the variation over all grid points.

\[
RATIO2_{k,p} \equiv \frac{|\theta_{k,p} - \theta_{k,p-1}|}{\max_p \theta_{k,p} - \min_p \theta_{k,p}} \leq TOLER2
\]

(A.9)

where the angle \(\theta_{k,p}\) is defined as

\[
\theta_{k,p} \equiv \tan \left( \frac{v_{k,p+1} - v_{k,p}}{x_{p+1} - x_p} \right)
\]

(A.10)

and \(x_p\) is the spacial coordinate at grid point \(p\).

If either of these two conditions fail, then a new grid point is added in the interval be-
tween $x_{p-1}$ and $x_p$. This ensures that grid points concentrate in regions where the solution and/or its gradients change abruptly. Selected values used in this project are: $TOLER_1 = TOLER_2 = 0.5$. 
