Thermodynamic Analysis for Combustion at High Gas Densities

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1 Introduction

Combustion of hydrocarbons at high pressure is becoming more common. There are several issues that are not mastered in the combustion literature and must be addressed. (1) The critical pressure of a mixture is commonly substantially higher than the critical pressure of any component. Thus, two phases can easily exist at so-called “supercritical” conditions. (2) Since critical pressure varies with composition, a volume (even at uniform pressure and temperature) can have subcritical portions and supercritical portions in space and/or time. (3) At subcritical mixture conditions, large amounts of ambient gas will dissolve in the fluid and diffuse away from the liquid-gas interface into the liquid interior. Thus, an injected liquid cannot be assumed to have its original composition or any uniform composition; its density, surface tension, specific heat, and transport properties can change with time and space. (4) Consequently, because of density gradients on both sides of the interface, an experimental image showing a fuzzy interface cannot be sufficient proof of single-phase behavior. (5) Even at true supercritical conditions, there can be a pseudo-two-phase behavior. A narrow domain can exist in temperature-pressure space across which sharp changes in density and can occur. Although the changes are not discontinuous like the true two-phase case, there can be similar consequences. (6) Transport rates decrease and chemical rates increase with increasing pressure. Therefore, the rate-controlling mechanism can change. (7) It is known that, at high densities and pressures, fugacity and not partial pressures should appear in the chemical equilibrium laws of mass action. Clearly, one would expect therefore that chemical kinetic laws should be expressed in terms of fugacity; otherwise, they can not drive towards accurate equilibrium at long times.

In the presentation, most of these issues will be discussed. They are not all addressed in this first Abstract submission.

2 High Pressure Phase Equilibrium

The fuel often enters the combustion chamber at sub-critical temperatures but supercritical pressures, resulting in a “trans-critical” situation [1]. While droplets can be immersed in a gas, the situation is not simply traditional non-premixed combustion. The ambient hot fluid is supercritical but the cold liquid is not supercritical although existing at supercritical pressure. The gaseous mixture in the film neighboring
can have a higher critical pressure than any component of the mixture. So, the mixture critical pressure can vary significantly both spatially and temporally. For the same nearly uniform pressure and at the same instant, there can be fluid regions at sub-critical conditions and other regions that are supercritical.

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

\[ T^\ell = T^g ; \quad P^\ell = P^g ; \quad \mu^\ell = \mu^g \]  

The relationship between chemical potential and fugacity is:

\[ \mu^\phi - \mu = R_u T \ln \frac{f_i}{\phi_i} \quad \text{and} \quad \lim_{P \to 0} \left( \frac{f_i}{P_i} \right) \to 1 \]

The chemical potential equality may be expressed in terms of the fugacity as \( f^\ell_i = f^g_i \), in which, bringing in the fugacity coefficient gives \( \chi^\ell_i \phi^\ell_i = \chi^g_i \phi^g_i \). From basic thermodynamic relations, the fugacity coefficient can be expressed in terms of temperature and volume (or temperature and pressure):

\[ R_u T \ln \phi_i = \int_V \left[ \left( \frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{R_u T}{V} dV \right] - R_u T \ln Z \]

The Redlick-Kwong EoS, or one of its variants, has been recommended for the sub-critical, near-critical and super-critical regions [2].

\[ P = \frac{R_u T}{v - b} - \frac{a}{T^{0.5} v (v + b)} \]

where a and b are computed by certain mixing rules [3][4].

At high pressure values and a given temperature, the energy required to vaporize one mole of component \( i \) from the liquid mixture 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

\[ \Delta H_{v,i}^l = \frac{f_i^g - f_i^l}{W_i} = R_u T^2 \left( \frac{\partial}{\partial T} \ln \frac{\phi_i^g}{\phi_i^l} \right) \]

**Two Species.** 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 results into curves that are sharper, and the range of pressures for which two phases are obtained is narrower. This effect can be seen in Figure [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 [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.

The critical temperature values vary monotonically between the maximum and the minimum critical temperature of the two pure species (see Figure [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 [2b]). In this last plot, the normalizing pressure for each hydrocarbon is the critical pressure.
Figure 1: Hydrocarbon Fuel and Oxygen Phase Equilibrium (Normalizing pressure corresponds to Fuel).

Figure 2: Critical properties of hydrocarbon/oxygen mixtures vs. mole fraction.

Figure 3: Hydrocarbon Fuel and Oxygen Enthalpy of Vaporization (Normalizing pressure corresponds to Fuel).
of the pure hydrocarbon. The variation of the enthalpy of vaporization with temperature and pressure is given in Figure 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 4 shows density and surface tension variations for decane with oxygen. In Figure 4a, the composition is varied from the liquid/gas phase equilibrium values at prescribed pressure and temperatures. A discontinuity in the density value and in the composition occurs across the liquid-gas interface. However, a continuous variation in those values occurs on both sides of the interface. The observation of a density gradient in an experiment therefore does not imply the absence of two distinct phases. Density increases with increasing decane fraction both for the liquid and for the gas phases. Density increases faster in the gas than in the liquid with increasing fuel fraction. Figure 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.

Four Species. A 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 make 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, 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 CO_2.
Figure 5: Decane, Oxygen and Products Phase Equilibrium ($P_r = P/P_{c_{DECANE}} = 2$).

References


