JOURNAL OF PROPULSION AND POWER
Vol. 25, No. 3, May–June 2009

Technical Notes

TECHNICAL NOTES are short manuscripts describing new developments or important results of a preliminary nature. These Notes should not exceed 2500 words (where a figure or table counts as 200 words). Following informal review by the Editors, they may be published within a few months of the date of receipt. Style requirements are the same as for regular contributions (see inside back cover).

Condensation-Induced Surface Boiling of Alcohol Fuel Droplets in Combustion Chambers

Daniel E. Rosner* and Manuel Arias-Zugasti†
Yale University, New Haven, Connecticut 06520-8286

DOI: 10.2514/1.40544

I. Introduction

FOR ordinary hydrocarbon liquid fuels, droplet energy-balance considerations have previously been used to clearly delineate combustion-chamber conditions under which injected fuel droplets will be driven to either a stable (wet-bulb) temperature less than both its boiling point and its thermodynamic critical temperature or to a transcritical state with vanishing latent heat (see, for example, Rosner and Chang [1]). When one is far from criticality, the notion of a stable wet-bulb droplet temperature that is systematically less than the prevailing fuel boiling point is based on the physical notion of *evaporative cooling* [2,3]. Although energy is indeed necessary to evaporate the fuel component for combustion, when the fuel is (or contains) an alcohol [as in the case of ethanol (C_2H_5OH, hereafter abbreviated as EtOH) used for the historic German V-2 liquid-propellant rocket motor], it can also condense/absorb its own combustion product: H_2O.

In the course of our recent theoretical studies of the performance of idealized high-pressure spray combustors (see, for example, Rosner et al. [4] and Rosner and Arias-Zugasti [5]), we have encountered combinations of fuel composition and chamber conditions in which the heat of H_2O condensation is actually capable of driving injected droplets to their prevailing bubble points. Indeed, when condensation heating contributes to the droplet energy balance along with Fourier heat diffusion, the following quantitative algebraic condition plays the role of a singular locus: $T_{wb} = T_{bp}$. Here, T_{wb} (a function of droplet composition and chamber conditions) is the droplet temperature at which the net *rate* of droplet heating vanishes in the prevailing environment, and T_{bp} (a function of droplet composition and chamber pressure) is the prevailing thermodynamic bubble point of the multicomponent liquid-fuel feed at pressure p. This condition is shown here to delineate the boundary between two interesting domains of possible operation: one in which small injected droplets will tend to be driven to a stable temperature below the prevailing bubble point (during which diffusion-controlled evaporation can proceed in nearly quasi-steady fashion [1,4]) or one in which small droplets are driven to an unstable state of surface boiling beyond which the normal laws of nearly isobaric diffusion-controlled vaporization no longer apply. It is perhaps not fortuitous that the V-2 rocket and some of its higher-performance derivatives (e.g., the Russian RD-101) [6], operated rather close to, but apparently not on, this singular locus (see Sec. IV and Fig. 1).

Although the simplified predictive methods outlined/illustrated subsequently are tailored to the comparatively well-studied binary $EtOH/H_2O$ system, we believe that this condensation-induced boiling (CIB) condition is an important and rather general one and that the possibility of such situations should be anticipated early in the design stage for any spray combustor.

II. Background and Objectives

Most earlier research on the role of H_2O uptake and condensation heating on alcohol droplet evaporation was focused on near-atmospheric-pressure, low-H_2O-pressure environments without appreciable recirculation of combustion products [7–9]. Even in these mild environments, such condensation heating produced noticeable increases in initial vaporization rate, causing characteristic departures from the familiar d^2 law, even when quasi-steady (QS) assumptions are valid for the vapor phase at every instant. In these studies, droplet temperatures were far below the prevailing boiling points, and in some cases, methyl alcohol (CH_3OH) droplets initially associated with envelope flames ultimately became so diluted with water that vapor-phase flame extinction occurred [8].

Also studied were the consequences of preferential loss of the more volatile constituent from the outer portions of large multicomponent droplets [10,11]: a phenomenon that occurs even in the absence of H_2O condensation. Further heating of such droplets was shown to lead to the possibility of internal bubble formation (and droplet fragmentation), provided that an appreciable local critical superheat was attained [11]. Such superheats [perhaps as high as approximately 60 K above T_{bp} (liquid composition and p) for the $EtOH + H_2O$ system] are not necessary at the outer surface of a droplet, considered further subsequently.

Despite this earlier work on several interesting consequences of H_2O uptake and its associated droplet heating, the possibility and significance of encountering the aforementioned singular-locus condition $T_{wb} = T_{bp}$ for high-pressure alcohol-fueled spray combustors appears to have escaped the attention it deserves as a design/operability criterion. Our purpose is to call attention to this criterion and to observe that several familiar EtOH-fueled propulsion systems were operating quite close to this threshold condition, perhaps not fortuitously.

III. Analysis

Recall that T_{bp} is the thermodynamic bubble-point temperature for a droplet of the feed composition at the prevailing chamber pressure: that is, the liquid temperature at which the sum of the constituent equilibrium species vapor pressures at the vapor/liquid (V/L) interface equals the prevailing total pressure [12]. In contrast, T_{wb} is the droplet temperature at which the rates of energy gain (by Fourier conduction and vapor diffusion/condensation) are balanced by the energy required to vaporize the fuel content. Parameters used in our present numerical estimates are summarized in Tables 1 and 2. In

---

Received 25 August 2008; revision received 23 December 2008; accepted for publication 10 January 2009. Copyright © 2009 by Daniel E. Rosner. Published by the American Institute of Aeronautics and Astronautics, Inc., with permission. Copies of this paper may be made for personal or internal use, on condition that the copier pay the $10.00 per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923; include the code 0748-4658/09 $10.00 in correspondence with the CCC.

*L. W. Jones Professor of Chemical Engineering; Director, High Temperature Chemical Reaction Engineering Laboratory; daniel.rosner@yale.edu.

†Visiting Assistant Professor, Yale High Temperature Chemical Reaction Engineering Laboratory; Departmento Física Matemática y de Fluidos, Universidad Nacional de Educación a Distancia, Madrid, Spain.

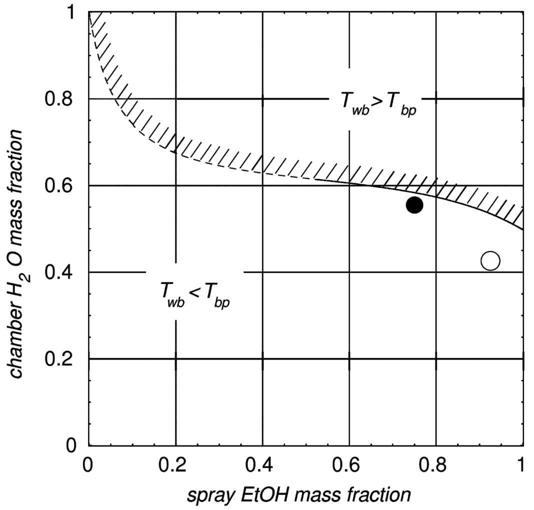

Fig. 1 Estimated $T_{\mathrm{wb}} = T_{\mathrm{bp}}$ CIB locus on the $\omega_{H_2O}(G)$ vs $\omega_{\mathrm{EtOH}}(L)$ plane at $p = 15$ and 20.9 atm for near-stoichiometric $\mathrm{EtOH/O_2}$ combustion; ● (V-2) and ○ (RD-101) operating points.

these calculations, radiation energy transfer and heat of solution effects could be neglected. Under the conditions examined, the value of T_{wb} is, mercifully, droplet-size-independent.

We note that the conditions for vapor/liquid equilibrium (VLE) [12] play a decisive role in the calculation of both T_{bp} and T_{wb} appearing in our CIB condition. Although, in many cases, thermodynamic nonideality can be neglected in the *vapor phase* at combustion gas temperatures, *liquid phase* nonideality *is* quite important in our present examples. Indeed, the EtOH activity coefficient at infinite dilution in H_2O is as large as about 6 near the $p = 1$ atm azeotrope temperature of 351.3 K [13]. The corresponding H_2O activity coefficient at infinite dilution in EtOH is about 2.5 near 351.3 K. A two-parameter van Laar fit [12] was used to represent the composition dependence of these temperature-insensitive activity coefficients in the present VLE calculations.

For present purposes, we abandon the idealized/unrealistic envelope flame picture for each liquid droplet and instead adopt a physical evaporation rate-controlled mechanism via molecular diffusion into the presumed combustion products, consistent with the approximate equality of vapor-phase energy and mass molecular diffusivities (cf. [14], Sec. 2.4, p. 85). Briefly, we use a QS equation for each of the two required species fluxes and energy flux, including the radial isobaric Stefan flow and allowing for the fact that the Fick diffusivity D (H_2O mix) is larger than D(EtOH mix) by a factor of about 2. Variable thermophysical property effects were approximately accounted for using a film condition with weighting factors of $\frac{2}{3}$ (V/L interface) and $\frac{1}{3}$ (external condition). Present molecular weight and temperature disparities were not large enough to enable appreciable Ludwig–Soret and Dufour contributions to the aforementioned diffusion fluxes [15].

In view of our present illustrative purposes, only the 4 dominant vapor species [EtOH(g), $H_2O(g)$, $CO_2(g)$, and $O_2(g)$] were explicitly considered, and any supplementary dissociation/recombination effects in the vicinity of each droplet were neglected at the pressures of interest (here, 15 and 20.9 atm). Finally, we have confined ourselves to the tractable internally well-mixed limit of spatially uniform instantaneous composition and temperature *within* each droplet during QS-species transfer. (Under actual propulsion conditions, this may indeed be more realistic than considering the opposite limit of purely radial liquid-phase *diffusion*.)

All of the aforementioned simplifications could, of course, be relaxed for situations in which increased accuracy is required and warranted by the quality of the available data. However, our simplified theoretical model is expected to adequately capture the dominant trends relevant here. Further details of our procedures and defense of our principal assumptions may be found in our bivariate population-balance analysis of the theoretical performance of such ethanol-fueled combustors [5].

The (pseudo) critical pressure corresponding to the V-2 $\mathrm{EtOH/H_2O}$ fuel is over 63 atm, so that $p/p_{\mathrm{crit},F}$ (less than 0.24) for this operational system was actually small enough to eliminate appreciable vapor-phase non-QS effects [4]. The size-independent singular temperature T_{wb}, which plays the role of an attractor for the evolving droplet temperature, retains its significance even when vapor-phase non-QS effects are *not* negligible (see [1]).

IV. Results/Discussion

To illustrate the implications of the algebraic CIB condition $T_{\mathrm{wb}} = T_{\mathrm{bp}}$, we examine the position of this singular locus for the $\mathrm{EtOH} + H_2O$ system on the $\omega_{H_2O}(G)$ vs $\omega_{\mathrm{EtOH}}(L)$ plane at two specified near-stoichiometric chamber conditions: $p = 15$ atm and $T_{\mathrm{ch}} = 2970$ K (V-2) and $p = 20.9$ atm and $T_{\mathrm{ch}} \approx 3200$ K (RD-101). Superimposed on this plane are the actual estimated operating points of these illustrative liquid-propellant rocket motor systems.

Table 1 Selected thermophysical property data and conditions assumed for the present $\mathrm{EtOH/H_2O}$ spray combustor illustrations (cf. Fig. 1)

Property	Units	EtOH	H_2O
Heat of combustion	MJ/kg	26.82	——
Latent heat of vapor at T_{nbp}	MJ/kg	0.838	2.26
Molecular weight	kg/kmol	46.069	18.016
Critical pressure p_c	atm	63.0	218
Critical temperature T_c	K	513.9	647.3
$(pV/(RT))_c$	——	0.248	0.229
Boiling point at 1 atm	K	351.4	373.15
Liquid density at T_{nbp}	$\mathrm{kg/m^3}$	0.742×10^3	0.958×10^3
Vapor heat capacity	$\mathrm{kJ/kg \cdot K}$	$3.07(T/1000)^{0.49}$	$2.29(T/1000)^{0.32}$
Fick diffusivity × (p atm)	$\mathrm{m^2/s\ atm}$	$1.1 \times 10^{-4}(T/1000)^{1.75}$	$2.2 \times 10^{-4}(T/1000)^{1.75}$

Table 2 Nominal chamber conditions (V-2 system) [6]

Characteristic	Units	Numerical value used	Notation
Chamber pressure	atm	15	p_{ch}
Latent heat of vapor at T_{nbp}	K	2970	T_{ch}
Mean molecular weight	kg/kmol	24	M_{ch}
Assumed H_2O mass fraction	——	0.55	$\omega_{H_2O}(G)$
EtOH mass fraction in fuel	$\mathrm{(m^2/s)atm}$	0.75	$\omega_{\mathrm{EtOH}}(L)$

Note that the two CIB loci are nearly indistinguishable on these coordinates and that the V-2 operating point comes remarkably close to this calculated locus, being just below it at the chosen feed composition (mass fraction): $\mathrm{EtOH}(L) = 0.75$. This raises the interesting historical question of whether, along with considerations of regenerative coolant effectiveness, the present algebraic CIB condition played some implicit or explicit role in the actual selection of the fuel ethanol mass fraction: $\mathrm{EtOH}(L)$.

We make no attempt here (or in [5]) to predict fuel vaporization-rate behavior within the interesting shaded domain of Fig. 1, in which one (or more) assumption(s) underlying all presently used methods for predicting individual droplet evaporation rate behavior fail.

Note that whereas the uptake of the combustion product $H_2O(g)$ by EtOH (or MeOH) is *energetically significant*, the corresponding uptake of, say, $CO_2(g)$ by liquid hydrocarbons at elevated pressures [16] is much less so because of drastic differences in the relevant latent heats of condensation. Thus, although product vapor uptake by injected fuel droplets at high chamber pressures is itself not unusual, the energetic consequences highlighted here (i.e., condensation-induced surface boiling) can be quite important for the alcohol/H_2O combinations considered here.

V. Conclusions

The observation that vapor condensation heating can lead to the surface boiling of injected liquid-fuel droplets in $H_2O(g)$-laden high-pressure combustion chambers seems to have escaped the attention it deserves and has motivated our present development and discussion of the simple droplet-size-independent condensation-induced boiling condition: $T_{\mathrm{wb}} = T_{\mathrm{bp}}$. Evidently (Sec. IV and Fig. 1), the EtOH-fueled German V-2 rocket (and at least one of its higher-pressure derivatives) operated rather close to this operational threshold. Although the water content of these EtOH-based liquid fuels was probably partially dictated by the efficacy of the resulting fuel as a regenerative (and partially film) coolant, we conjecture that other combustor performance factors (probably including stability [14,17]) might have been influenced had this threshold EtOH concentration been exceeded.

Acknowledgments

This Note is a byproduct of our ongoing studies of multivariate population-balance methods in chemical reactor engineering, supported in part by the National Science Fund under grant CTS 0522944 at Yale University. The participation of Manuel Arias-Zugasti was supported in part by projects S-0505/ENE/0229 and ENE2005-09190-c04-02 at Universidad Nacional de Educación a Distancia (Madrid) and Reservoir Engineering Research Institute (Palo Alto, CA) at Yale University. The authors wish to acknowledge helpful discussions with F. A. Williams, R. L. McGraw, M. B. Labowsky, and C. Anderson.

References

[1] Rosner, D. E., and Chang, W. S., "Transient Evaporation and Combustion of a Fuel Droplet Near Its Critical Temperature," *Combustion Science and Technology*, Vol. 7, No. 4, 1973, pp. 145–158. doi:10.1080/00102207308952353

[2] Rosner, D. E., *Transport Processes in Chemically Reacting Flow Systems*, Dover Mineola, NY, 2000.

[3] Law, C. K., *Combustion Physics*, Cambridge Univ. Press, New York, 2006; Secs. 6.3, 6.4.

[4] Rosner D. E., Arias-Zugasti, M., and Labowsky, M B., "Intensity and Efficiency of Spray Fuel Fed Well Mixed Adiabatic Combustors," *Chemical Engineering Science*, Vol. 63, No. 15, 2008 pp 3909–3920. doi:10.1016/j.ces.2008.04.027

[5] Rosner, D. E., and Arias-Zugasti, M., "Bi-Variate Population-Balance Model of Ethanol-Fueled Spray Combustors," American Institute of Chemical Engineers Paper 156d; Nov. 2008.

[6] Sutton, G. P., *History of Liquid Propellant Rocket Engines*, AIAA, Reston, VA, 2006.

[7] Law, C. K., Xiong, T. Y., and Wang, C. H., "Alcohol Droplet Vaporization in Humid Air," *International Journal of Heat and Mass Transfer*, Vol 30, No. 7, 1987 pp. 1435–1443. doi:10.1016/0017-9310(87)90175-X

[8] Lee, A., and Law, C. K., "An Experimental Investigation on the Vaporization and Combustion of Methanol and Ethanol Droplets," *Combustion Science and Technology*, Vol. 86, No. 1, 1992 pp. 253–265. doi:10.1080/00102209208947198

[9] Mani, S. V., Kulmala, M., and Vesala, T., "Evaporation of Poly-Dispersed Ethanol Aerosols in Humid Environment," *International Journal of Heat and Mass Transfer*, Vol 36, No. 3, 1993 pp 705–711. doi:10.1016/0017-9310(93)80046-W

[10] Landis, R. B., and Mills, A. F., "Effect of Internal Diffusional Resistance on the Evaporation of Binary Droplets," *Proceedings of the Fifth International Heat Transfer Conference*, Japan Society of Mechanical Engineers, Tokyo, 1974, pp. 345–349.

[11] Law, C. K.,"Internal Boiling and Superheating in Vaporizing Multi-Component Droplets," *AIChE Journal* Vol. 24, No. 4, 1978 pp. 626–632. doi:10.1002/aic.690240410

[12] Prausnitz, J. M., Lichtenthaler, R. N., and Gomes de Azevedo, E., *Molecular Thermodynamics of Fluid Phase Equilibria*, 3rd ed., Prentice–Hall, Upper Saddle River, NJ, 1999.

[13] Resa, J. M., Goenaga, J. M., Gonzalez-Olmos, R., and Iglesias, M., "Measurement and Modeling of Phase Equilibria for Ethanol + Water + Methanol at Isobaric Condition," *Journal of Chemical and Engineering Data*, Vol. 51, No. 6, 2006 pp 2114–2120. doi:10.1021/je0602521

[14] Harrje, D.T. (ed.), *Liquid Propellant Rocket Combustion Instability*, SP-194, NASA, 1972, pp. 74–100.

[15] Rosner, D. E., La Mantia, B., and Israel, R., "Heavy Species Ludwig-Soret Transport Effects in Air-Breathing Combustion," *Combustion and Flame*, Vol. 123, No. 4, 2000 pp 547–560. doi:10.1016/S0010-2180(00)00179-6

[16] Rosner, D. E., and Arias-Zugasti, M., "Soret-Shifted Dew-Points for Surfaces Exposed to Hydrocarbon Vapors Dilute in Compressed CO_2," *Chemical Engineering Science*, Vol. 63, No. 18, 2008, pp. 4475–4479. doi:10.1016/j.ces.2008.06.012

[17] Yang, V., Habiballah, M., Popp, M., and Hulka, J. (eds.), *Liquid Propellant Rocket Thrust Chambers: Aspects of Modeling, Analysis and Design*, Progress in Astronautics and Aeronautics, Vol. 200, AIAA, Reston, VA, 2004.

V. Yang
Associate Editor