



AIAA 2002-3880

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Ignition and Flameholding Combustion
Processes

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**38th AIAA/ASME/SAE/ASEE Joint
Propulsion Conference and Exhibit**

7-10 July 2002
Indianapolis, IN

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REVIEW OF AIR VITIATION EFFECTS ON SCRAMJET IGNITION AND FLAMEHOLDING COMBUSTION PROCESSES

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ABSTRACT

This paper offers a detailed review and analysis of more than 100 papers on the physics and chemistry of scramjet ignition and flameholding combustion processes, and the known effects of air vitiation on these processes. The paper attempts to explain vitiation effects in terms of known chemical kinetics and flame propagation phenomena. Scaling methodology is also examined, and a highly simplified Damköhler scaling technique based on OH radical production/destruction is developed to extrapolate ground test results, affected by vitiation, to flight testing conditions. The long term goal of this effort is to help provide effective means for extrapolating ground test data to flight, and thus to reduce the time and expense of both ground and flight testing. The contents of this paper will also be published as a Chapter, entitled "Air Vitiation Effects on Scramjet Combustion Tests," as part of the final report of the NATO RTO AVT WG-10 Scramjet Subcommittee.

1. OVERVIEW OF THE PHYSICS AND CHEMISTRY OF VITIATION EFFECTS

In ground tests, stored high-pressure air must be heated significantly before it is expanded through a facility nozzle to simulate hypersonic flight conditions. Resultant "vitation effects" thus refer to particular chemical kinetic and thermodynamic effects on scramjet combustion caused by the use of artificially-heated (vitated) air. Such heating may be accomplished in various ways. Two electrical techniques are by arc or by inductive electric (e.g., Plasmatron technology) heating. Both techniques are relatively expensive in terms of initial investment. A less expensive, simpler technology involves combustion preheating of beds of bricks or ceramic pebbles, followed by the input/heating of dry compressed air (as in Japan's NAL facility at Kakuda RC). Finally, an even lower cost air heating technique is to burn fuel (e.g., H₂, CH₄, or C₃H₈) with a predetermined equivalence ratio, and then expand the resultant vitiated air, with or without oxygen makeup, through a facility nozzle. The question we face here is how to characterize and control the resultant effects on scramjet test performance, since the vitiated air will differ from inlet-processed ambient air fed to a combustor in actual flight.

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1.1 Highlights of Some Key Physical-Chemical Effects

Several physical-chemical “facility processing effects” are currently recognized, starting with common knowledge that a number of species introduced to a typical test airstream differ from those emerging from inlet-processed natural air. The classic paper by Edelman and Spadaccini in 1969 [1], entitled “Theoretical Effects of Vitiated Air Contamination on Ground Testing of Hypersonic Airbreathing Engines,” addresses many key phenomena and is an essential starting point for any serious study of air vitiation effects. A comprehensive summary of their findings and many other papers appears later in Section 4.2. Below, we present an abbreviated discussion of some key homogeneous and heterogeneous gas phase effects that are detailed in Section 4.2.

1.1.1. Steam At high altitude the air composition is extremely dry, whereas large amounts of steam are present in combustion-vitiated air. Analyses in [1] showed that steam (and resultant H_xO_y radicals) could not only condense, which is clearly undesirable, but also spoil the duplication of flight conditions in scramjets by altering various thermodynamic and chemical kinetic effects on ignition, flameholding, combustion rate, and energy release from radical recombination in both the combustor and (especially) exit nozzle. In particular, Ref. 1 deduced that large amounts of steam *may* exert strong kinetic effects; the reduced molecular weight *will* lower mass capture in an inlet; and thermodynamic heat capacity and steam-dissociation effects *will* cause loss of thrust.

Quite recently, kinetic analyses of scramjet combustion by Mitani at NAL [41,42,94] indicate that steam alone (without added H_xO_y radicals) inhibits ignition. Steam acts as a very efficient third body in recombining $H + O_2 + M \rightarrow HO_2 + M$, and $H + HO_2 + M \rightarrow H_2 + O_2 + M$; and steam also reacts directly with H-atom in the chain-propagation step, $H + H_2O \rightarrow OH + H_2$. Although steam from vitiation heaters can inhibit ignition at moderately low temperatures near atmospheric pressure, such inhibition becomes unimportant at reduced pressures. For example, for Mach 6 “simulated air” at ~ 0.3 atm, variation of steam mole fraction from 0.0001 to 0.4 has essentially no effect because ignition delay is *already much longer* at this pressure, even at low steam contents [42]. Thus if T and P are such that (ignition delay) + (combustion time) $>$ (mixing residence time), ignition will be suppressed; and this tends to occur at static $T < 1100$ K and 1-atm for H_2 /air combustion. Alternately, at static $T > 1100$ K, steam has progressively less effect on ignition delay, because the critical kinetics become substantially faster than mixing rate. Thus the Damköhler number (\equiv mixing time/reaction time), which varies with T , P , and characteristic flow/mixing rate, may be used to characterize steam effects on ignition / flameholding-combustion (a Damköhler approach is developed in Section 4.3.2.).

A complementary view of how steam and H_xO_y radicals perturb H_2/O_2 ignition chemistry can be obtained by examining chain-branching explosion-limit behavior. Numerical simulations of ignition delays in H_2 /air mixtures [63,85] indicate typical scramjet ignition “potentials” closely follow the classical P vs T explosion limits of H_2/O_2 systems [93]. Thus to explode under quasi-steady conditions (or ignite under, e.g., strained counterflow conditions), the P and T must fall within the classic second-limit explosion peninsula (or within a strain-rate-dependent “extended second limit” peninsula [63]). Just above the upper boundary of the second explosion peninsula, e.g. at pressures between ~ 0.2 to 2 atm and initial temperatures < 850 K, H_2 /air mixtures no longer explode or ignite. In such cases, initial temperatures must be raised enough to reach the dynamic, extended second limit [63].

At even higher pressures, where $H + O_2 + M \rightarrow HO_2 + M$ is further favored, temperatures must be raised enough to intersect a so-called dynamic third limit [67] that resembles, but actually differs significantly from, the classic third explosion limit [93]. Reliable, definitive scramjet ignition data, that are either characterized by the extended second limit, or intersect the dynamic third limit, are scarce (see Chapter by T. Cain). However Cain did obtain and analyze a unique set of high-pressure ignition data, using a free-piston rapid-compression device [67]. He concluded ignition kinetics at high pressure do *not* follow the classic third

explosion limit, which depends on assumed-steady-state concentrations of H, OH, HO₂, H₂O₂. (Note the hydrogen peroxide may form either by HO₂ + HO₂ → H₂O₂ + O₂, or HO₂ + H₂ → H₂O₂ + H. And it may be destroyed by OH + H₂O₂ → H₂O + HO₂ and H + H₂O₂ → H₂O + OH.) Instead, Cain concluded that a high-pressure *dynamic* third limit exists in which H₂O₂ accumulates rapidly, and then, as temperature increases to ~1150 K, undergoes *rapid* dissociative chain branching (not steady state) via H₂O₂ + M → 2 OH + M. Not surprisingly, substantial disagreements exist in descriptions of the ignition mechanism, and also in rate coefficients, at these elevated pressures (see Section 4.2.3.10 for additional details).

Even very small amounts of steam significantly catalyze O₂ and N₂ vibrational relaxation processes [92] that affect predictions of aerodynamic heating by clean air. For example, the larger the vibrational disequilibrium, the lower the resultant thermal load on a downstream external surface or on a scramjet inlet surface, provided vibrational relaxation is relatively slow. Such relaxation effects may also play a role with short scramjet test models and small tactical missiles. In these cases convective transport times may be comparable to “clean-air” vibrational relaxation times for O₂ and N₂, which effectively reduces “clean-air” thermal loads. *However* when steam shortens these relaxation times by orders of magnitude, wind tunnel tests can overestimate thermal loads. Calculations performed at DLR-Goettingen [83] show this effect is significant enough to warrant further investigation for high-speed flight [84].

1.1.2. Precombustion Free Radicals Free radical species (from both well- and poorly-designed vitiation-combustion preheaters), such as H, O, and OH when H₂ fuel is used, and also C_xH_yO_z radicals when hydrocarbons (HC) are used, may significantly alter ignition delay times and flameholding/combustion in a scramjet combustor [1]. Recent simulations indicate OH introductions may reduce ignition delay time by 10x or more [41,42,89,90,99], especially at typical low inlet temperatures and pressures (largest effect occurs at ~ 0.3 to 1 atm and ~ 900 K, i.e., at flight Mach numbers of order 3-4). Depending on vehicle type and mission profile, a switch from ramjet to scramjet mode is often planned in this range, which further emphasizes the need to consider possible OH effects on ignition and flameholding. The effect of added H is similar, due e.g. to competition between H + O₂ → OH + O chain branching, and chain termination by H + O₂ + M → HO₂ + M, both of which are critical to flammability limits, ignition and flame propagation. Finally, O-atoms influence the branching reaction, O + H₂ → OH + H, which is also very important for ignition and flame propagation.

Very rich H₂ (or HC) precombustion in a Rocket-Based Combined Cycle (RBCC) scramjet system may be an effective means to anchor flames in high speed flows, due to high fluxes of H-atoms (and HC radicals) injected into the leaner H₂-air mixture of the main combustor [48,49,91,99] and many others. Resultant chain branching competes favorably with chain termination, which lengthens ignition times. Thus increased concentrations of H-atom and other radicals in *vitiated* air may further enhance both ignition and flameholding in fuel-rich, RBCC systems.

1.1.3. Nitrogen Oxides, NO_x Nitric oxide, NO, produced in amounts of 0.3 to 3 mole percent, can exert particularly strong effects on ignition and flameholding processes at low input temperatures. Nitric oxide results from any high-temperature combustion or (especially) arc heating processes involving air. In addition, residual C_xH_yO_z radicals stemming from incomplete preburning of HCs are not only very reactive with O₂, but also N₂, forming various CN intermediates and excess NO_x. Thus resultant NO_x (estimated mostly in simulations, less from experiments) promotes ignition as a function of *T*, *P*, and equivalence ratio [9,17,18,80]. Note the percentage of NO_x needed for significant reduction of ignition delay approaches 1%, which is close to the upper ‘thermal’ NO_x limit for a well designed HC-preheated wind tunnel. Note also, a theory of the effect of additives on HC combustion [101] defined families of NO_x-releasing molecular species that are typically very effective combustion promoters. Thus, despite our lack of detailed NO_x-effects data on scramjet ignition and flameholding over a useful range of *T*, *P*, and input composition/flows -- and considering the typical diffusive flame character of H₂-air and (much more complex) HC-air flameholding -- the NO_x in HC-

vitiated air may have strong and unexpected effects on scramjet combustion. Much further work is needed in the HC-fueled scramjet area (see [49] for discussion of some known problems).

1.1.4. CO₂ and Steam When large amounts of *both* CO₂ and steam are present in vitiated air, their larger heat capacities, C_p , and molecular dissociation at high T , will not only lower the maximum T and P of H₂-fueled scramjet combustion [1,38,47], but also decrease reflected shock angles [47]. These thermodynamic effects should be most pronounced at higher test Mach numbers, where temperatures are higher.

In opposition to the negative C_p -effects of CO₂ and steam, steam has a *positive* third-body kinetic effect on H₂-air flames at 1 atm and relatively low T (say 1300 to 1400 K), where “non-robust” flameholding may occur and fail intermittently. Both independent measurements and computations indicate replacement of N₂ in air by steam increases (1) non-premixed “flame strength,” i.e. the aerodynamic strain-rate limit for extinction of H₂-air counterflow diffusion flames [24], and (2) the burning velocity of premixed flames over a range of equivalence ratios [6]. Thus steam promotes local temperature increases in these respective flames near the airside edge, or forward-flame edge -- primarily via the enhanced third-body recombination, $H + O_2 + M \rightarrow HO_2 + M$, which is followed by a series of exothermic reactions that overwhelm the negative “ C_p effect.” Under the same conditions CO₂ weakens both diffusion and premixed flames via the C_p effect. Finally, the higher molecular weight of CO₂, relative to 28.95 for air, partly offsets the lower one for steam. Thus the effect of vitiation preheating with HC/air combustion is complex, and *may or may not be* more ‘neutral’ in its effects on scramjet combustor performance than preheating with H₂/air, based on a combination of thermodynamic and kinetic effects [80,24].

By now it should be clear that an important set of questions arise, based on competitive processes, that ask whether preheater-combustion may improve or worsen the anchoring of turbulent diffusion flames in critical flameholding regions, and in turn affect thrust performance. In *practical* ground-based testing, the promoting effects of excess C_xH_yO_z radicals downstream of a HC/air preheater, and the respective negative and positive effects of steam on ignition and flameholding, would compete with cooling due to C_p effects at moderate temperatures, and dissociation of H₂O and CO₂ at higher temperatures. Clearly it is important to separate and quantify the various competing effects. Russian practice at ITAM in Novosibirsk (where scramjet combustion studies began in the mid-60s) was to use kerosene to produce high-temperature (vitiated) air. Whether, or not, this use ever reflected a deliberate technical judgement to minimize possible vitiation effects is not known by the authors.

1.1.5. Condensed Species Test facilities may also introduce metallic / condensed-oxide species in the airstream. Arc heating typically releases copper oxide particles [39]. Even the stainless steel walls of shock tubes may release nickel-containing particles via shock tube erosion [96]. Fortunately, copper and nickel appear to be ineffective recombination catalysts in H₂-air flames, based on a detailed study of metal oxide/hydroxide catalysts. A ranked listing (most efficient elements down to neutral ones) includes Cr, U, Ba, Sn, Sr, Mn, Ca, Mg, Fe, Mo, Co, and then Cu and Ni which are effectively neutral [102]. Note, however that Cr, a significant component of stainless steel, was found most efficient, and probably acts heterogeneously [102]. Air heating, by passing cold air over preheated ceramics (e.g. pebble heaters, as in Japan’s NAL-KRC facility) will release ceramic powder. Such “inert” particle effects on combustion were recently analyzed theoretically [41,95]. The heat sink effect was found negligible (dust must exceed 10% of total mass flow to exert an impact), but the effect on radical termination (recombination) on particle surfaces became important at dust mass fractions > 0.001 and particle sizes < 3 microns. At sufficiently high temperatures these phenomena are reduced by ceramic softening, that prevents particles from being eroded; such may occur with zirconia bricks [41,95]. Thus in planning scramjet tests using ceramic heating facilities, one should consider the potential magnitude of particulate effects.

1.1.6. Charged and Electronically Excited Species Charged and electronically excited molecular species may also influence test results. In arc-heated wind tunnels oxygen and nitrogen ions can be present. In general, their concentrations should be relatively low because Coulomb forces are long-range, and recombinations of positive ions and electrons are very fast. However, some neutral electronically excited species survive for long times. An example is O_2 in the singlet delta state, a species observed during either homogeneous third-body or surface catalytic recombination of O. This state of O_2 can persist for the order of seconds [103]. At present, relatively little is known about the possible effects of electronically excited species on combustion kinetics. However, if present in critical concentrations, they may reduce ignition delay time, because typical recombination / relaxation energies tend to be very high (of order 10 eV vs 1 eV for recombination of radicals). Finally, ions can be exploited locally to promote combustion and anchor a flame. Examples of past work in this area are by P. Tret'yakov at ITAM in Novosibirsk, and T. Wagner and W. O'Brian at VPI & SU.

1.2. Some Practical Generalizations and Projections Thus Far

Although the primary experimental goal of any facility should simply be to supply high-enthalpy "air" with the reactive properties of a "real" inlet, appropriate knowledge of vitiation effects, coupled with careful testing and analysis, may reveal *new* ideas on stabilizing and anchoring flameholding/combustion modes. Thus, if variations of inlet air temperature and/or suspected changes in radical concentrations cause unexpected improvements in flame anchoring and more efficient scramjet combustion, a good research plan should allow focused investigation of possible free radical and inlet/combustor effects.

Excess radicals in vitiated air may, for example, recombine catalytically on upstream inlet surfaces leading to the combustor. Heat released on the walls will alter expected surface heat flux and local wall temperatures. Specific tests for surface recombination on relevant materials, using reactive probes, and measurement of wall temperatures and heat fluxes, may reveal the effects of significant excess radical concentrations. Ideally, such tests should be performed prior to routine combustor testing to assess the presence of excess radical species in wind tunnel runs with vitiated air.

Looking ahead to the detailed review of scramjet combustion processes that follows, it should become apparent that likely homogeneous (and heterogeneous) air vitiation effects have not been adequately quantified to the point of being accepted and useful. Typically, specific quantitative variations (e.g. partial derivatives) of key ignition, flameholding, and performance variables have not been adequately mapped as a function of temperature, pressure, and fuel/air inputs. Thus realistic and reliable "vitiating-compensation" offset procedures are simply not available to assess and compare data from different facilities; and hypothetical relationships between ground-based and free-flying scramjet combustor tests remain very uncertain and untested. Better information is needed on the merits of H_2 vs. HC combustion preheating, and refined methodology needs to be developed and certified to enable improved testing and utilization of test facilities.

2. DETAILED CHARACTERIZATION OF IGNITION, FLAMEHOLDING AND COMBUSTION PROCESSES

2.1. Characteristics of Ground Test Facilities and Vitiating Processes

The total temperatures (enthalpies) required to ground-test air-breathing (aero-propulsion) engines at high Mach number flight conditions can be achieved in a number of ways. Among these are:

- heat exchangers, including pre-heated ceramic beds,
- direct electrical heating, e.g., arc discharge, inductive, and resistance heaters,
- compression heating,
- shock heating, and
- in-stream combustion, with oxygen replenishment to match air content.

Each method has distinct advantages, disadvantages and limitations. All have a common characteristic of being designed for intermittent flow, due to the extreme energy required for continuous operation at simulated Mach numbers above about 3. All also distort the composition of atmospheric air to some degree, due to the high temperatures that occur in a plenum section prior to flow-expansion to simulated flight conditions. In the case of in-stream combustion, the resulting test medium is commonly referred to as "combustion-vitiated air," being composed of oxygen, nitrogen and some fraction of combustion products.

2.1.1. Typical Air Contamination in High Enthalpy Facilities Table 1 lists mole percentages of several gaseous air contaminants in wind tunnels due to typical methods of generating high enthalpy supersonic flow. The presence of very large amounts of steam, and much smaller but potentially reactive quantities of nitric oxide (NO) and free radicals, e.g. OH and O (not shown), are of concern for both hydrogen- and hydrocarbon-vitiated air. Nitric oxide formation with attendant O₂ depletion are major contaminant "sources" in facilities using arc heaters (possible ionic and electronically-excited species are not shown). Carbon dioxide, CO, and residual C_xH_yO_z molecular/radical species are additional air contaminants in hydrocarbon-vitiated air. Furthermore, deviations in the control of O₂ makeup, departures from complete mixing and combustion in a facility heater, and incomplete recombination in a facility nozzle, may cause significant deviations in downstream test simulations. Finally, methods for producing very high enthalpy flow, e.g. a piston-driven reflected shock tunnel or a shock/detonation-driven expansion tube, may alter the test gas drastically. Significant O-atom production may profoundly affect ignition/combustion kinetics. Also, relaxation rates of vibrationally-excited O₂ and N₂ are greatly accelerated by steam. Thus various generated air contaminants introduce uncertainty in scramjet testing, and may require compensation to achieve "clean air performance."

Table 1. Mole Percentages of Contaminants in High Enthalpy Vitiated Air Simulated* for Mach 4-7 and 1-atm Static Pressure

SPECIES	FLIGHT	Method / Fuel for Producing High Enthalpy Air				
		AIR+ARC HEATER	H ₂ + AIR/O ₂	CH ₄ + AIR/O ₂	C ₃ H ₈ + AIR/O ₂	CH ₃ N ₂ H ₃ + N ₂ O ₄ + O ₂
H ₂ O	<< 1	.1	5 - 33	3 - 21	2 - 15	3 - 21
CO ₂	.03	.03	.03	1.4 - 10	1.7 - 11	1.1 - 7
CO	0	0	0	≤ 0.2	≤ 0.3	≤ 0.1
NO	< .01	.2 - 3.5	≤ 1.4	≤ 1.6	≤ 1.8	≤ 1.5
O ₃	<.001					

*Calculated using equilibrium combustion and frozen expansion from 8 atm.

CH₄ ----- methane
 C₃H₈ ----- propane
 CH₃N₂H₃ ----- monomethyl hydrazine
 N₂O₄ ----- nitrogen tetroxide

2.1.2. Advantages of In-Stream Combustion Heating The ubiquitous use of combustion-vitiated air facilities warrants special attention to the advantages and disadvantages of this method for achieving high total enthalpies. These facilities have several very important advantages relative to other methods for achieving comparable total temperatures:

- Low capital investment
- Low technical risk
- Low operating costs
- High productivity
- Wide operating range
- Long run duration
- High versatility

Paramount among these is the relatively low capital investment required to design and build the heater component of a test facility - often the most expensive component. The cost of an in-stream combustion heater is lower, by a factor of four or more, than for any other method of achieving comparable temperatures in large masses of air.

The most commonly used fuel for in-stream combustion heating is hydrogen, because there is relatively low technical risk associated with designing an efficient hydrogen burner that operates over a wide range of conditions (i.e., temperatures, pressures, mass flow rates). Burners developed some thirty years ago at GASL have been operated over simulated Mach 2 through 8 conditions ($444\text{ K} \leq T_t \leq 2500\text{ K}$). Although higher temperatures are also possible, pressure constraints on the burner vessels ($P \leq 12,400\text{ kPa}$) bound the practical limit of higher temperature operation.

The use of chemical heat release also contributes significantly to the lower cost. Typical combustion heaters are equivalent to 200MW arc heaters in terms of heat transferred to the test medium, but with far lower direct operating costs per heating unit. Although shock heating can have even lower operating cost per run, run times may be unacceptably short for full development of ignition and flameholding in recirculation/combustor regions, and for applications such as engine durability testing.

Run times for heaters employing in-stream combustion are typically limited only by the supplies of air, fuel, replenishment oxygen and cooling water. Other factors, such as model survival, vacuum/exhauster capability, etc., usually cause limitations on run time.

In-stream combustion heaters also offer high facility productivity, although factors such as the replenishment of gas supplies and vacuum, model changes, data reduction and analysis, etc., limit turnaround time. The heaters typically attain operating conditions in tens of seconds, and turn off almost as quickly. Direct electrical heaters offer comparable productivity, but storage heaters typically require several hours to heat up prior to each run.

Finally, the versatility of in-stream combustion heaters should be recognized. The heater-mixer-plenum chambers are quite compact and relatively lightweight compared to other systems. Pressure and temperature in the plenum can be varied in "real time" during a run by scheduling the mass flow rates of the gas supplies. This permits real-time simulation of flight total pressure and total temperature corresponding to a segment of a flight trajectory (or even an entire flight trajectory, in principle). Furthermore, gas supplies can also be brought into a unit by flexible hoses, enabling relatively easy movement of the heater-mixer-plenum-nozzle assembly for real-time simulation of the flight Mach number approaching a stationary engine model, in concert with variations in total pressure and total temperature. (Movement of the engine model is seldom practical due to problems with ducting the hot exhaust stream from the engine into a diffuser/exhauster system, and with moving the force measurement system).

2.1.3. Disadvantages of In-Stream Combustion Heating Given the compelling advantages of in-stream combustion heating, one must ask what price is paid in terms of the fidelity of the resulting simulations and engine data. Whereas high speed aeropropulsion test facilities should at least duplicate the flight environment (speed, total temperature, total pressure), matching all the non-dimensional simulation parameters required for complex chemically reacting, supersonic or hypersonic flow through an engine, is virtually impossible.

Thus the first and most obvious disadvantage posed by the use of vitiated air is that it requires selection of the most appropriate thermodynamic parameters to duplicate, since not all can be matched due to the differences in gas composition. Although 21 molar percent oxygen content is presumably "correct" from the reactivity standpoint (to be examined), a portion of the nitrogen content is displaced by water vapor. And if a hydrocarbon fuel is used, carbon dioxide is formed, and the molecular weight is altered, so that mass capture and thrust may be affected by gas properties (discussed below). Other variations in chemical species/distributions may also occur, depending on the fuel or propellants employed (Table 1), the degree to which complete combustion is achieved, and the degree to which chemical recombination occurs in the nozzle expansion process.

Consequently, the molecular weights and specific heats of test gas mixtures will not match those of air. Thus, selections must be made about which properties of the flight environment will be duplicated and which will be relaxed to some extent. Given the importance of chemical reactions in an engine, duplication of static temperature and pressure (or density) is almost always selected, while some degree of relaxation is accepted in the local Mach number or sound speed and (sensible) enthalpy. Unfortunately, attempts to examine the effects of vitiation by comparing data between two types of facilities invariably run into the problem of selecting a proper basis for comparison. Can the effects of "vitiation" *per se* be separated from the effects of inherent or inevitable differences in test conditions? How are the data to be extrapolated to flight?

With regard to the definition of a "correct" oxygen content, it is not possible to match both the mass and mole fractions of oxygen in air due to differences in molecular weight between vitiated air and real air. Maintaining 21 molar percent of oxygen permits proper stoichiometry and reactivity with the fuel on a molar basis, but the fuel-air mixture ratio (on a mass basis) changes as the vitiated air temperature (and distribution of vitiation-combustion gases) is changed. On the other hand, maintaining 0.23 mass fraction of oxygen requires smaller

changes in fuel-air mixture ratio with changes in air temperature, but the mole fraction of oxygen changes. This is a dilemma that, although generally minor in its practical consequences, must be recognized, and the implications of the selection must be resolved during data reduction and interpretation.

The second disadvantage of in-stream combustion heating is that important thermochemical and chemical kinetic processes associated with combustion heat release in the engine may be affected by chemical species present as "contaminants" in vitiated air, but not in atmospheric air. The key thermo-chemical processes are auto-ignition / flameholding and subsequent formation of near-equilibrated combustion products, which then expand and recombine in the engine nozzle. For example, auto-ignition and flameholding may be enhanced significantly by the presence of trace amounts of free radicals in the test medium, due to incomplete combustion and/or some degree of dissociation in the heater that is not followed by near-complete recombination in the facility nozzle (the "freezing" phenomenon). Similar problems can also occur in other high temperature heaters due to the formation of nitric oxide, which remains frozen in the test gas, and sometimes substantial atomic oxygen. If auto-ignition and flameholding are marginal, the benefit obtained by testing in vitiated air may be decisive, and misleading. On the other hand, if auto-ignition and flameholding are vigorous, the benefit may be inconsequential. From a thermodynamic standpoint, the final state reached after complete combustion will be affected by the difference in specific heat between dry air and vitiated air. In general, the excess water vapor (and CO₂) in vitiated air will tend to absorb more enthalpy and thereby suppress the pressure rise produced by combustion. Finally, vibrational relaxation (of N₂) and chemical recombination (of H, O, and OH) processes in a nozzle expansion are very efficiently catalyzed by water vapor. This is a positive benefit in the facility nozzle, but in an engine nozzle the excess water vapor in vitiated air may produce misleading effects. The latter effect will clearly be dependent on the amount of water vapor produced by the engine as compared to that in the vitiated airstream.

The third disadvantage is that condensation of the combustion products may occur in the facility nozzle or test cell, at the simulated altitude-temperature. Condensation to a liquid (or solid) releases heat, produces a corresponding static pressure rise, and reduces total pressure. Expansion of the flow to atmospheric flight conditions invariably drops the temperature below the equilibrium saturation state for water vapor. (At Mach 8 conditions, about 33% of the test gas may be water vapor in a hydrogen-fired combustion heater.) Fortunately, there are two mitigating circumstances that are recognized. First, condensation is a finite-rate process. Studies of condensation in early supersonic and hypersonic tunnels employing humid atmospheric air showed that up to 111 K (200 R) of supercooling (or supersaturation) could occur before the first signs of condensation, if the rate of expansion exceeded about 1 million degrees per second. This supercooling limit is more than sufficient for simulation of typical atmospheric air temperatures; facility nozzles having an exit area of one or two feet in diameter readily exceed the required expansion rate to avoid condensation (although much larger nozzles may not). Thus, if an engine inlet is at or very near the facility nozzle exit plane, condensation will not ordinarily occur under most conditions. Second, the compression process in the inlet quickly raises the temperature (and pressure) above the condensation "line." Finally, airframe-integrated engines are typically tested at conditions simulating those downstream of the vehicle bow shock, which are also usually above the condensation line.

Therefore, for a wide range of practical test conditions, condensation should not occur in a vitiated airstream ingested by an engine. Nevertheless, it may occur in the external flow further downstream in the test cell, or in the diffuser, resulting in a higher back-pressure and poorer diffuser performance than with dry air.

Finally, hot water vapor or carbon dioxide may react with hot structural materials (e.g., carbon) differently than with either hot oxygen or nitrogen. This may or may not have consequences for materials testing, and ultimately engine durability testing, in facilities heated by in-stream combustion. Although there are no known indications of a problem of this type, it should not be dismissed out-of-hand for new flight-weight, high-temperature materials.

In the following sections, published studies of vitiation effects on (mostly) H₂-air ignition, flameholding and related modes of combustion, and high-speed engine model testing are first summarized in a referenced overview, and then examined in a detailed, roughly-chronological review of major findings.

2.2. Early Studies of Facility/Vitiation Effects on Ignition, Flameholding and Combustion

2.2.1. Brief Overview of Vitiation-Contamination Studies up to 1990 Early studies of vitiated-air contamination effects on engine combustion processes employed various techniques. The pioneering study by Edleman and Spadaccini included analytical assessments of equilibrium, vibrational and chemical relaxation, finite-rate condensation, combustion and mixing efficiency, and overall scramjet engine performance [1]. Early measurements and analyses of contaminant effects under a variety of premixed combustion conditions involved: Laminar burning velocities from conical flames [2-6]; ignition delays for H₂/O₂ explosions sensitized by NO_x in batch reactors [7]; ignition delays in reflected shock tubes, shortened by H₂O at 1000 to 1500 K and unaffected by CO₂ [8], and sensitized by NO_x [9]; blow-out residence times from well-stirred reactors [10]; calculated ignition and reaction times (5% and 95% of steady-state) from plug-flow reactor models [11-16], in which [13] used a global model to assess ignition for several complex scramjet flameholding geometries, [15,16] used detailed kinetics to assess effects of NO, H₂O, temperature and pressure, [15] also included O₃ and H₂O₂ air additives, and [16] included analyses of well-stirred reactor and premixed supersonic ignition/combustion cases; and finally, [17,18] provided refined kinetic analyses of effects of NO_x, H₂/O₂ equivalence ratio, temperature, and pressure on the catalytic NO, and non-catalytic NO₂, autoignition of H₂/air mixtures. Notably, none of the above contamination studies relate to nonpremixed turbulent ignition and flameholding, which are particularly important when H₂ and H atom are major reactants. Although some very recent studies of diffusion-influenced combustion processes have appeared, relevant information is still scarce.

In one area of non-premixed combustion, one of the authors (GLP) has conducted experimental studies of NO, CO, CO₂, H₂O and O₂ air-contaminant effects on extinction limits of laminar aerodynamically-strained H₂/N₂ vs "air" counterflow diffusion flames, using an axisymmetric tube-based Opposed Jet Burner (OJB) [19-24]. The results provide quantitative flame-strength offsets on highly-strained nonpremixed flames, which apply at density-weighted input flow conditions (nominally 1-atm) and relatively-low peak temperatures (1300-1400 K) that fall between those typically needed for ignition and those in adiabatic flames. The resultant flame strength (equivalent to airside strain rate at extinction) offsets for steam, CO₂ and O₂ are significant [22,24]. For example, increasing O₂ from 21 to 22 molar % increases flame strength by 7.5%, which compares (noteably) with a 7.4% increase in the burning velocity of a stoichiometric H₂-"air" flame (GLP analysis of Ref. 35 data). Respective near-linear offsets, at 21% O₂, for 33% steam and 10.5% CO₂ are +4.8% and -9.9%. These results [24] have recently been further generalized (unpublished manuscript) in light of a comprehensive summary of "clean air" baseline characterizations [25] derived from five sets each of tube- and nozzle-OJBs. To date, only limited numerical simulations of CO₂ and H₂O effects on H₂-air counterflow diffusion flame structure and extinction limits have been available using detailed chemistry [26]. These numerical results are being supplemented by new 1-D and 2-D simulations.

2.2.2. Detailed Review of Vitiation-Contamination Effects Studies up to 1990 Edelman and Spadaccini were first to address the high-speed-combustion problem in a study of "Theoretical Effects of [hydrogen- and propane-] Vitiated Air Contamination on Ground Testing of Hypersonic Airbreathing Engines" [1]. Using 1-D analyses for a Mach 7-10 flight regime, they concluded scramjet thrust levels in H₂-vitiated air with O₂ makeup would be lower

than for clean air due to (steam) heat capacity and dissociation effects. They also concluded the presence of free radicals such as OH, O, and H would accelerate flameholding and subsequent combustion in a test engine, while H₂O and CO₂ would “either increase or decrease reaction time, depending upon initial temperature, pressure and concentration level.”

Kuehl, in a 1962 pioneering study, found that steam enhanced (anomalously, compared to expected C_p effect) the laminar burning velocity, S_u , of H₂-air flames at 1/4 atm, 700 K input, when *substituted* for part of the N₂ in air [2]. He postulated internal thermal radiation transfer was the major contributing factor (now considered incorrect even for 1-atm flames; discussed later). Later, Reed et al. measured effects of air vitiation on S_u and flammability limits of methane/air/diluent mixtures [3,4]. Erickson and Klich conducted analytic chemical kinetic studies of water vapor and CO₂ effects on H₂-air constant-pressure combustion [11]. And Carson analytically assessed effects of O, H, and OH on H₂-air combustion [12].

Slack and Grillo investigated the sensitization of H₂-air ignition by NO and NO₂ using a reflected shock tube technique [9]. They found an order-of-magnitude reduction of the ignition-delay induction period with ~ 0.5 mole-% NO or NO₂ at < 1000 K and 2 to 1 atm. Sensitization occurred via the Ashmore and Tyler mechanism [7]: Initiated by $HO_2 + NO \rightarrow OH + NO_2$, $H + NO_2 \rightarrow OH + NO$, and also $H_2 + NO_2 \rightarrow HNO_2 + H$ when NO₂ is present; supported by $H_2 + OH \rightarrow H_2O + H$; and terminated by $OH + NO + M \rightarrow HNO_2 + M$ and $OH + NO_2 + M \rightarrow HNO_3 + M$. Sensitization was most pronounced in the vicinity of the second explosion limit for H₂-air, where rates of $H + O_2 + M \rightarrow HO_2 + M$, and $H + O_2 \rightarrow OH + O$ are balanced at the crossover temperature; e.g. ~ 925 K at 1 atm.

Jachimowski and Houghton employed a reflected shock tube to investigate the respective effects of CO₂ and H₂O vapor on the induction period of the H₂-O₂ reaction, using up to 1:1 H₂ vs CO₂ or H₂O in Ar diluent at 1000 to 1500 K and ~ 1 atm [8]. Experimentally, CO₂ did not produce a noticeable effect, whereas H₂O appeared to shorten the induction period. However, their kinetic analysis for H₂O depended upon assumed adjustments of two rate coefficients, and was inconclusive at both low and high temperatures.

Subsequently, Jachimowski [27] analyzed Slack and Grillo's shock tube ignition data [9] (based on “real” H₂-air mixtures instead of “simulated” mixtures containing Ar) to deduce a refined set of rate coefficients that fit both the ignition data, and also some H₂-air burning velocity data [28,29]. Using the refined mechanism, [27] concluded that chemical kinetic effects can be important at representative scramjet combustion conditions (up to Mach 16) and that combustor models which use non-equilibrium chemistry are preferable to models that assume equilibrium chemistry. Also, for Mach numbers up to 16, [27] concluded “an ignition source will most likely be required to overcome the slow ignition chemistry.”

Huber et. al. examined the "Criteria for Self-Ignition of Supersonic Hydrogen-Air Mixtures" [13]. They derived a correlation of available self-ignition data (64 runs) obtained in representative scramjet combustors. Their correlation was based on a pressure-length scale product as a function of combustor-entrance stagnation temperature, and a global reaction rate to approximate finite rate chemistry. Their principle findings are quoted as follows.

“(1) For the typical case of fuel stagnation temperature much less than air stagnation temperature, the ignition very likely occurs in those regions where the mixture equivalence ratio is approximately 0.2. (2) Self-ignition is extremely sensitive to the mixture temperature at the pertinent ignition locations. As a result, wall temperature and recirculation-zone temperature recovery factor have dominant influence on the phenomenon, and it is desirable for both to be as high as possible. (3) For the typical case of highly cooled walls, the ratio of boundary-layer thickness to jet penetration height, step height, or base half-height has strong influence on ignition since it directly influences recirculation-zone recovery temperature. (4) The likely regions for self-ignition in the combustor seem to have an order of merit as follows: (a) strut bases and steps where the fuel is injected well upstream, (b) the upstream recirculation regions of strong transverse

jets on plane surfaces, (c) behind steps with transverse fuel injection, and (d) bow-shock regions of transverse fuel jets.”

Ogders and Kretschmer, in their paper "Considerations of the Use of Vitiated Preheat," reviewed available combustion data, and assessed applications in gas turbine development [14]. They concluded, for a gas turbine combustor, “no model currently available in the literature has been established which will describe the combustion behavior with an accuracy sufficient for vitiated preheating to be used to assess unvitiated performance at the same nominal conditions.”

Rogers and Schexnayder performed a "Chemical Kinetic Analysis of Hydrogen-Air Ignition and Reaction Times" in the presence of contaminants [15]. They found “for mixture equivalence ratios between 0.5 and 1.7, ignition times (5% of temperature rise) are nearly constant; however, the presence of H₂O and NO can have significant effects on ignition times, depending on the mixture temperature. Reaction time (95%) is dominantly influenced by pressure but is nearly independent of initial temperature, equivalence ratio, and the addition of chemicals” (e.g. H₂O, NO_x, H₂O₂, and O₃).

Later, Rogers numerically examined several important aspects of "Effects of Test Facility Contaminants (NO and steam) on Supersonic Hydrogen-Air Diffusion Flames" [16]. Static input temperatures ranged 850 to 1250 K, and static pressures 0.2 to 2.5 atm. A plug flow reactor (PFR) model was used to determine temperature vs time for ignition (5%) and reaction (95%), and a well-stirred reactor (WSR) model was used to assess overall flame stability (blow-off) at 1-atm. Rogers concluded: (a) 0.5 to 1 mole-% NO enhanced PFR ignition for stoichiometric ($\phi = 1$) H₂/air mixtures, and increased WSR flame stability for $\phi > 0.3$ at < 1100 K and ≥ 1 -atm; and (b) H₂O retarded PFR ignition for $\phi = 1$ at < 1100 K and < 1.5 atm, and slightly enhanced PFR ignition and combustion at > 1100 K. However, for WSR inputs at 1000 K and ϕ of 0.3 to 2 at 1-atm, H₂O progressively enhanced WSR flame stability (to 14% less residence time, for 25 mass-%), both with and without 1% NO.

Finally, Rogers numerically simulated diffusive supersonic combustion of a central core of H₂ flow (240 K, Mach 2) and coaxial air (1000 K, Mach 2.2), at 1-atm [16]. Most cases were synthetically pre-seeded with a H₂/air ignition source near the H₂ tube lip, and all required a small initial turbulent intensity (0.01 or 0.02) for the "k-epsilon" model. After the ignition seed cooled from 1800 to nearly 1000 K, onset of significant downstream combustion occurred: (a) sooner with 1% NO in the air, and (b) later with 8 mass-% H₂O, compared to clean air. Combustion onset always moved upstream with increasing turbulent intensity; and unseeded autoignition with H₂O-contamination occurred later than in clean air. These retarding effects of H₂O were consistent with the PFR ignition studies at < 1100 K.

Twenty-four years after Kuehl reported a *positive* effect of added steam on S_u relative to N₂ [2], Koroll and Mulpuru conclusively confirmed that steam has an anomalous and extraordinary chemical kinetic effect on flame structure and S_u of H₂/O₂ mixtures when steam replaces N₂-diluent [6]. Notably, before Kuehl, steam was considered an inert heat sink that lowered S_u by reducing flame temperature [30,31]. Sometime after Kuehl, but before [6], Liu and MacFarlane [5] reported detailed S_u measurements as a function of input temperature (296-523 K) and composition (18 to 65 mole-% H₂-air *plus* 0 to 15% steam), using a 3 mm Mache-Hebra nozzle. They found a doubling of input temperature from 300 to 600 K tripled S_u . They also reported S_u decreased with steam addition (which consequently decreased O₂). A normalization (by GLP) of their S_u data correlation by resultant X(O₂) showed a net “apparent neutral effect” of steam addition. Despite this “neutral” finding for a 3 mm nozzle, Koroll and Mulpuru's comprehensive experimental / theoretical study [65], which used a larger (5 mm) more-ideal nozzle and *included* O₂ make-up, decisively showed that progressive reductions in S_u due to steam addition were not commensurate with changes in the heat capacity of the mixture. In fact, steam *enhanced* S_u by up to 16% when it replaced N₂ diluent in a mixture at fixed O₂ concentration.

Although the S_u results offer important chemical kinetic insight on the effect of steam in *premixed* H_2/O_2 flames (third body effect; discussed later), measured "strengths" of H_2 –(air + steam) *diffusion* flames are also important [24]; i.e., because early stages of flameholding are essentially non-premixed, and significant differences in flame structure exist which effectively control the respective effects of air contaminants on H_2 + air burning velocity and H_2 –air flame strength [25].

2.3. Detailed Review of Contamination-Effects, Ignition / Combustion Studies Since 1990

During the 1990's several detailed studies of non-premixed / premixed fuel-air systems significantly advanced our understanding of ignition and combustion processes, and possible air contamination effects relevant to testing of high-speed hydrogen-fueled (mainly) airbreathing propulsion devices.

In what follows, we first highlight the fundamental basis of scramjet efficiency. Second, we briefly review two representative studies of highly-complex non-premixed flames with vortex and turbulence interaction, and four studies of premixed flames affected by pressure, composition, stretch and diffusion. We then focus on eleven detailed studies of facility-based contamination effects on Scramjet ignition and flameholding/combustion, and thirteen experimental flame stabilization studies with bluff bodies and cavities. Next, we review a study of chemical reaction effects on numerical simulation of supersonic combustion flows, in which at least 8 reactions were required to properly simulate ignition during the transverse injection of H_2 in a generic scramjet configuration. We also identify some results on O_2 dissociation and O-atom and NO production in very-high-speed pulsed facilities. Near the end of the review, we examine several detailed ignition studies involving non-premixed diffusion and turbulence. We also review a premixed high-pressure ignition study, two catalytic ignition studies, and numerical simulations of ignition and combustion in high-speed shear layer flows. These recent ignition studies offer several new and important insights. Finally, we attempt to summarize the principal findings of this review.

2.3.1. On the Fundamental Basis of Scramjet Efficiency In contrast to rocket combustion at relatively high pressures, Harradine et al. point out that due to inherently-low gas densities, three-body recombination kinetics remain important during ignition, flameholding, supersonic combustion, and nozzle expansion [32]. Their study on the chemical basis of scramjet efficiency compared equilibrium assumptions with detailed finite-rate kinetics for premixed combustion, and then conducted a sensitivity analysis. They concluded slow three-body recombinations of H_2O dissociation products (H, OH, and O) during combustion and nozzle-expansion represent a major obstacle towards achievement of high efficiency.

2.3.2 Non-Premixed H_2 –Air Diffusion Flames w/Vortex, Turbulence Interaction Ref. [33] describes an experimental / numerical investigation of vortex interaction and flame quenching patterns that occur when a pulse of air is injected, from a 5-mm diameter syringe tube, to generate a vortex that passes coaxially through a steady opposed-jet (25-mm diameter) H_2/N_2 –air counterflow diffusion flame. Changes in flame structure due to various vortex normal velocities were followed using OH PLIF. When an air-side vortex was forced toward the flame at relatively high speed, point-quenching of the flame occurred at the stagnation point. At moderate speeds, the flame surface deformed and quenching developed in an annular ring away from the stagnation surface; here, extinction was not caused by a strain rate mechanism per se, but from the combined effect of preferential diffusion and flame curvature.

Ref. [34] applied an unsteady laminar-flamelet model in numerical simulations of a steady, turbulent, H_2/N_2 –air jet diffusion flame. Differential diffusion was neglected, and unity Lewis

numbers were assumed. Transient effects were considered in terms of relevant timescales. Radiation effects were unimportant, and flame structure was hardly affected by transient effects, but slow processes like NO formation were affected. Predictions by the unsteady model agreed reasonably with experimental data for temperature and concentrations of major species, OH, and NO. In contrast, while steady flamelet libraries yielded good results for flame structure and OH concentrations, NO was overpredicted by an order of magnitude. However, reasonable NO results were obtained by solving an unsteady flamelet in a postprocessing mode. A needed step is to include nonequal Lewis numbers to explore wide ranges of scalar dissipation rates.

2.3.3. Premixed H₂/O₂/N₂ Flames: Effects of Pressure, Composition, Stretch, Diffusion A comprehensive experimental / numerical study of laminar premixed H₂/O₂/N₂ flames (spherical, *outwardly* propagating) examined effects of pressure and composition on flame / stretch interactions [35]. Fuel equivalence ratios ranged 0.45 to 4.0; pressures 0.35 to 4.0 atm; volumetric O₂ 12.5 to 21%; and Karlovitz numbers 0 to 0.6. Both measured and predicted ratios of laminar burning velocities, for large-radius nearly-unstretched (S'_u) flames to stretched (S_L) cases, varied linearly with Karlovitz numbers (= flame stretch * mass diffusivity / S_L^2). Resultant Markstein numbers (slopes) varied from -4 to 6 with equivalence ratio (and pressure). These results implied that flame stretch and preferential diffusion interacted strongly with burning velocity.

Ref. [36] computationally examined *inward*-propagating laminar spherical flames, in both lean and rich H₂/air mixtures, to investigate the extinction of fuel pockets and formation of unconsumed reactants through flame-vortex interaction in turbulent flames. The first set of results, assuming *quasi-steady* propagation, showed the lean ($Le < 1$) flame becomes progressively weaker such that extinction is stretch-induced and accompanied by substantial unconsumed H₂ and O₂. In contrast, the burning intensity of a rich ($Le > 1$) flame is so enhanced by stretch that the flame can survive to a much smaller radius -- where extinction is caused by depletion of O₂ *ahead* of the flame, and practically no unconsumed O₂ remains. Second, for the more realistic case of *transient* propagation, a flame can persist almost to the center for both lean and rich flames, and all deficient reactants are consumed upon flame extinction. The authors extended the transient results to hydrocarbon flames, within the context of stretch and nonequidiffusion, and suggested that formation of unreacted fuel pockets may also be of limited importance there because complete consumption of the deficient reactant may occur upon extinction of the inwardly propagating flame.

Ref [37] numerically computed the effects of stretch and preferential diffusion on the structure and extinction of a laminar counterflow, *premixed* H₂/air, symmetric double-flame system. They demonstrated use of local adiabatic equilibrium temperature as a basis for measuring energy loss and gain in stretched flames, caused by preferential diffusion (mass and thermal) and reaction incompleteness (quantified by the difference between actual flame temperature and local equilibrium temperature). Energy gain was quantified by the difference between local free stream and burned gas equilibrium temperatures. With increasing stretch, lean hydrogen flames gained energy through preferential diffusion; and continuously lost energy through reaction incompleteness, which finally caused extinction (e.g. 3400 s⁻¹ at $\phi = 0.3$). For rich mixtures, energy loss through reaction incompleteness leveled off at high stretch rates; thereafter, energy loss by preferential diffusion led to extinction (e.g. 30,600 s⁻¹ at $\phi = 1.3$). Note the latter extinction limit is roughly double that for extinction of a H₂-air counterflow diffusion flame (which resides on the airside) [25].

A recent numerical study of air contamination effects examined premixed combustion in a plug flow reactor [38]. The authors developed 50 plots to illustrate the effects of NO, CO₂ and H₂O contaminants on effective ignition and reaction times, for 21% O₂ and respective H₂, CH₄ and C₂H₆ fuels, at pressures from 0.1 to 100 atm and initial premix temperatures from 800 and 1200 K. Findings included: NO > 0.2% exhibited pronounced sensitizing effects; 0 to 20% H₂O inhibited ignition monotonically below 1100 K, but slightly accelerated combustion

above 1000 K; and H₂O + CO₂ (in 2:1 ratio) had very little additional effect over H₂O on either ignition or reaction times.

2.3.4. Facility-Based Contamination Effects, H₂-Fueled Scramjet Combustion Studies

Facility-based studies have addressed some of the more obvious contamination issues. In this review of recently studied H₂-fueled scramjet configurations, it should be apparent that even “well-controlled” experiments are frequently compromised with respect to important controlled conditions, ranging e.g. from undesired boundary layer phenomena to the generally assumed tight control of O₂ level. Also, they often lack the singular cause and effect relationships we seek to pinpoint.

Nitric oxide (NO) production in air attained ~3 mole-% in an arc-heated supersonic tunnel during Mach 8 flight simulations [39]. The combined effect of 3% NO production (with destruction of 1.5% O₂ and N₂) was then assessed analytically. A 1-D finite-rate kinetics code, coupled with a 3-stream mixing code, revealed a very slight *net* enhancement of calculated thrust performance [39]. Notably, NO is predicted to cause a significant increase in calculated performance, due to enhanced nozzle recombination kinetics [40], that is partially “compensated-for” by decreased O₂ and combustion heat release [39].

Scramjet ignition difficulties related to heated air containing H₂O, radicals, and dust were assessed theoretically by Mitani using a reduced kinetic model [41], and experimentally at Mach 6 by Mitani et al. [42]. In [41] an analytic expression was developed based on steady-states for HO₂ and O atom. It predicted ignition delay in terms of O₂ and H₂O concentrations, and three rate coefficients: i.e. for $H + O_2 + M \rightarrow HO_2 + M$, and $H + O_2 \rightarrow OH + O$ (and $O + H_2 \rightarrow OH + H$), which have equal chain-branching vs termination rates at the crossover temperature, T_c, that closely corresponds to the “second explosion limit” for H₂-air; and for $H + H_2O \rightarrow OH + H_2$, which has steam as a reactant. The retarding effect of high steam concentrations (15-30 mole %) on ignition increased significantly with higher pressure and (of course) lower temperature [41,42]. Also, synthetic addition of O atoms was 1.5 times more effective for ignition than addition of H atoms [41]. With respect to dust effects, radical termination on surfaces mimics heat loss, but can become significant when dust mass fraction exceeds 0.001 and particles are < 3 μm and chemically active, whereas the heat sink effect only becomes important after mass fraction exceeds 0.1 [41].

Mitani’s experimental assessment [42] featured tests of a H₂-fueled scramjet at Mach 6 flight conditions, with air from both a vitiation-combustion heater (**V** mode) and a storage heater (**S** mode). Although steam from **V** can have a strong third-body effect in retarding ignition at ≥ 1 atm, via third-body recombination of $H + HO_2 \rightarrow H_2 + O_2$, steam effects on ignition were irrelevant in their engine tests because ignition delay at *low* pressure (0.03 M Pa) was already 5x larger, and thus not further affected by steam. Furthermore, some “compensating ignition enhancement” was promoted by transport of equilibrated H_xO_y radicals from the steam-containing **V** mode.

Post-ignition combustion behavior in Mitani’s (et al.) engine was also affected by the test air [42]. Gas sampling showed that, as fuel flow increased, combustion changed from a *weak* boundary-layer mode along the engine walls, to an *intensive* mode where flame anchored near the backward-facing step. Because a detached flame coexisted with the weak-mode “semi-anchored” flame, the detached flame appeared to promote overall kinetic-control with enhanced sensitivity to test air composition.

Kanda, in a follow-up paper [43], refined his assessment of the [42] *intensive* combustion mode, which produced a much larger thrust than the *weak* mode after a sufficient increase in primary fuel was injected normally downstream of the backward-facing step. Note pilot fuel was always injected just upstream of the step, and parallel injection was also used with any short-isolator model. Kanda concluded the boundary layer downstream of the step interacted with the fuel jet (aided by a strut at Mach 6). Thus recirculation between the step and primary fuel jet, and particularly recirculation downstream of the jet, appeared to cause significant

heat release near the fuel injector, which greatly enhanced combustion efficiency (90% vs. 5%).

Ref. [44], in a collaboration with Japan's NAL, also investigated experimentally and numerically the effects of combustion on the change of flowfield in a similar model scramjet combustor with a backward-facing step. The main airflow was at Mach 2.0, and the total temperature was 1000 K for cold flow and 1800 K for hot flow (H_2 - O_2 -air vitiation heater). Parallel injection of hydrogen was through a slit on the backward step face. To paraphrase the principal findings, as follows: The weak combustion (WC) mode was not accompanied by a shock wave, and the flowfield was similar to that for cold flow. The intensive combustion (IC) mode was accompanied by a precombustion shock wave, a large separation region generated just behind the step by the shock wave, and a resultant vortex that rolled the fuel up. The main reacting region was the shear layer just behind the shock wave, where the main airflow bumped the rolled-up fuel, and the temperature was elevated by the shock wave. This IC flowfield, controlled by the rate of mixing, led to a comparatively fast heat release and a raised pressure level in the combustor, which supported the shock wave. Thus a passive feedback occurred, and both the mixing efficiency and combustion efficiency became high. Alternately, in the WC mode, the reacting region spread more gradually over the thin shear layer downstream of the step, the heat release was lower, the flowfield was controlled by the lower reaction rate, and the combustion efficiency was lower.

To improve measurements of the combustion performance of scramjet engines using gas sampling, Mitani et al. [45] constructed four kinds of probes and quantified their degrees of reaction quenching in a Mach 2.5 supersonic combustor. They included freezing-oriented pitot probes (0.3 and 0.7 mm orifices), a freezing-type static probe, and a reaction-oriented pitot probe (1.0 mm orifice, heated nickel). The probes were tested in a slightly-diverging supersonic flow reactor duct that contained two swept-ramp H_2 injectors, and was directly connected via a contoured nozzle to a H_2 - O_2 -air vitiation heater. The heater and nozzle produced a Mach 2.5 "airflow" (containing 20% H_2O , and H_xO_y radicals), with airflow total temperature T_t from 750 to 2200 K. Autoignition was observed in the reaction-oriented probe for $T_t > 910$ K. The freezing-oriented probes yielded gas compositions having partially burned H_2 and O_2 , even at $T_t = 2190$ K. The calculated combustion efficiency increased from 0% to 100% as T_t increased with the freezing-oriented probes. The pitot pressure measurements indicated combustion actually occurred in the supersonic combustor, not in the 0.3 mm freezing-oriented probe. They concluded, by comparing with static pressure measurements, that the 0.3 mm freezing-oriented pitot probe indicated the correct combustion efficiency for scramjet engine conditions. The similar 0.7 mm probe failed to quench H_2 - O_2 reactions, misled the occurrence of combustion at $T_t = 1000$ K, and yielded an incorrect higher combustion efficiency at $T_t = 1200$ K.

Takahashi et al. [46] tested active control of flameholding by secondary air injection downstream of a rearward-facing step, and effectively reduced pressure oscillations from unstable flameholding and/or blowoff in a fixed-geometry, rectangular scramjet combustor at an off-design point. Injected air controlled the effective cross-sectional area of the combustor, and also improved self-ignition at low total temperatures.

A numerical assessment of H_2O and CO_2 vitiation effects on mixing and combustion efficiency, at Mach 7 flight conditions, involved simulations of a premixed diverging-duct combustor flowfield, using a single 30° angled injection of H_2 for both a hydrocarbon-vitiated air stream and clean air [47]. The temperature rise due to combustion was lower in the vitiated air case, due to the higher heat capacity and more extensive dissociation of H_2O and CO_2 . Also, both combustion-induced pressure rise and reflected shock angles were lower, due to the same cause. Finally, only small differences in overall mixing efficiency and combustion efficiency were found, both in the near and far field. Thus [47] concluded observed differences were mainly due to thermodynamics; and whereas vitiation-combustion facilities are useful in simulating scramjet flow fields, appropriate analysis is necessary.

2.3.5. Contamination Effects, Hydrocarbon-Fueled Scramjet Combustion Chinitz and Erdos examined the effects of NO and steam contaminants on ignition and combustion, with 1-atm “air,” of several **neat** hydrocarbon fuels [48], and of the simulated products of Norpar-12 endothermic-decomposition [49]. Ref. [48] used pure steam and NO, and also assessed possible chemistry effects on detonations. Unfortunately, the respective effects of NO and steam on neat hydrocarbon fuels [48] were too variable in magnitude and direction to permit generalizations. As a result, the principal conclusion from that study was that “careful pre- and post-test analyses, using validated chemical kinetic mechanisms, will be required to ensure that wind tunnel experiments using hydrocarbon fuels achieve the result desired and that the data obtained are correctly interpreted.”

In [49], the authors adopted a recommended surrogate fuel mixture of H₂, CH₄, C₂H₄, C₂H₆, C₃H₆, and C₃H₈ to represent the typical catalytic decomposition products of Norpar-12 at 867 K. Separately, they calculated heater-vitiate at 500-psi, and expanded it through a 10° half-angle nozzle (7.3 area ratio), assuming frozen composition to the nozzle throat and finite-rate recombination in the expansion. The resultant vitiate was assumed to enter an engine model and then “process” to combustor inlet conditions at constant composition, with initial temperatures of 800 and higher.

Four separate kinetic effects were identified in [49]. First, they examined the effects of NO concentration and initial temperature on ignition delay times (5% temperature rise) and combustion times (95%). Unlike with the neat fuels, the enhancing effect of NO on ignition delay was greatest at 800 K, but at higher temperatures was relatively slight and somewhat complex.

Second, [49] examined the effects of steam and its H_xO_y dissociation products on ignition delay and combustion times as a function of initial temperature and Mach number based on total enthalpy. Notably, both ignition and combustion times were dramatically increased by steam at initial temperatures below 1200 K; e.g., at 800 K these delay times were longer by two (or more) orders of magnitude. Thus the effects of steam and its dissociation products appeared highly significant below model-engine combustor entrance temperatures of ~ 1100 K, because both ignition and reaction times may be orders-of-magnitude higher, giving the appearance of a poorly functioning, or non-functioning engine configuration. Above about 1100 K, little effect of steam contamination on ignition and combustion may be expected. In conclusion with respect to steam effects, “combustion may not occur at these temperatures in vitiated-air wind tunnel tests, whereas combustion would occur in flight.”

Third, [49] examined the effect of atmospheric ozone on ignition and combustion times, and showed the effects were relatively small. Fourth, [49] showed some moderate effects of excess steam on species recombination in exhaust nozzle expansions, to form CO, CO₂ and steam, and to affect the axial temperature and pressure distributions. This excess steam-enhanced recombination and heat release would augment measured thrust in a vitiated air facility.

Finally, regarding the computational assessment of NO chemical kinetic effects on ignition of hydrocarbon fuels in [49], it can be concluded that an adequately complete and properly optimized (for ignition) kinetic mechanism must be utilized. That is, both “complete” and reduced mechanisms are required wherein *all* potentially important reactions between NO and the remaining constituents are included or accounted-for, and the rate coefficients have been validated *under ignition conditions*. The size of such a mechanism is considerable when hydrocarbon fuels are used. In the absence of a relatively complete and properly validated mechanism, erroneous conclusions are easily drawn regarding predicted effects of NO in ground tests designed to replicate hypersonic flight. Clearly, supporting analytical studies using *proven* reduced mechanisms are required to either “correct” the scramjet test data for the effects of flow contaminants if they are minor, or flag the data if they are profound.

2.3.6. Experimental Flame Stabilization Studies with Bluff Bodies and Cavities A very early paper by Winterfeld [104] examined the stabilization of flames in recirculation zones behind bluff-body flame holders situated in a tube. Attention was paid to the separation point and downstream onset of flame, the main flame, the recirculation flow and its contour, and the rear stagnation point. Data plots characterized the dimensionless length, diameter, and residence times of recirculation zones behind discs, 45° and 90° cones, and a cylinder, with various degrees of (flow) blockage, in both the presence and absence of flame. The mean residence time varied inversely with the velocity of the approaching flow. The presence of a flame increased the residence time considerably, and reduced the exchange of mass and energy. Flame holders that deflected flow the most produced the greatest exchange.

More recently, several flame-holding/stabilization studies have appeared in the literature, involving low- and high-speed, and unheated and heated air flows past fueled ramps, struts, cavity flameholders, and trapped vortex combustors.

In one parametric study, the flame stabilization characteristics of a separated strut were examined at Mach 1.5 [50]. Two opposing triangular prisms (with 15 and 10 mm bases) were configured as if a single stepped-strut was sliced at the backward-facing wall. With parallel injection of H₂ from the larger base, shadowgraph and schlieren imagery demonstrated no shocks or expansion waves existed within the gap. Variations of the airflow total temperature, H₂ flow rate, and gap length were examined in conjunction with LDV measurements. Flame stabilization characteristics changed drastically with gap length, and were controlled by competition between reaction rates and mass transfer rates (residence time), as measured by local Damköhler number. Progressive widening of the gap increased residence time, altered air entrainment and effective equivalence ratio, and eventually created two stable flameholding regions. The technique provides a unique parametric research tool for examining tradeoffs involving residence time, air entrainment, fuel equivalence ratio, and drag penalty in the development of flame stabilization approaches.

A trapped-vortex combustor concept has been used to assess (mostly) low-speed flame stabilization in a cavity between two axisymmetric disks mounted in tandem [51,52]. Fuel injection with co-flowing air, from one of the disks, into a variable-length cavity, bounded by the other disc and surrounded by a primary airflow, resulted in trapped-vortex combustion with various degrees of stability. Detailed experimental measurements and computations illustrate the effects of geometry and primary/annular airflows on primary equivalence ratio, lean blowoff of flame, velocity and temperature distributions, combustion efficiency, and pollutant emissions. Optimal cavity size resulted in increased residence time, restricted entrainment of primary-air into the cavity despite outside unsteadiness, and reduced drag. Lengthening of the cavity increased entrainment of primary-air, but produced vortex shedding that led to unstable flames and increased drag.

In a simple basic study of subsonic CH₄-air diffusion flames stabilized behind a backward-facing step, a halon fire suppressant was pulse-injected into the air flow while CH₄ issued from a porous plate downstream of the step [53]. The critical mole fraction of agent needed for flame extinction varied strongly with injectant period, air input velocity and step height. Also, two distinct regimes of flame stabilization were observed, i.e., a rim-attached wrinkled laminar flame, and a wake-stabilized turbulent flame. This simple device allows the characterization of air contaminant residence time and flame structure on subsonic flame stability.

An excellent review and initial assessment of cavity flameholders, for ignition and flame stabilization in high speed flows, describes previous scramjet research, present concepts for flame stabilization, and the use of ultra-high-speed schlieren imaging to identify two basic flow regimes [54]. The authors' phenomenological assessment includes the following. For open cavities ($L/D < 10$) the turbulent shear layer separates from the upstream lip and reattaches to the back face, and small cavity drag results. For closed cavities ($L/D > 10$) the free shear layer reattaches to the *lower* wall, resulting in significantly increased drag. Self-sustained cavity oscillations depend on both L/D ratio and Mach number. In a short cavity, transverse oscillations may dominate, but longitudinal oscillations may be present. In a long cavity,

longitudinal oscillations dominate, but these may be caused either by reflected acoustic waves or shedding vortices. Finally, [54] discusses some key fundamentals of resonant frequencies, fluid injection, exchange of heat and mass, use of passive and active control methods, and the adequacy of short duration pulse facilities.

Following the above [54] review and initial study, [55] describes an experimental effort to characterize the flameholding process of an underexpanded H_2 jet injected into a supersonic cross flow of air, for different jet-to-free-stream momentum flux ratios. An expansion tube was used to accelerate "radical-free air" to flight Mach 10 and 13. Schlieren images showed the shock structure around the jet, and periodic coherent structures in the jet/free-stream interface. Overlaid OH-PLIF (side and top view) and schlieren images showed that initial OH signals appeared in the recirculation region upstream of the jet exit, and in the bow shock region, compared to previous experiments at lower total enthalpy where no strong OH signal was observed within 10 jet diameters. At Mach 10 the OH signal decreased significantly as the mixture expanded around the jet flow field, indicating a partial quenching of ignition. The authors concluded combustion of hydrogen and air at high enthalpy conditions was a mixing limited process, and that improved injection schemes would be required for practical applications in scramjets.

Ref. [56] used OH PLIF and schlieren imaging to investigate shock-induced combustion phenomena on a 40° wedge in an expansion-tube flow. Stoichiometric H_2/O_2 mixtures, with N_2 dilutions of 75, 80, and 85%, were tested at two different flow conditions. "Three test cases yielded shock-induced combustion behind an attached shock at the tip of the wedge. Depending on the sensitivity of the mixture, the flame front either rapidly converged with the shock or slowly diverged away from it. Measured wave angles and surface pressures were, in general, well modeled by shock-polar theory using frozen thermochemistry. Two other test cases, using the most sensitive gas mixtures, produced a closely coupled flame front behind a detached shock wave near the wedge tip. In this case surface pressure was better modeled using equilibrium chemistry. And finally, simple finite-rate chemistry modeling of the ignition zone agreed well with the experimental results in all cases.

Baurle and Gruber [105] began a systematic study of "Recessed Cavity Flowfields for Supersonic Combustion Applications," to better understand the cold flow characteristics of cavity flowfields. They used the VULCAN Navier-Stokes code (Viscous Upwind Algorithm for Complex flow Analysis), to investigate the effects of cavity geometry, cavity length to depth ratio, and the incoming boundary layer. "In general the cavity geometry had a minimal effect on the cavity entrainment rates and residence times. The cavity length had the largest influence on the mass entrainment rate, while the cavity depth essentially determined the cavity residence time. Larger cavities had significantly higher drag coefficients than the smaller cavities considered. Standard two-equation turbulence models showed the tendency to overpredict the turbulent viscosity near the separation point and within the cavity, resulting in steady flowfields for all geometries considered. Comparisons with unsteady laminar calculations showed the enhanced diffusion of the turbulent simulations allowed much larger mass entrainment rates into the cavity even though the flowfields were steady."

Baurle et al. [106] continued using VULCAN to conduct an initial "Numerical and Experimental Investigation of a Scramjet Combustor for Hypersonic Missile Applications." Pre-test CFD simulations of cold flows, and reacting flows using 3- and 10-step reduced models for ethylene kinetics, were performed for a baseline combustor pilot concept. Thus a staged, multi-port low-angle flush-wall-mounted fuel injection system was combined with a variable-size cavity flameholder, and the combustor was tested in a new Mach 4-6 direct-connect scramjet test facility. The simulations, using the VULCAN code compared favorably with experimental results for cold-flow injections of N_2 and ethylene. Several early conclusions and possible directions for future work were discussed. Although "reasonable mixing levels" were obtained with "minimal total pressure losses," reacting simulations showed that "further refinements are needed to the combustor geometry to prevent thermal choking under certain conditions."

A follow-on study [107] of “Supersonic Combustion Experiments with a Cavity Based Fuel Injector” used the same baseline combustor pilot as [105,106]. Ethylene was injected through the low-angle flush-wall multi-ports, located just upstream of the cavity-flameholder that was mounted in a direct-connect supersonic test facility. Combustor inlet properties simulated flight conditions between Mach 4 and 5 at a dynamic pressure of 1000 psf. Besides the upstream injection, ethylene was also injected normal to the cavity floor through five holes located just upstream of the cavity aft ramp. Conventional spark plugs were mounted in the cavity floor to facilitate ignition. After stable combustion was achieved in the cavity, and main fuel was added, stable main stream combustion occurred without further use of sparkplugs, and equivalence ratios ranged from 0.25 to 0.75. Video records were used to document flame spreading. Net thrust levels were measured and reported along with 1-D performance analyses, which suggested combustion efficiency up to 80% at the highest equivalence ratio.

Next, Baurle et al. [108] applied a (VLES) Very Large Eddy Simulation modeling approach to better describe the cold flow characteristics over recessed cavities for scramjet flameholding applications. This was done because ... “Early efforts using standard two-equation eddy viscosity models were not capable of predicting the self-oscillatory unsteady flow features associated with fluid flow over recessed cavities.” Cavity aft wall angle, and cavity length-to-depth ratio were varied, and both were shown to have a significant effect on the mass exchange process. Notably “the VLES model captured the large scale unsteadiness known to exist for recessed cavity flows.” Also “the expected result of reduced mass exchange with shallow cavity wall angles was predicted,” whereas the opposite effect was observed when a Reynolds Averaged Navier Stokes approach was utilized previously.

Finally, Gruber, Baurle, Mathur and Hsu [109] very recently summarized, using 46 references, several important aspects of “Fundamental Studies of Cavity-Based Flameholder Concepts for Supersonic Combustors.” The paper describes both experimental and computational studies of flowfields associated with several open (length-to-depth ratio < 10) cavity-based flameholders in nonreacting supersonic flows. A number of offset ratios (upstream-to-downstream step-height ratios) and aft ramp angles were used. Shadowgraph and schlieren photographs are shown along with computed stream traces and pressure contours, and both experimental and computational wall static pressure distributions. As the aft ramp angle decreased from 90°, with an unity offset ratio, it strongly affected the shear layer that spanned the cavity. In addition, the pressure on the cavity fore wall decreased steadily, and the recompression process occurred more gradually, all of which led to higher drag coefficients and shorter residence times.

2.3.7. Computational Flame Stabilization Studies Ref. [57] investigated the effects of certain chemical reaction sets (0, and 7 vs 8) on numerical simulation of supersonic combustion flows. The generic configuration included transverse injection of a 1.5-mm under-expanded jet of H₂, at 300 K total temperature, three step-heights downstream of a 5-mm rearward-facing step. Air inlet conditions were 800 K and 0.5 atm static pressure at Mach 2. Results from the 3-D version of SPARK, which simulated turbulence using the Baldwin-Lomax model, compared favorably with experimental wall pressure distributions. Deletion of the eighth reaction, $H + O_2 + M \rightarrow HO_2 + M$, strongly induced thermal choking. Thus “the oblique shock generated at the step became stronger, the pressure constantly increased, and the flow became subsonic in a continuously larger region.” Once the eighth reaction was included, “the flow reaccelerated back, the upstream interaction disappeared, and the solution marched towards the characteristic supersonic flow bounding the subsonic reacting region” near the injection wall. Transition from a nonreacting to an 8-reaction case increased the size of the circulation zone, decreased local velocities, and thus increased flameholding residence times. Also, the fuel jet expansion changed significantly, the usual barrel shock disappeared, and the jet penetrated (80 %) deeper into the main flow. Finally, an oblique shock wave system was created that was characteristic of a weaker expansion and significantly higher (70 %) back pressure in the test section.

2.3.8. Very High-Speed Pulsed Facilities Various hypersonic pulsed-flow shock facilities have also been used. Effects of test gas composition on combustion of injected H₂ were examined using simplified scramjet combustor models in both the T4 free-piston reflected-shock tunnel, where 50 mass-% of O₂ is dissociated to yield O-atom and NO, and in the HYPULSE shock expansion tunnel, where < 3% of O₂ is dissociated [58]. Ref. [58] concluded the static pressure rise upon combustion was significantly greater when dissociated oxygen was present (T4 free-piston RST), and “this is attributed principally to the heat of formation of the oxygen adding to the combustion heat release of the fuel at these test conditions.” Approaches for reducing and compensating the O₂ dissociation effect are discussed. It seems the influence of high (to very high) O-atom concentrations on combustion kinetics needs to be more thoroughly assessed.

In an independent study [59], transverse jet mixing and combustion in a duct model were compared in both the T5 free-piston shock tunnel and the HYPULSE tunnel. Here, test results agreed closely, and “no significant effects of the dissociated oxygen and NO production in the T5 flow have been detected compared to the clean-air HYPULSE expansion tube flow.” Notably, H₂ combustion efficiencies were very low in these tests, ranging from 25% in a high pressure case with $\phi = 2$, to 10% with $\phi = 1$. Thus the conclusion seems quite conditional.

Ref. [60] analyzed H₂-air combustion for the shock expansion and reflected shock tunnels, using a one-dimensional quasi three-stream-mixing combustor code (SCRAM3) with finite chemistry. For a simulated Mach 17 flight condition, the results indicated “the combustion process is kinetically controlled in experiments in both tunnels, and the presence of the nonequilibrium partially dissociated oxygen in the reflected shock tunnel enhances the combustion.” Notably, the presence of nitric oxide at the respective low-pressure levels of the experiments did not affect the combustion process. Finally, the analytic studies in [60] suggested “the effect of partially dissociated air can be compensated either by altering the oxygen content of the reflected shock tunnel test gas or by reducing the hydrogen content of the fuel by dilution with an inert gas such as helium.” However, it was concluded that ... “additional experimental studies, however, are needed to verify the proposed methods for controlling the effect of dissociated oxygen.” Similarly, methods of compensating for the oxygen dissociation effect are also discussed in [40].

M. V. Pulsonetti and Stalker reported a “Study of Scramjet Scaling” [97] that was based on the first author’s dissertation [98]. Experiments were conducted on two centrally injected scramjet combustors in a reflected shock tunnel, T4. The two scramjet models had a 5:1 scale in all dimensions. Ten conditions were used to test a hypothesized pressure-length scaling law. Five were at the same nozzle stagnation pressure (36.9 MPa), while the stagnation enthalpy varied from 3.59 to 10.7 MJ/kg. Another five were at the same stagnation enthalpy (5.61 MJ/kg), while the nozzle stagnation pressure varied from 5.9 to 37.5 MPa. For each of these conditions the Mach number, temperature, and reactant conditions were maintained essentially the same.

Resultant pressure distributions in [97] indicated combustion occurred both in the mixing-limited and reaction-limited regimes. The ignition delay time was well characterized by the hypothesized pressure-length scaling law. The *rate* of pressure rise due to combustion was higher in the large scramjet for the reaction-limited cases; and the *scaled* pressure rise due to combustion was slightly larger in the large scramjet, with one small exception. The authors conjectured that the lower rate of pressure rise in the small scramjet may have been due to its higher *absolute* pressure, which enhanced three-body recombinations [e.g., $H + O_2 + M \rightarrow HO_2 + M$] and depleted the supply of free radicals. The authors concluded ... “the pressure-length scaling law seems to provide, with reasonable accuracy, a relation for predicting the fundamental phenomena occurring in a scramjet combustor. Thus, while there are second order effects, the pressure-length scaling law is effective as a first order approximation for scaling scramjet performance.” Note in Section 4.3.2.2 the pressure-length scaling law is derived from kinetic considerations, using three bimolecular reactions (two chain branching and one chain propagating). However, it is also shown that inclusion of the $H + O_2 + M$

recombination leads to a (pressure-squared)-length dependency, which agrees qualitatively with the above observations.

2.3.9. Detailed Ignition Studies, Nonpremixed Diffusion There have been several recent detailed ignition studies that significantly increase our understanding of nonpremixed ignition processes in H₂-air systems. Although none of the studies discussed below pertain directly to air vitiation effects, it should be recognized that the newly developed fundamental knowledge should be considered in any future assessments of ignition.

Recently, linear bifurcation and numerical techniques [61] were used to determine critical conditions for ignition in steady laminar counterflowing H₂/N₂ vs air systems at temperatures *larger* than T_c. An analysis of the radical pool at ignition revealed that, regardless of dilution, the steady-state assumption for O-atom fails before that for OH on the airside of the mixing layer. Thus after neglecting initiation, and assuming steady-state for HO₂ and OH, an earlier seven-step scheme was reduced to a minimum of three global steps needed to describe ignition. These were: H₂ + O₂ → O + H₂O; O + 2H₂ → 2H + H₂O; and 2H + M → H₂ + M. Excellent agreement was obtained at all fuel dilutions with numerical solutions based on detailed chemistry.

Very recent experimental and computational ignition studies of 6 to 38% H₂/N₂ vs heated-air *laminar* counterflowing jets showed the existence of mild oxidation regimes, and multiple ignition and extinction states, at pressures between 0.3 and 8 atm [62]. Experimentally, LDV, thermocouple, and Spontaneous Raman Scattering Spectroscopy measurements of H₂O indicated that up to three stable stationary states could be achieved for identical boundary conditions! For example, measurements of steam for 9% H₂ at 4 atm, with a density-weighted input strain rate of 300 1/s, identified a frozen lower branch of the Damköhler S-curve, a mild oxidation regime, and a flame. Computationally, strain rates ranged 10 to 40000 1/s, and air input temperatures varied 950 to 1100 K. Moreover, by changing input strain rate, up to five steady-state multiplicities, and up to two ignition and extinction states resulted from thermokinetic and transport effects.

Additional computational [63] and experimental [64] studies of *inhomogeneous* ignition in *turbulent* counterflowing hydrogen vs heated-air provide further valuable insight. First, Kreutz and Law [63] derived a number of “skeletal” and “reduced” reaction mechanisms to simplify a detailed kinetic mechanism having 9 species and 19 bidirectional elementary steps. They found use of homogeneous approximations, such as steady-state or partial equilibrium, can lead to *significant* errors in the inhomogeneous system when deriving reduced reaction mechanisms. Typically, ignition is controlled by processes that occur within a localized ignition kernel, where H₂ mixes and reacts rapidly with air. Kreutz and Law demonstrate H + HO₂ → 2OH is a critical step in kinetically-controlled ignition. A 6-step skeletal mechanism is presented to represent the *smallest* set of elementary reactions that provides proper turning point behavior in the first and second inhomogeneous ignition limits. Resultant density-weighted strain rate limits for diffusion flame ignitions are shifted in pressure and temperature (as displaced Z curves) along the classic crossover-temperature condition, which defines (within 2x) the upper bound of the second homogeneous steady-state chain-branching explosion limit. Transition to a third dynamic ignition limit involves additional propagation (2HO₂ → H₂O₂ + O₂ → 2OH + O₂) and branching (HO₂ + H₂ → H₂O₂ + H → 2OH + H) pathways that compete with chain termination. This 9-step skeletal mechanism appeared to capture all three limits very well over 3 orders of magnitude in strain rate.

Based on the above, Kreutz and Law drew several conclusions [63], paraphrased as follows. Mass transport of radicals out of the ignition kernel affects the ignition process, particularly in the first and third ignition (explosion) limits where the dominant chemistry is relatively slow. Thus radical build-up associated with these limits is sensitive to aerodynamic straining. An important feature of nonpremixed ignition is the radical pool is extremely small at the ignition turning point. Thus heat release from chemical reactions is so small that essentially no “thermal feedback” occurs in the system at the ignition turning point, and concentrations of

major species are effectively unperturbed. In summary, [63] developed a new view of the ignition turning point as a “decoupled ignition environment” in which major molecular species and temperature are “totally frozen” just before ignition, and the chemistry of minor (radical) species controls the process. They also developed a new “Steady-State-Ratio” sensitivity analysis that, used in conjunction with a previous flux analysis, quantifies system response near the ignition turning point to important parameters in the conservation equations.

Next, the measurements of ignition of turbulent nonpremixed H₂ by heated counterflowing atmospheric air [64] showed that, for fuel approaching 15% H₂/N₂, ignition temperature (of air) was no longer sensitive to *turbulent* intensity. This was consistent with earlier laminar counterflow results, where the dominant (second-limit) chemistry was rapid enough, compared to transport rates, that ignition temperature was insensitive to local strain rate. Below 14% H₂, ignition was *intermittent* in that flows repeatedly ignited and extinguished over a range of input temperatures, and the range of intermittence widened with decreasing fuel concentration, increasing turbulent intensity, or increasing global strain rate. Thus *local* strain rate in the ignition kernel “...can alternately traverse beyond the ignition and extinction turning points [in Damköhler S-curves], causing the flow to intermittently ignite and extinguish.”

Ref. [65] performed some very revealing 1-D and 2-D direct numerical simulations of autoignition, of counterflowing N₂-diluted-H₂ vs heated-atmospheric-air, in mixing layers with both laminar and homogeneous turbulent flows. The air temperature (1100 K) was higher than the crossover temperature (e.g., 928 K), and simulations were performed with and without heat release. Three turbulent intensities were used: weak, moderate, and strong, with characteristic timescale ratios ($\tau_{\text{turb}}/\tau_{\text{ig}}$) of 3, 1, and 0.3. Peak concentrations of radicals increased by more than 7 orders of magnitude before the temperature showed any noticeable change due to reaction; then temperature rose substantially (by ~200 K) to ignition, while radical concentrations changed only by ~2x. As a result, the ignition delay w/ and w/o heat release was almost identical up to the ignition point for laminar flow (137 & 126 μs), and for all three turbulence levels (129 & 121; 130 & 122; and 139 & 130 μs , respectively).

The authors of [65] concluded: (1) for weak to moderate turbulence, ignition was only slightly facilitated by turbulence due to enhanced mixing; (2) for stronger turbulence, ignition was retarded due to excessive scalar dissipation and diffusive loss at the ignition location; (3) ignition of nonpremixed hydrogen and air in turbulent flow fields can be characterized *purely* by radical runaway as opposed to thermal runaway; and (4) ignition delays are quite insensitive to a wide range of initial turbulent fields. Note that (4) agrees with above-discussed experimental measurements using a counterflow technique [64]. In addition, the ignition kernel always occurred where hydrogen was “focused,” and peak HO₂ was aligned closely with scalar dissipation rate. This peak HO₂ shifted toward the cold fuel stream as ignition approached, and then vanished with onset of intensive burning. Thus the study ... “confirmed the important role of the branching reaction, HO₂ + H → OH + OH for chemical ignition” ... which became increasingly important as the ignition point was approached. And finally, it was shown ... “that the ignition kernel tends to be located where the mixing layer is convex toward the fuel side, due to the high diffusivity of the hydrogen molecules.”

The extinction limits of stoichiometric H₂-O₂ and H₂-air counterflow diffusion flames at elevated pressures (1 to 100 atm) were numerically evaluated to determine the effects of pressure and O₂ content [66]. Also, the effects of acoustic-pressure oscillation on peak temperature and strain rate were determined. The extinction strain rate for H₂-O₂ increased linearly with pressure, up to 100 atm, whereas for H₂-air it became asymptotic around 50 atm. Similar behavior was retained with four-, three-, and two-step mechanisms. Finally, a sensitivity analysis showed that (a) H + O₂ → OH + O and OH + H₂ → H₂O + H control extinction strain rate at 50 atm, and (b) a (hypothetical) depression of the rate of recombination via H + O₂ + M → HO₂ + M would favorably stabilize local acoustic oscillations.

2.3.10. Ignition of Premixed H₂/O₂/Inert Mixtures Autoignition of H₂/O₂/He mixtures at high pressure (3.5 to 7 M Pa) was investigated using a free-piston compressor to rapidly increase temperature and pressure [67]. Measurements of a so-called *dynamic*-ignition temperature (~1150 K) were independent of pressure. A fundamental difference was cited between (a) ignition delay in the author's new analytic "dynamic third-limit" simulation, where rapid breakdown of accumulating H₂O₂ occurs via $\text{H}_2\text{O}_2 + \text{M} \rightarrow 2\text{OH} + \text{M}$, and (b) the "classic third explosion limit" characterized by a quasi-steady chain-breaking mechanism. The latter did not correctly predict radical concentrations on the non-explosive side of the ignition limit. The author argues the quasi-steady limit doesn't apply to the dynamic experimental conditions, and furthermore is based on data from a reaction vessel technique that "is notoriously unreliable and completely unsuited to determining the third limit." Expressions for the new dynamic third limit, derived in terms of critical OH concentrations that ranged 0.5 to 5 x 10⁻⁹ mole/cm³, were consistent with the data. These were located at temperatures ~1150 K @ 50-atm, well above (into) the classic third explosion limit (that varied from ~840 K @ 0.5-atm to 740 K @ 50-atm). Finally, the author contends (personal communication) the "correct third limit" is an extension of the second dynamic ignition limit that does not turn back on itself until temperatures approach 1200 K.

Ref. [68] examined the *catalytic* ignition of H₂/O₂ mixtures at 1-atm with emphasis on dynamic behavior. The authors measured ignition progress, using a Pt wire technique that served as both thermometer and calorimeter. They also simulated its temporal evolution from a pre-ignition kinetically controlled regime to a post-ignition state controlled by mass transport. Good agreement was obtained between experimental results and simulations. Early on, the surface was considered covered by H atoms, which poisoned the surface by preventing dissociative adsorption of O₂. Increasing temperature promoted desorption of H₂ and created more free sites for O₂ dissociation, which eventually led to ignition. The authors conclude catalytic ignition is "primarily governed by coupling between (i) the heat balance, (ii) the kinetics of adsorption of H₂ + O₂, and (iii) the desorption kinetics of H₂." Their model is offered for application to coupled gas-phase, heterogeneous-ignition, combustion processes.

Ref. [69] studied the *catalytic* ignition of H₂/O₂ mixtures, diluted by N₂, on a small platinum sphere at 1-atm. Temperature-time histories were measured using a thermocouple junction which supported the sphere. A "well known" significant difference in reactivity was observed between the first exposure of a catalyst and subsequent exposures. Plots of ignition temperature vs. relative hydrogen, H₂/(H₂ + O₂), showed evidence of a minimum ignition temperature not seen by other investigators, including those who used H₂-air mixtures. A simple overall reaction model with an Arrhenius expression was used with modest success to relate ignition temperature to reactant concentration (dilution ratio).

2.3.11. Ignition and Combustion in Shear Layer Flows Ref. [70] analyzed thermal ignition in a supersonic mixing layer, using a numerical model that employed a single reaction with Arrhenius temperature dependence, constant gas properties for specific heat and density-weighted viscosity, and unity values for the Lewis and Prandtl numbers. A large-activation-energy asymptotic analysis was also performed. The study demonstrated that "for small values of viscous heating, the ignition distance scales approximately linearly with the freestream Mach number, whereas for large viscous heating, it decreases rapidly due to the temperature-sensitive nature of the reaction rate." These results illustrated the "potential of using local flow retardation to enhance ignition rather than relying solely on external heating." The effects of flow nonsimilarity were also assessed, and found to be more prominent for the mixing layer flow in comparison to a previously studied flame-plate configuration.

Ref. [71] followed [70] with *detailed* numerical simulations of supersonic laminar-shear-layer flows. They used finite-rate kinetics to characterize diffusive ignition/reaction, to examine the roles of viscous heating, radical proliferation, and thermal runaway relative to the H₂/O₂ second explosion limit. Results showed ... "the state of the H₂/O₂ second explosion limit has the dominant influence in the system response in that, for all practical purposes ignition is not

possible when the air stream temperature is lower than the crossover temperature, even allowing for viscous heating. On the other hand, when the air stream temperature is higher than the crossover temperature, the predicted ignition distance indicates that ignition is feasible within practical supersonic combustion engines.” “Furthermore, for the latter situations, the ignition event is initiated by radical proliferation (runaway),” ... “instead of thermal runaway.” Finally, whereas the above results agreed qualitatively with the [70] results described earlier, the “analytically-predicted ignition distances (asymptotic analyses) are much shorter than the (detailed) computed values because the [70] analysis overemphasized the viscous effect through the constant $\rho\mu$ and unity Prandtl number assumptions.”

3. SCALING OF AIR VITIATION EFFECTS ON SCRAMJET COMBUSTION

3.1. OVERVIEW OF SCALING

The above review of air vitiation effects, and the fundamentals of ignition, flameholding and Scramjet combustion processes, shows that ignition delay and flameholding / combustion chemistry may be affected substantially, depending on the type and operational mode of a particular facility. Thus, in the context of this NATO Subgroup, a major goal is to provide technical bases for extrapolating ground test data to predict flight performance.

The extrapolation process consists in identifying, deriving and applying appropriate scaling procedures. Scaling in the scramjet context means to develop appropriate characterizations of the essential physics and chemistry of inlet compression, ignition, and flameholding / combustion that apply when the key parameters of vitiation are varied, e.g. fuel-air input composition, temperature, pressure, and facility-nozzle / test-section geometry. Thus our ultimate scaling goal is to (1) Assess the magnitude of vitiation effects on combustor performance, and (2) deduce feasible compensatory effects involving deliberate variations of vitiation/test parameters.

3.2. SCALING OF COMBUSTION FLOWS IN SCRAMJETS

Although aerodynamicists are familiar with the scaling of external flows in wind tunnels, scaling tasks become vastly more complicated when combustion occurs. Logically, scramjet scaling should at least include the effects of vitiate-composition on classic Damköhler, Reynolds and Mach numbers, and scaling efforts should consider “commonly-accepted” similarity-laws in designing combustors (except those at very low pressure) [82]. For gas phase kinetic effects due to H_2O , CO_2 , NO_x and H_xO_y radicals, scaling laws seem quantifiable for H_2 -air combustion [97,98]. However, for particulate effects (soot, ceramic particles, droplets) scaling is much more complex because two-phase processes are involved [41]. Despite all the complexities introduced by combustion, an attempt at scaling may still be a reasonable and worthwhile approach to anticipate and account-for vitiation effects during scramjet testing and development.

Such an approach might begin with trying to maintain *all* the major similarity parameters between a subscale model and its subsequent flight application. For combustors, dimensionless parameters can include Re , M , Pr , Sc , Da_i , Le , and St numbers. However, even a cursory analysis indicates using all seven parameters represents an impractical requirement, e.g. in [82]. Thus variations in temperature and pressure impact both chemistry

and gasdynamics, which pose impossible constraints on the problem. The question thus becomes, which parameters to fix and which to float?

Notably, some engine and/or vehicle designers take a dim view of “parameter selection processes.” Faced with the unknown consequences of preferentially relaxing similarity requirements, it sometimes “seems safer” to fix certain well-known physical quantities. Among the major choices for scramjets are stagnation temperature, T_0 , Mach number, M , and stagnation enthalpy, h_0 . Such an approach appears more intuitive than technically driven; i.e., it is tacitly assumed that chemistry and turbulence *will be the same* at fixed total temperature, or combustor entrance velocity. In fact, the analytic reason for using Da , Re or M similarity is based on the opposite assumption – namely, one maintains relevant time ratios, not absolute time. Thus faced with the unpredictability of flight performance, at least a simplified similarity approach seems justified if nothing else can be developed.

3.2.1. Simplifying Assumptions We now attempt to delineate which similarity parameters might be maintained in the simplified analysis of a scramjet combustor. First, we assume both key combustion kinetics for supersonic flameholding, and overall heat release for thrust, are of paramount importance. For a well-designed combustor, we also assume (at 0-th order!) friction is less critical than thermal choking, and vorticity due to turbulence will be mostly streamwise. In agreement with experimental data at $M \gg 1$, turbulence intensity should be relatively small in *most* of the combustor space. Exceptions occur, however, in regions where (1) supersonic mixing is purposefully enhanced in some way (e.g., by shock trains, or induced unsteadiness), and (2) flameholding is aided (and sometimes accomplished) in cavity flows and blunt-body fuel injector wakes. Thus considering the gross supersonic transport of species, the primary balance will occur between convection and chemical kinetics, and this leads to application of the Damköehler similarity parameter, the Da_i number of first kind, associated with key species i .

In a rigorous consideration of turbulent mixing, one might define a spectrum of convective times, each relative to a turbulent scale. This would produce a spectrum of Da_i , and require a matrix of Da_i with size equal to the number of species times the number of turbulent scales. In our 0-th order analysis we neglect this multiplicity, and assume the turbulent spectrum is very limited (unlike for subsonic flows) to justify use of a single Damköehler number. The above limitations imply we are considering “true” scramjet configurations, where ignition and flameholding occur *without* a purposely designed subsonic recirculation region. These are strong and perhaps unacceptable assumptions for some applications, but they may be adequate for the initial design of certain advanced combustors in high M -vehicles.

As for energy release, the same rough assumptions lead to a rate balance between chemical heat release and both convection and enthalpy change; thus a single Da_i number also applies. Finally, similarity also occurs between the molecular transport of energy and species, so that local transport rates are scaled by a Lewis number.

Perhaps a weak point in this similarity approach is the assumption that mixing occurs *without* strong interaction with combustion kinetics effects, which are influenced by vitiation. Most experimentalists would take strong exception to such an assumption; after all, scramjet combustion is precisely a case where reaction times are similar to convection times, and heat addition enhances mixing. The justification in making such an assumption is that strong interaction will be unlikely inside the shear layer *immediately* downstream of fuel injection, but will occur once air and fuel are mixed further downstream. When such mixing has occurred, the correct quantity to observe is not absolute ignition (or combustion) time, but the ratio between available convection time and reaction time (Damköehler number, related to combustor size).

Notably, the above Damköehler approach is frequently used in assessing nonequilibrium effects within shock waves, or possible surface catalytic effects over re-entry vehicles [100]. Thus either the characteristic vibrational relaxation time, or surface catalytic recombination

time, may be less important than the relevant Da (ratio) number [81]. For example, in a small (a few cm long) subscale model inside a wind tunnel, vibrational relaxation past the bow shock may occur downstream over the *entire* model; during a Shuttle re-entry, this takes place only a few centimeters downstream of the bow shock. Thus if we maintain the same Mach number and stagnation temperature in both situations, the absolute times are the same, but the effects on flowfield will be very different.

3.2.2. Simplified Damköhler Number (Da) Scaling Based on species mass conservation for a scramjet combustor, and using the above assumptions, the balance between the convective transport rate of species i (e.g. OH) and its rate of formation, w_i , can be written one-dimensionally by

$$\rho Y_i U / L \sim w_i \quad (1)$$

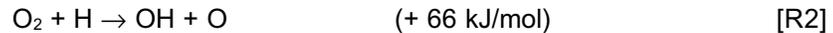
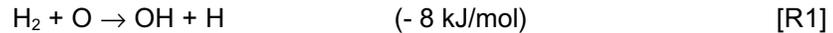
where U is the axial velocity, L the combustor length scale, Y_i the mass fraction of species i , and ρ the density. Arrhenius kinetics for w_i are given for any reaction by $w_i \sim A_i \rho^n \exp(-E_a/RT)$, where $n=2$ for chain propagating or branching reactions, $n=3$ for third-body recombination reactions, and A_i is the pre-exponential factor (A_i^* includes the T^b factor for simplicity).

By letting $U = M c$ (where c , the speed of sound varies as $T^{1/2}$), the Da_i number is obtained for a single reaction as the ratio between w_i and the transport rate. Substituting,

$$Da_i \sim A_i \rho^{n-1} [L / (Y_i M T^{1/2})] \exp[-E_{a_i}/RT] \sim A_i^* \rho^{n-1} L / (Y_i M T^{1/2}) \quad (2)$$

This indicates, for bimolecular ($n=2$) radical pool formation reactions (that presumably dominate during the ignition delay period), Da_i scales as ρL for the “conventional” binary or pressure-length scaling law; whereas for radical-termination/recombination kinetics dominated by termolecular ($n=3$) reactions, Da_i will scale as $\rho^2 L$. This is also the conclusion of [97,98].

3.2.2. Introduction of Key OH Formation Kinetics for Ignition The next step is to select appropriate scramjet ignition kinetics. A key goal is to specify the rapid rate of OH formation via two well known bimolecular chain-branching H_2 /air reactions [88,63]; i.e.,



For the initiation of H_2 -air combustion, the most accredited step is $H_2 + O_2 \rightarrow HO_2 + H$, which provides needed H-atom for the chain branching reaction [R2]. Note the effect of vitiated air containing O-atom is to bypass [R2], which is 6x slower than [R1] at 900 K, and “jump-start” chain branching via [R1].

If OH is also present in vitiated air, its effect is felt via the reversible chain propagating reaction,



that provides H atom for [R2]. All the above OH formation reactions are 2nd order, so the multi-reaction Da_i scaling suggested in Eqs. 1 and 2 leads to the pressure-length scaling expression,

$$Da_{OH} \sim (\rho L / U) [A^*_1 Y_{H_2} Y_O / Y_{OH} + A^*_2 Y_{O_2} Y_H / Y_{OH} + A^*_{-3} Y_{H_2O} Y_H / Y_{OH} - A^*_3 Y_{H_2}] \quad (3)$$

The reverse of the branching reactions [R1,R2] have been neglected due to the small radical concentrations. At early times the rate of OH formation will be fast. Subsequently it slows down, and OH is consumed by [R3].

In this provisional attempt at using similarity, none of the other H₂-air reactions are included, especially the three-body recombination, $H + O_2 + M \rightarrow HO_2 + M$, which would introduce a “ $\rho^2 L$ ” weighting as discussed in connection with Eq. (2). Notably, the pressure-length scaling relationship of Eq. (3), *and* evidence of a minor second order effect due presumably to the $H + O_2 + M$ recombination, was confirmed experimentally in [97] (see section 4.2.3.8; and detailed analyses in [98]).

Some first order effects of air vitiation on ignition processes can now be approximated, using Eq. (3). For similar ignition performance in ground testing and in flight, the Da number should be the same. Thus for ground tests, e.g. at 1 atm pressure, the ground-test combustor length scale L must be increased relative to that of the “real vehicle,” if the inlet of the real vehicle supplies the engine combustor with air at $P > 1$ atm.

Using *vitiated* air, where initial O, H, H₂O and OH concentrations can be estimated, ignition kinetics can be started with finite Y_O , Y_H , Y_{H_2O} and Y_{OH} values, which may significantly reduce ignition delay. Similarly, an initial “effective” Da_i in a particular ground testing condition / facility can be deduced.

For the much smaller initial values of radical concentrations under flight inlet conditions, a different initial flight Da_i will be predicted. Thus if we wish to achieve equivalent flight *ignition* performance on the ground, the respective initial Da_i should be equal. This may mean increasing the $(\rho L/U)$ factor, or even initial Y_{H_2} , Y_{O_2} concentrations, accordingly. The maintenance of both initial *and* later stages of flameholding becomes much more complex and effectively impossible, using the Dämkoehler scaling approach, because radical concentrations change drastically once combustion is initiated.

Alternatively, one may start with an achievable, functional ground-test (initial) Da_i for ignition, and then scale a flight test article so the target flight (initial) Da_i is reproduced. Such an exercise may suggest flight test conditions should be “modified” to achieve the flight Da_i , e.g. by using a silane, plasma, or photolytic ignition aid. Finally, high-recombination-rate coatings might be employed for thermal protection system models to assess catalytic recombination effects during an actual re-entry [81].

4. RECOMMENDATIONS

4.1. Overview Summary of Air Vitiation Effects

The results detailed in this paper make clear that test medium effects on ignition, flameholding and steady combustion in a scramjet test article continue to be a moving target. On the experimental front, uncertainties stem from differences in: Methods of achieving high total enthalpies; test facility configurations; test article configurations, including relative scale; nature of vitiated-combustion mixing processes; geometric and chemical aids to cold-start ignition, flameholding and combustion (e.g., bluff-body injectors, cavities, steps, use of heaters, pyrophorics etc.); simulated-flight inlet conditions (static pressure and temperature; velocities); mixing schemes and relative velocities in shear layer combustion; and possible effects of flow-separation, reattachment, turbulence, skin friction and heat loss. In addition, measurement fidelity is a question hanging over all experimental studies.

Theoretical studies of test medium effects are clouded by questions of definitive chemical kinetic mechanisms and associated reaction rate coefficients, especially for hydrocarbon-fueled test articles. Additional questions arise in connection with detailed theoretical modeling of actual test conditions. For example, in the majority of hypersonic test facilities, the "air" passes through a facility nozzle, with an exit-flow chemical composition somewhere between that of a "frozen" expansion and that for a "shifting equilibrium" expansion. Even refined 2-D computational studies that start at the facility nozzle throat entrance, and proceed through the test article, are still suspect (until thoroughly validated). This is because numerous methodological questions surround the application of chemical kinetic mechanisms for ignition, combustion, and nozzle-expansion processes, "accurate" turbulence modeling, the treatment of assorted viscous and shock wave effects, and other reactive-flow phenomena which are extraordinarily difficult to deal with computationally (e.g., separation-reattachment effects).

It seems fair to conclude that the presence of "extra air species" can affect both the chemistry and flow properties in test articles meant to simulate flight conditions. Test media having thermodynamic and transport properties (e.g., average specific heat, viscosity, thermal conductivity and diffusivity) that differ from those derived from inlet-processed ambient air will certainly impact attempts to replicate flight conditions for a test article.

Finally, high plenum temperatures, dissociation of the test medium, whether combustion-initiated or not, becomes a potential problem. Nitric oxide is one product of concern. Atomic oxygen may be co-produced, which even in minute quantities (e.g. 10^{12} atoms/cm³) can significantly reduce ignition delay times. In-stream combustion will produce hydroxyl radicals at equilibrated or superequilibrated concentrations, which are as active as atomic oxygen. The importance of such contaminants is, again, dependent on the test conditions, engine conditions and configuration. One important generalization that can be drawn is that, if auto-ignition and flameholding-combustion are marginal, due to some combination of local temperature and pressure and mixing time/length, the presence of free radicals may dramatically improve engine performance in ground tests. But, on the other hand, if autoignition and combustion are vigorous, the effects of free radical seeding in the flow may be insignificant and not evident under a given set of test conditions.

4.2. Required Future Research

The many years of study of test medium effects on ignition, flameholding and combustion and processes, in test articles designed to replicate hypersonic flight, have yielded only a few definitive answers. It seems clear that many attempts to sort out the complex phenomena occurring within test articles, while perhaps yielding some information relevant to the specific model and test configuration, often fail to supply satisfactory answers to many of the questions raised herein. What is required are unit-process experiments that separate, to the maximum extent possible, the chemical kinetic effects associated with "contaminant" species from the complications of thermo-fluid dynamics and "synthetic" turbulence approximations.

As an example, benchmark-quality ignition experiments in pulse facilities (e.g. shock tube/tunnels and expansion tube/tunnels, at thermodynamic conditions corresponding to hypersonic flight) that focus on the effects of NO (and O-atom) on the ignition of well-characterized hydrocarbon fuel mixtures in air, might help resolve the nitric oxide question. Definitive chemical kinetic mechanisms must be developed, validated, reduced for some applications, *and* used to characterize key scramjet combustion processes as more detailed kinetic mechanisms and computational power become available. Such attempts to validate mechanisms have been made in the recent past, but disagreements and inconsistencies persist.

Key reaction rate coefficients for elementary reactions in "complete" mechanisms should be validated using modern assessment techniques such as those employed by Baulch *et al.*

[77], Curran *et al.* [78], Kreutz and Law [63], and Yetter, Dryer and Rabitz [79]. Furthermore, reduced models need to be developed / tested in careful kinetic sensitivity / validation studies under *relevant* conditions -- e.g. near ignition turning points for ignition studies, and at typical "intermediate" temperatures for burning velocity and flame extinction studies. Where the scatter of available data is unacceptably large, detailed data reviews may be needed, and numerical approaches based on quantum-mechanical theory should be used to resolve such discrepancies.

In a climate of austere budgets and insecure support for hypersonics, the above recommendations will likely seem impractical by many in this community. The price to be paid for "shortchanging" fundamental studies is continuing uncertainty on what might be achieved during actual flight. Efforts to reduce or eliminate uncertainties in key unit processes could be carried out systematically at modest cost over a reasonable length of time. To ignore such uncertainties in the long run is to compromise the promise of airbreathing hypersonic flight.

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