CHEMICAL KINETICS, FLUID MECHANICS, AND HEAT TRANSFER IN THE FAST LANE

The Unexpurgated Story of a Long-Range Program of Research in Combustion

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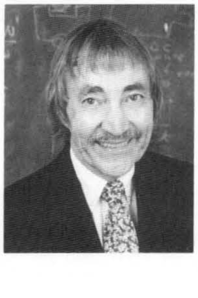
The presentation of experimental and theoretical findings in a journal usually implies that the path of the investigation of which they are the culmination was well-planned and straightforward. Such is rarely the case, however, particularly with exploratory research for which unanticipated results are the justification and the reward. Indeed, the most useful results are often the consequence of a deviation from the original objective in order to explain, resolve, or explore an apparent anomaly. Most discoveries and innovations so arise.

This paper utilizes the history of a long-term (40-year) investigation of combustion inside tubes to illustrate the true, unvarnished path of exploratory research with all of its turnings, windfalls, misdirections, triumphs, and disasters. The primary objective of this recounting is to persuade doctoral students (and perhaps their advisors) that the anomalies observed in experiments or in comparing experiments and theoretical solutions are not to be ignored, hidden, or deplored, but rather should be taken as a signal of possibly important unknown behavior that may actually justify a diversion in, an addition to, or even a complete redirection of the research. A second, related objective is to demonstrate the helpful (and indeed, essential) role of theoretical modeling in explaining experimental results and, particularly, anomalies.



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ACOUSTICALLY RESONANT COMBUSTION

The research program that supported me as a graduate student involved the ignition of solid propellants by a stream of gas at high temperature. We rationalized that a mixture of O_2 and inert gases was equivalent in that respect to the products of combustion of a primer. My curiosity was provoked and unsatisfied as to the possible effects of combustion itself on heat transfer, and sometime thereafter I persuaded Donald W. Sundstrom to investigate this subject for his doctoral research. Supported equipment-wise by an unrestricted grant from the Esso Engineering and Research Company, we chose a geometry unrelated to the ignition of propellants but of more general interest—namely heat transfer from a flame of premixed air and propane stabilized on a central bluff body inside a 25.4-mm-ID stainless-steel tube. The choice of combustion inside a tube, which was arbitrary on our part and at that time relatively unexplored, proved to be serendipitous not only in terms of the immediate results, but also in precursing the entire subsequent chain of events described herein.

Although acoustic resonance was not anticipated to be a significant factor, Sundstrom observed a correlation between the local rate of heat transfer and the aurally-sensed amplitude of the noise generated by the flame, and he promptly acquired the appropriate instrumentation for characterization of the latter. The local rate of heat transfer was found to depend primarily on the pattern of flow generated by the combustion, but that pattern was found in turn to be influenced strongly by the flame-generated acoustics.[1] The latter were rationalized to be initiated by the periodic shedding and combustion of the vortices generated by the flameholder, and to be enhanced by the resulting resonant oscillations in pressure. Theoretical calculations indicated that the frequency of the oscillations corresponded to the lon-

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gitudinal (organ-pipe) mode. This identification and pursuit of an unexpected aspect of behavior by an alert, motivated student was an important, if not essential, element of the entire ensuing program of research.

A study of the literature on flame-generated oscillations suggested that the "screeching" combustion associated with jet engines might have a similar cause, but be due to tangential rather than longitudinal oscillations. Sundstrom was unable to produce screeching combustion in his apparatus, but William N. Zartman, the following student, determined from crude, preliminary experiments with a flame stabilized on a bluff body inside plain, uninstrumented and uncooled pipes of various sizes, that screeching combustion could be made to occur for pipe diameters greater than 100 mm. Hence, stainless-steel pipe with a diameter of 127 mm was chosen for his doctoral research. Amplitudes of as great as 160 db at a frequency of 4125 Hz were attained.

The research itself documented a linear increase in the local heat-transfer coefficient within the tube with the amplitude of the resonant oscillations, and indicated that these oscillations could be dampened by the installation of 1/4-wavelength tubes radially at the theoretically-identified nodes.[2] The work of Zartman was distinguished in character by his use of inexpensive and brief preliminary experiments to choose the conditions for detailed study and by the use of theoretical analysis not only to explain but also to develop a method for controlling the experimentally-observed behavior.

A PRELIMINARY MODEL FOR THERMALLY STABILIZED COMBUSTION

In order to eliminate the source of the acoustic resonance, rather than just dampen it, I speculated on the possibility of stabilization without backmixing. I thereupon persuaded two students to attempt to model (as a term project in a seminar-type course) the stabilization of a flame inside a ceramic channel by thermal feedback only. One of them, Ward O. Winer, concluded from a very idealized model based on the postulates of plug flow with perfect radial mixing, an infinite rate of combustion following the attainment of an arbitrary temperature of ignition, and a tube of infinite length with an emissivity of unity and a negligible conductivity, that a flame could be stabilized within the channel by wall-to-wall radiation only.

THERMAL STABILIZATION IN A CERAMIC TUBE

The promising (if somewhat hypothetical) result of Winer gave me the courage to persuade Thomas D. Bath to undertake experimental research on radiative stabilization in a ceramic tube for his doctorate. Bath succeeded in establishing a flame from premixed propane vapor and air inside a 25.4-mm ceramic tube, but (as contrasted with the experiments of Sundstrom and Zartman) the temperature of the wall approached that of the flame. As a consequence, every tube cracked during the process of startup, raising the spectre that the stabilization might be due to recirculation downstream from the crack. We were disappointed that the flame fluctuated and was somewhat noisy, but concluded this behavior might also be attributable to the cracks. Because of the poor definition of the conditions inside the tube, we chose not to publish these results in the archival literature.

THERMAL STABILIZATION IN A CERAMIC BLOCK

As a consequence of such a discouraging experience, I might not have resumed research on thermally-stabilized combustion at the University of Pennsylvania (where I had now relocated) had I not discovered, as a consultant to the Marathon Oil Company, that the ceramic Wulff furnace elements used by them for the thermal cracking of methane would withstand (because of their considerable porosity) temperatures and temperature gradients as high as those encountered in the experiments of Bath. Marathon graciously donated several elements for our research. These consisted of 254-mm-long blocks perforated by round 9.52-mm holes in a triangular array. Cementing three such elements together produced a burner with seven channels. The central one was used for the measurements, and the outer six functioned as guard heaters.

With this promising device in hand, I persuaded Joseph L.-P. Chen to undertake as his doctoral research a continuation of the work begun by Bath. Considerable patience and ingenuity were required to establish a stationary flame in this ceramic block the first time; without the confidence generated by the idealized theoretical solution of Winer and the experiments of Bath with tubes, we might not have persisted through the many failures. Once we learned how, establishing a stationary flame became routine (if time-consuming), and Chen determined by tedious trial and error the limits of flow for a stable flame of premixed propane and air within the block. For all of these conditions, the process of combustion was noticeably clean, quiet, and non-fluctuating as compared to conventional processes, all of which involve backmixing—by diffusion in laminar flames, by recirculation in bluff-body-stabilized flames, and by turbulent fluctuations in jet-mixed flames.

Following this phase of the work, Chen decided to investigate the dependence of the range of stable flames on the diameter of the channels by cementing in ceramic liners with an ID of 4.76 mm. Although combustion could be established in these smaller channels, the flame was (to our surprise and disappointment) diffuse and oscillatory. This difference in behavior was clearly associated with the regime of flow upstream from the flamefront, being laminar in the 4.76-mm channels and barely turbulent in the 9.52-mm ones.

In retrospect we were lucky. If the original channels in the Wulff furnace elements had been 8 mm or less in diameter, we might have abandoned this line of research as uninteresting owing to the relatively poor combustion which occurs in the laminar regime. Instead, because of the clean-cut behavior observed in the 9.52-mm channels, we realized that we had discovered a new and promising process of combustion.[3] Even so, we did not yet even begin to appreciate all of its unique characteristics.

MODELING OF THERMALLY STABILIZED COMBUSTION

Despite the above-mentioned accomplishments, I was somewhat critical of Chen because of his failure to attain a high degree of reproducibility for his data (which is an essential requirement of good experimental work), particularly in the determinations of the location of the flamefront for various conditions. I was also somewhat impatient with his failure to produce a numerical solution for an extended theoretical model. Both of these judgements proved to be quite unfair. As shown by later work, the irreproducibility was inherent in the process. As regards the numerical solution, the model involved an integro-differential equation with split boundary conditions for the temperature in the solid phase, together with differential equations for the temperature and composition in the gaseous phase, and was truly formidable at that stage of development of numerical methods.

Despite no previous experience with either computers or numerical methods, Chen eventually did devise an ingenious and successful procedure that produced a solution in close accord with his experimental results. The model incorporated a number of idealizations including global kinetics, plug flow, and perfect radial mixing, but only one significant empiricism—the effective energy of activation, which he chose to force agreement with respect to location of the computed and measured longitudinal profiles in temperature in the ceramic block.

One disturbing aspect of the numerical procedure was the dependence of this effective energy of activation on grid size. Even more startling was the prediction of six additional stable solutions for the same external conditions. Three of these multiple states were closely grouped upstream and four downstream in the tube. We speculated in print[4] that two of the seven solutions, *i.e.,* one from each grouping, might have physical validity by analogy to those for a perfectly mixed exothermic reactor, but that the other five were probably artifacts of the approximate and iterative method of solution—a not uncommon experience with integral equations.

The numerical solution revealed that the temperature of the burned gas just beyond the flamefront exceeded *the adiabatic flame temperature.* This result, which is perhaps startling at first glance, is not a violation of the second law of thermodynamics but simply a consequence of the refluxing of energy backward across the flamefront by wall-to-wall radiation and in-wall conduction. The temperature of the burned gas leaving the burner is of course below the adiabatic value by an amount equivalent to the total heat losses from the ceramic block to the surroundings. The calculations revealed that about one-third of the thermal feedback was by conduction in the ceramic block and two-thirds by wall-to-wall radiation, and indeed that (contrary to the approximate model of Winer that encouraged this line of research) the contribution of thermal conduction through the ceramic block was essential to the existence of a stable flame.

Chen also carried out calculations for a variety of parametric conditions beyond the range of his experiments. His prediction of the limiting flamespeeds for a 25.4-mm channel agreed closely with the measured values of Bath, validating them retroactively. Numerical calculations with Chen's model were not attempted for a 4.76-mm channel since the postulates of plug flow and perfect radial mixing were obviously not applicable for the laminar regime.

Chen's experimental work revealed a new process of both intrinsic and practical value, and his modeling and numerical solutions were a valuable complement. Most of the characteristic elements of behavior of thermally stabilized combustion were totally unexpected when we began. Luck, my perhaps excessive confidence in the asymptotic solution of Winer, and the persistence and ingenuity of Chen (both experimentally and theoretically) were all essential to the great success of this research.

THE SEARCH FOR MULTIPLE STATIONARY STATES

Melvin H. Bernstein undertook the task of searching for the predicted multiple stationary states as his doctoral research[5] with a newly-acquired set of Wulff furnace elements. First, he reproduced Chen's data within its band of variability. Then he searched for and found the expected second stationary state, then the five more which we had not expected despite their prediction by the numerical solution. One curious and (to this day) unexplained aspect of these measurements was the observation of four closely grouped upstream states and three even more closely grouped downstream states, whereas Chen's model predicted four downstream and three upstream.

The Mobil R&D Company responded favorably and graciously to my request to analyze several samples of the burned gas from Bernstein's experiments since we did not then have equipment for such measurements. We were excited to learn from these analyses that the thermally stabilized burner (TSB) produced no residual hydrocarbons since (as contrasted with all conventional burners) none of the fuel bypasses the zone of high temperature. Also, the TSB was found to produce essentially no "prompt" NO in the flamefront owing to its negligible thickness, and to produce exceptionally low concentrations of "thermal" NO_x (5-30 ppm) thereafter owing to the short post-flame times of residence. The concentration of total NO_x was found to be directly proportional to the post-flame residence time, as would be expected for a zero-order reaction. On the other hand, these low values of NO_x constituted a tradeoff with CO in that the same post-flame residence times were insufficient for complete oxidation to CO_2.

I encouraged Bernstein to improve upon Chen's computer program, but he was unable to make even the original one operational. Finally, in desperation and impatience I telephoned Chen and solicited his help. He offered to retest his program as a first step and to call back the next day. After a suspicious delay of several days he called and shamefacedly reported that he had inadvertently printed a preliminary inoperable computer program in his dissertation, but that he was sending us the original, correct one, which he had retested and found operational.

However, Bernstein, in his struggles with the inoperable program, had discovered two significant errors. They were found to exist in the "original" program as well. Both of the errors inflated the heat-transfer coefficient for convection downstream from the flamefront as estimated from a standard correlation. When these errors were eliminated, no stable solutions could be computed. After much agony, we concluded that an inexplicably high coefficient was necessary to produce stable solutions, at least with Chen's model. (It took another decade of work to explain this anomaly.)

We were now in the unbelievable situation of having found seven stationary states experimentally only because we were inspired to search for them by a theoretical model which now appeared to be invalid! But for the errors in his computer program, Chen might never have attained a solution, and Bernstein would never have searched for or found all of the six additional stationary states. (The subsequent history of our research suggests that we would have eventually searched for and found at least one additional state.) In retrospect, the irreproducibility of Chen's data arose from the establishment on successive days of different members of the closely-grouped set of upstream states. The particular state depended upon minor variations in the process of startup that we had no reason at the time to consider relevant.

Again, luck was obviously an important element in our success, but two lessons stand out. First, the interaction of experimental and theoretical work is often synergetic and may produce more than either one alone. Second, independent efforts by two or more investigators may identify and explain anomalies that escape attention and/or resolution by only one. These two lessons have been reinforced by our subsequent experiences as described below.

THERMALLY STABILIZED COMBUSTION OF A LIQUID FUEL

As his doctoral research, Byung Choi extended the investigation of thermally stabilized combustion to liquid fuels by burning droplets of hexane generated by vibration of a capillary tube. Stroboscopic visualization of droplets of water in a preliminary experiment was utilized to confirm a theoretical model, which was then used to guide the unobserved production of a chain of uniformly-sized and uniformly-spaced droplets of hexane within the burner. His results agreed remarkably well with those of Chen, suggesting that the thermally stabilized burner was essentially fuel-independent insofar as the droplets were small enough and volatile enough to evaporate completely ahead of the flamefront.

However, Choi was not able to establish more than one stationary state for a given set of conditions.[6] He extended Chen's model to encompass evaporation of the droplets and devised a greatly improved but still approximate method of solving the integro-differential equation (which proved to have general utility even outside of combustion and for solving purely integral equations as well).[7] With this method, the effective energy of activation required to match the computed location of the flamefront with the experimental one was not dependent on grid size. He avoided the "stiffness" associated with the steep gradients of temperature and composition in the flamefront by using steps in composition rather than distance in the numerical integration. Even so, extreme sensitivity was encountered in the computational procedure; the stable solution was found to be dependent on the eighth significant figure of the temperature of the wall at the inlet, which quantity was used as the variable of iteration.

The numerical solution provided a complete, essentially fuel-independent locus of flamefronts versus the rate of flow of fuel and air in close agreement with the data for both gaseous propane and droplets of hexane.[8] However, this relationship predicts only two stable locations for a given fuel-to-air ratio and rate of flow, one near the inlet and one near the outlet of the channel. The other five stable states predicted by Chen and observed by Bernstein are only slightly displaced from this locus, and we now postulate that the slight approximation which expedited the process of solution eliminates the fine structure which would have resulted in their prediction.

As contrasted with *blowoff* and *flashback* for conventional burners, the above-mentioned locus of stability predicts another unique characteristic for thermally stabilized combustion: for increasing rates of flow, both of the computed stable locations of the flamefront are predicted to shift inward toward a common point near the longitudinal midpoint of the channel followed by extinguishment; for decreasing rates of flow, both of the computed stable locations are predicted to shift outward to the respective ends of the channel, with extinguishment occurring somewhat short of the ends. The predicted limiting behavior was not tested by Choi, even for the single downstream stable flame he established, because of the difficulty of adjusting the fuel and air proportionately while maintaining the same size and spacing for the droplets.

Choi also computed the chemical process of combustion using a global model for conversion of the hexane to CO and H_2O, and pseudo-steady-state free-radical models for the formation of NO_x and the oxidation of CO. The predicted concentrations of NO_x were greatly in excess of, and those of residual CO were grossly below, the measured values, suggesting that these models were inadequate, at least for the high temperatures and minimal backmixing encountered in thermally stabilized combustion.

The previously noted lessons concerning the conduct of research were reinforced in a slightly different context by the work of Choi. Again, a fresh approach by a second investigator, this time in solving the general model with some extensions, was very productive. The resulting solution included a complete locus for the stable flamefronts, and thereby the prediction of unique and unexpected limiting behavior. It also provided theoretical confirmation for the observed fuel-independence of the thermally stabilized burner. In addition, theoretical modeling of the atomization was a critical element in the design of the experiments.

THE SEARCH FOR MULTIPLE STATIONARY STATES WITH DROPLETS OF HEXANE

John W. Goepp, as his M.S.E. thesis, and with the help of Shu-Kin (Harry) Tang, completely reconstructed the experimental apparatus of Choi in order to provide more precise and flexible control of the rates of flow of air and hexane, and thereby facilitate the search for multiple stationary states in that system. Wulff furnace elements were no longer available, but a geometrically equivalent burner was cast from a commercial ceramic cement. Equipment for online analysis for NO, CO_x, CO, CO_2, and O_2 was added. The improved control permitted identification of as many as three upstream and two downstream multiple stationary states with hexane.[9] Presumably, two more might have been found with better control and care. The locations of all of these stable flamefronts were in good accord with the predictions of Choi. The online chemical analyses were in agreement with those by Mobil, eliminating the nagging possibility that the latter were affected by the storage and transportation of samples in Teflon bags.

CHEMICAL MODELING OF THE POST-FLAME ZONE

Tang utilized the improved apparatus constructed by Goepp and himself to investigate as his doctoral research the effects of an addition of small concentrations of fuel-nitrogen and fuel-sulfur to hexane on the formation of NO_x. He covered a more complete range of residence times than his predecessors by making periodic, pseudo-steady-state measurements while the flamefront drifted upstream from a stable location near the outlet or downstream from one near the inlet as a result of a perturbation in the rate of flow. He also investigated a wider range of equivalence ratios (fuel-to-air ratios divided by the stoichiometric fuel-to-air ratio). He found that the conversion of fuel-nitrogen to NO_x occurred primarily in the flamefront, was almost quantitative for equivalence ratios from 0.6 to 1.0, and fell off outside that range.[10] Fuel-sulfur was found to reduce the formation of thermal NO_x slightly and fuel-NO_x significantly,[11] a result which was in contrast with prior observations for other types of burners.

Tang initially resisted my proposal to model the post-flame reactions with a complete set of free-radical mechanisms, but relented when I mentioned that the alternative was explanation and possibly reinterpretation of his experimental results by another student. By trial-and-error he found that a kinetic model incorporating twenty-one reversible reactions was sufficient for the post-flame region for the combustion of pure hexane, and that twenty-three additional reactions were necessary for fuel-nitrogen and sixteen more for fuel-sulfur. He postulated a global model for the combustion of hexane to CO and H_2O. When the mole fraction of hexane fell to 1 ppm due to combustion, the fuel-nitrogen and fuel-sulfur were postulated to be converted quantitatively and instantaneously to HCN and H_2S respectively. The post-flame model was then initiated.

The predictions of NO_x by Tang were in good agreement with his measurements for equivalence ratios up to 1.1, but in disagreement beyond.[12] The details of the computations revealed significant deviations of the concentrations of all of the free radicals from their pseudo-steady-state values throughout the post-flame zone, thus explaining the failure of prior predictions. The model predicted negligible formation of NO_2 (less than 10 ppb) in contrast to a significant fraction of the NO_x in the measurements. Subsequent calculations suggested that all of the measured NO_2 was formed in the sampling tube, and this presumption has since been verified by spectrographic measurements within a burner. The deviation of the predicted concentrations of NO_x for very fuel-rich mixtures from the measured values was presumed to be due to the failure of the postulate of quantitative conversion of the fuel to CO and H_2O. This speculation was eventually confirmed as described below. The predictions of NO_x for hexane with added fuel-nitrogen were in good agreement with the measurements (except for very fuel-rich mixtures for the same reason as above).[13] The predictions for added fuel-sulfur were in qualitative agreement with the measurements, but the reductions in NO_x were less.[11]

The work of Tang reemphasized the generalities noted above with respect to exploratory research. The synergetic value of combined experimentation and modeling was overwhelmingly apparent—particularly to Tang, who had initially resisted the incremental effort required by the latter. Again, common wisdom, this time in terms of the pseudo-steady-state postulate for the concentration of free radicals, was found to be misleading. The detailed kinetic model not only improved the predictions of NO_x and CO, but also explained the failure of the early models. The prediction of NO_2 brought the process of measurement into question, and subsequent modeling of the process of sampling demonstrated that the measurements of NO_2 and CO were indeed in error due to an inadequate rate of quenching.

On the other hand, the extended range of experiments with respect to equivalence ratio identified the limit of validity of post-flame modeling alone, and suggested a new direction for this research. The qualitative agreement between the experimental and the theoretical effects of fuel-sulfur on the formation of NO_x was essential in obtaining acceptance from the reviewers of an article for publication, since this result is contradictory to both experimental measurements and theoretical predictions for other types of combustion. On the other hand, the quantitative discrepancy between the measured and predicted effects of fuel-sulfur suggested an error in the modeling which was examined and resolved in subsequent work. The results for fuel-sulfur suggest another generality with respect to exploratory research. One must be prepared to justify (in great detail and beyond any question) radical results which invalidate prior theories or generalities, particularly those of the reviewers themselves.

CHEMICAL MODELING OF THE PREFLAME ZONE

Lisa D. Pfefferle proposed modeling chemical kinetics in the preflame region as her doctoral research. Since prior work had indicated the behavior of the thermally stabilized burner to be essentially fuel-independent, methane (for which the rate mechanisms were presumed to be the simplest and most reliable) was chosen as a fuel. This research appeared in advance to be straightforward, but (as indicated below) unexpected results and difficulties arose at every turn. First, a clean and non-oscillatory flame could not be stabilized in the new, longer (508-mm) burner which had been cast. Several weeks were spent recalibrating the metering devices, analyzing the fuel, making a new 254-mm-long burner, etc.—all to no avail. In despair, she turned back to propane, which proved to burn stably as before. She then tried ethane, which also burned satisfactorily, and chose it in preference to propane and methane for the subsequent studies.

Analysis of the data for methane revealed that the steady rate of flow fell in the laminar regime upstream from the flamefront as contrasted with the turbulent regime for ethane, propane, and hexane. She speculated (and later confirmed by modeling) that this difference in behavior for methane was due to the absence of a C-C bond. One productive consequence of this adventure (which was very disturbing at the time) was the construction of a graphical correlation for the regimes of stability in the TSB for various fuels, equivalence ratios, channel-diameters, and channel-lengths.[14] Another was a computational study of the adiabatic and non-adiabatic ignition of various fuels and mixtures thereof.[15,16]

The studies of stability confirmed that turbulent flow is barely achieved in a 9.52-mm channel, even with C_{2+} fuels. It may be inferred that turbulent flow is unlikely to occur in ordinary chemical reactors since the much lower rates of reaction compared to those for combustion cannot be compensated for entirely by a larger diameter.[17] Therefore, the postulate of plug flow cannot be justified on the basis of turbulent flow in either homogeneous or heterogeneous reactors despite that implication in most textbooks on chemical reaction engineering.

The computational studies of ignition by Pfefferle revealed that small concentrations of H_2 or C_{2+} in the mixture greatly enhance the ignitability. Had ordinary natural gas been used (rather than chemically pure methane) in her initial experimental studies in the thermally stabilized burner, the difficulties which caused such agony and led to the switch to ethane would not have been encountered. On the other hand, the long-range effects of this experience were many and all positive, including another example of the fundamental difference between thermally stabilized combustion and other processes, for which backmixing is a sufficient source of free radicals for rupture of the C-H bond.

Having established a model for the preflame region, Pfefferle encountered great difficulty with the stability of the solution of the set of differential equations representing the kinetic behavior ahead of the flamefront as contrasted with the single one for global kinetics. This characteristic difficulty in solving ordinary differential equations numerically is known as "stiffness" and arises from widely separated eigenvalues, or in physical terms in this instance from the critical dependence of the kinetics on minute concentrations of free radicals near the inlet of the burner. Brute-force calculations require intolerably small steps in space in that region. Pfefferle surmounted this difficulty by using an approximate analytical solution for the very inlet, followed by a standard scheme of marching.

Her computations revealed incredibly complex behavior near the flamefront and resulted in very good predictions of NO and CO even for very fuel-rich mixtures. The path of oxidation of ethane to CO and H_2O was found to proceed through many intermediates such as CH_2OH.[18] This work confirms that, while a global kinetic model with adjustable empirical constants is able to predict the thermal behavior with reasonable accuracy, it cannot possibly be used to predict the concentrations of CO, NO, etc., either locally or overall. Pfefferle also modeled the preflame as well as the post-flame zone for the combustion of ethane with additions of ammonia[19] and of ammonia and hydrogen sulfide.[20] The predictions of NO_x for pure ethane and for ethane plus ammonia were in good agreement with her own measured values, but the initial calculations for the added effect of hydrogen sulfide were not. She concluded that some important mechanisms were missing from the best current compilations. She also concluded that the greater reduction in fuel-NO_x by fuel-sulfur in the TSB as compared to conventional burners was due to the higher temperatures in the immediate preflame zone and to the minimal backmixing. The contrasting chemical behavior for various conventional burners was successfully modeled with the same kinetic mechanisms by postulating an adjustable combination of a plug-flow reactor and a perfectly mixed one.

The productivity of Pfefferle's research was greatly enhanced relative to original expectations by the completely unexpected behavior of methane *vis-a-vis* other fuels in the TSB. This result was a consequence of the fortuitous use of chemically pure methane rather than natural gas. Many important findings followed: 1) the absence of a C-C bond was identified as the source of fuel-sensitivity; 2) the absence of backmixing was identified as the source of the difficulty in burning methane in the TSB as contrasted with other burners; 3) the study of ignitability revealed the sensitivity of the TSB to small concentrations of C_{2+} and H_2; and 4) the generalized analysis of stability resulted in the recognition that turbulent flow is unlikely in conventional reactors.

Other difficulties and anomalies were also a precursor to discovery. The stiffness of the free-radical, preflame kinetic model as compared to a global one resulted in the development of a new technique for that purpose. The failure of the predictions of the effect of fuel-sulfur on the formation of NO_x to agree with experimental measurements in the TSB identified missing mechanisms as the culprit, and the different effects in a TSB and conventional burners were rationalized in terms of a combination of plug-flow and perfectly mixed reactors—a classical application of the methodology of chemical reaction engineering.

TESTING THE POSTULATE OF PLUG FLOW

The study of stability by Pfefferle[14] led to a further inference not mentioned above. Since the stable flow upstream from the flamefront is barely turbulent, at least for a 9.52-mm channel, the approximately seven-fold increase in absolute temperature and the associated approximately five-fold increase in dynamic viscosity result in a decrease of the Reynolds number behind the flamefront to much less than 2100 for all conditions. Laminarization was therefore to be expected. In all of the above-mentioned modeling, plug flow was postulated both upstream and downstream from the flamefront, except for the evaluation of the heat-transfer coefficient for convection, which was estimated from empirical correlations for fully developed turbulent flow upstream and for developing laminar flow downstream. The postulate of plug flow in the kinetic model was excused on the basis of the demonstration by Aris[21] that the error in the conversion of a reactant due to the postulate of plug flow rather than laminar (parabolic) flow is less than 11% for a first-order reaction and even less for higher orders.

Even so, I was very pleased when Lance R. Collins chose as his doctoral research to investigate laminarization behind the flamefront and its effect on the post-flame reactions. He computed the time-averaged field of velocity using a low-Reynolds-number k-ε model for turbulence[22] and then the corresponding chemical compositions using a free-radical kinetic model.[23] His measured pressure gradients and velocities at the centerline were in reasonable accord with the predictions, but both his measured and predicted concentrations of CO were as much as 25% higher than computed values based on plug flow. This unexpected result led to the realization that the generalization of Aris is not applicable to the residual concentration of a reactant. For example, the possible error in the residual concentrations of a reactant by a first-order reaction due to assuming plug flow rather than laminar flow is unbounded. The formation of NO_x is not affected significantly since it is effectively zero-order and as such is independent of the velocity distribution.

The lesson here is that an authoritative generalization, although valid *per se*, may not be valid for conditions that differ subtly. We were ourselves misled for over a decade by the accuracy of the predictions of NO to the extent of presuming a chemical-kinetic rather than a fluid-mechanical explanation for the observed errors in the predictions of CO. It is noteworthy that none of the reviewers of our several papers seriously challenged the applicability of the postulate of plug flow in our modeling.

GENERATION OF STEAM AND THE REDUCTION OF RESIDUAL CO

The very low concentrations of NO_x produced in the thermally stabilized combustor are, as noted above, somewhat at the expense of large residual concentrations of CO. Furthermore, NO_x continues to form in the products of combustion after leaving the burner insofar as they remain at high temperature. This period may be significant with conventional boilers, etc. As his doctoral research, Mark R. Strenger chose to investigate a process devised to quench the formation of NO_x in the boiler, but to allow continued oxidation of CO while generating steam. The equipment consisted of seven metal tubes (contiguous with the channels of the combustor) that passed through a pool of boiling water contained in a cylindrical jacket.

The process worked exactly as planned chemically[24] but the heat transfer coefficient for forced convection from the products of combustion was much higher than expected.[25] A theoretical solution for the fluid mechanics and heat transfer using the same k-ε model as that of Collins provided an explanation.[26] The flow inside the combustor is in transition from turbulent to laminar flow. As the gas is cooled inside the metal tubes, the viscosity decreases, the Reynolds number increases, and a transition back to turbulent flow occurs. Owing to this transition, a heat transfer coefficient higher than that for either fully developed laminar or fully developed turbulent flow is achieved.

The turbulent-laminar transition explains, at least in part, the excessive heat transfer coefficients required in the models of Chen[4] and Choi.[8] The heat transfer coefficient for forced convection inside small tubes is much greater than that for radiative transfer and unconfined convection in conventional boilers, even without enhancement by transition. The combined effect produces a reduction of **several orders of magnitude** in the size of the boiler.

Although the chemical behavior in Strenger's research was much as expected, the thermal/fluid-mechanical behavior produced a favorable surprise which could be explained only through the theoretical modeling.

CONCLUSIONS

Combustion is a worthy subject of research by chemical engineers. It is of obvious practical importance, but has been the subject of only limited fundamental work. As a result of recent progress in chemical kinetics and machine computation, it is responsive to modeling with the classical techniques of chemical reaction engineering, and as a result of recent improvements in instrumental techniques, the *in situ* measurements necessary to test critically such modeling have become possible.

Thermally stabilized combustion proved, as indicated herein, to be a fortunate choice for this program of research because the fluid mechanics are simple relative to all conventional processes of combustion, while the thermal/chemical behavior differs radically in almost every respect. The characteristics of thermally stabilized combustion, which are noted herein only in a historical context, are summarized elsewhere.[27]

Conclusions relative to the conduct of academic exploratory research were drawn above in connection with each of the separate undertakings, and only generalities in this regard will be listed here.

- **Most discoveries arise from experimentally observed anomalies (the existence of multiple stationary states was an exception in that it arose from modeling).**
- **Theoretical modeling is usually necessary to understand and explain observed anomalies, and thereby to determine whether they represent physical behavior or experimental error.**
- **The combination of experimentation and modeling is generally more productive than their separate performance.**
- **Consecutive individual efforts on a general problem often provide new insights.**

It follows that one of the most important roles of a faculty advisor is to encourage students to be on the alert for anomalies and to pursue and/or resolve them. A more difficult but worthwhile endeavor is to persuade theoretically inclined students to test their modeling experimentally, and experimentally inclined students to develop a model to explain and extend their measurements.

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REVIEW: Thermodynamics

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dard enthalpy change for reactions as a function of temperature. Further, the units are now essentially all SI. There has been some rearrangement of material that includes putting fugacity earlier and devoting more material to EOS and high-pressure phase equilibria. Finally, there are revised examples and problems.

Over the years we have used different editions of the text in our own teaching. A recent experience was with students whose first course was in the engineering core, so this book was used for a subsequent chemical engineering course in chemical thermodynamics. Our opinions on the success of the book are similar. In general, the examples and problems are very good—they are challenging but consistent with the text. The exposure to all combinations of phase equilibria is highly desirable. Also, the programs included in the second edition can be quite useful to students in addressing real (and therefore complex) systems, as well as fostering an exploratory mode of how nature actually behaves. This is especially valuable for students who must encounter the idealized or limited nonideal descriptions of physical chemistry thermodynamics.

The connections of the text to other courses is difficult to measure. Our experience is that differences of approach and notation usually overwhelm the similarities that may appear to students in later courses unless the same instructor is involved.

The text does achieve a significant level of detail, but this often leads to confusion about the fundamentals. The dilemma of how many formulae to put into the hands of students is solved by using extensive tables of equations for different cases. Often, the student's reaction is to try to use these tables to look up a formula rather than to quickly derive the one they need for a problem. Another effect of this is to inadequately distinguish between fundamental concepts, approximate relationships, and specific illustrations. The result is that students become unsure of which are the big things that should be focused on and remembered. It also leads to a great deal of the material being strictly mathematical, with little physical connections that are either macroscopic or molecular.

Teachers will undoubtedly have differences with the author about his selection of correlations—that is inevitable in this area. In any case, the correlations are often presented without indication of whether they are to be used in real work or whether they are merely illustrative. The corresponding states treatment involves graphs from Hougan, Watson, and Ragatz containing Z_c, but equations containing the acentric factor. While the treatment for mixtures is complete, it is quite mathematical and follows a considerable discussion of the fugacity of pure components, so the whole exposition appears less focused than it might be.

All of the above issues may be dealt with by an experienced instructor who is comfortable with this difficult subject. In particular, highlighting the important material and simplifying complexities will be necessary. This takes a high level of concentration and a willingness to sacrifice some of the rigor of the text—this might ask for more commitment from students than they want to give. They will also have to deal with the text and the teacher appearing to conflict with one another.

The qualities of the text are numerous. It has been adopted in a limited number of situations, according to the latest AIChE Education Survey, and it is worthy of serious consideration at least as a reference. ❐