

Combustion Metrology: A Manifesto

KERMIT C. SMYTH *Building and Fire Research Laboratory, National
Institute of Standards and Technology, Gaithersburg, MD 20899*

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Speaker 1: "If you don't know where the atoms and molecules are in a flame, you don't know anything!"

Speaker 2: "You must be a chemist."

In the fall of 1985 Jene Golovchenko from Bell Laboratories presented a staff colloquium at the National Bureau of Standards (now NIST) on scanning tunnelling microscopy. This was an exciting time in surface science, since the tunnelling microscope was yielding such fundamentally new insights that the Nobel Prize would soon be awarded for its invention and application. In his seminar Golovchenko made a key point that has stuck with me ever since. His argument went something like this: Investigations of surface processes had been largely empirical and had made little headway before the advent of scanning tunneling microscopy. The field simply could not progress beyond a certain point without a detailed knowledge at the scale of atomic dimensions. Tunnelling microscopy was unleashing a flood of information which was forming the basis of a new surface science.

I made a brief note of these remarks and placed it beside my desk, where it remains to this day. Golovchenko's sentiments have served as a beacon and a worthy goal for my own efforts. When I was asked in 1976 whether or not I wanted to become the Center for Fire Research's "laser diagnostician", I'd never heard the term and didn't have a clear idea of what it meant. Although I said yes at the time, it was not until Golovchenko's seminar that I could effectively articulate the direction we had recently embarked upon (Smyth *et al.*, 1985). Despite that fact that we have never created a group at NIST devoted to "Combustion Metrology", I've been fortunate to have spent much of the last decade probing the chemical structure of diffusion flames. What better place to do this than the government's laboratory for physical measurements!

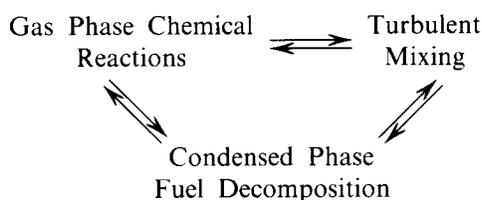
Predicting the next 25 years in combustion is a daunting prospect, particularly when one considers the advances which have occurred over the last quarter century. However, it seems clear that while the science of combustion will push forward with unexpected and exciting consequences, progress will be largely incremental (as opposed to revolutionary) without much improved measurements in flames of all types. This means more accurate, more detailed, and more comprehensive *in situ* data on atomic and molecular species, combined with improved measurements of temperature and velocity fields. Current efforts in laser diagnostics are making important contributions, but the impact could be much greater. Such investigations in themselves may not merit a Nobel Prize no matter how successful, yet quantitative species, temperature, and velocity information constitute the defining and most demanding tests of what we think we know. Flame measurements are the ultimate arbiter of how well we understand the controlling chemical mechanisms and transport processes. Just as we cannot

construct a comprehensive chemical mechanism by simply assembling all the best kinetic rate data and thermodynamic properties (although this is a necessary first step), so we cannot claim to understand combustion by patching together chemical mechanisms and turbulence models and making only global comparisons against experimental results.

The advancement of combustion science also faces formidable obstacles arising from its multi-disciplinary nature. For example, chemists and fluid mechanics (speakers 1 and 2) may not use a common language. Researchers from different backgrounds often stick close to their specialties and select relatively small pieces of problems they know best; tighter budgets can foster more conservative approaches. Despite such natural tendencies, the lure of successful collaborations is helping the combustion community broaden its viewpoint and overcome traditional practices. The future of combustion science rests to an important degree upon how well different perspectives and individual efforts can be integrated.

THE UNBALANCED COMBUSTION TRIANGLE

In the general case of burning condensed phase fuels, combustion involves the coupled interaction between gas phase heat release, turbulent mixing, and the chemical and thermal decomposition processes:



Combustion science has often attempted to isolate these basic ingredients and focus on one specific area—the high-temperature chemical reactions or the fluid mixing processes or the production of gaseous fuels. Even more challenging is the elucidation of the complex coupling between these components. CO formation is an apt illustration of this coupling: We know very well the kinetic rate coefficients for CO production and destruction at elevated temperatures, yet we cannot predict CO emission from any turbulent flame over a range of conditions even for purely gaseous fuels. What we don't know is placed in the black box called chemistry-turbulence interactions.

Figure 1 is a personal view of what we've learned about combustion's troika in recent years, obtained from my own vantage point in gas-phase chemistry. Plotting the rates of knowledge accretion against time illustrates several points:

1. The greatest accumulated knowledge (the areas under the curves) has occurred for gas-phase chemistry. Most advances have come from experimental measurements of rate constants and thermodynamic properties in non-combusting environments.

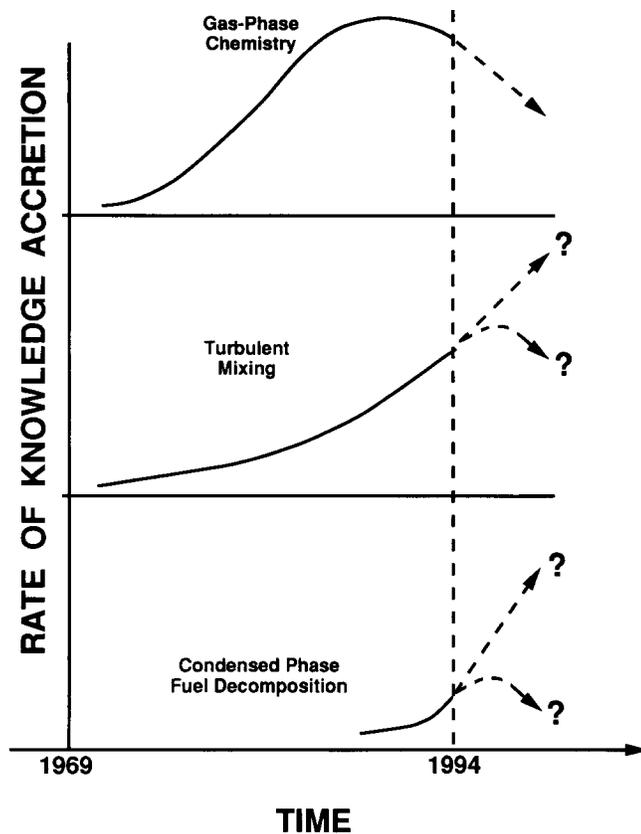


FIGURE 1 A personal view of the rate of knowledge accretion plotted versus time over the last 25 years for the three basic components of combustion.

2. The rate of knowledge growth for gas-phase chemistry peaked several years ago, as some of combustion chemistry's classic problems were convincingly framed and major chemical pathways identified. Soot production in hydrocarbon flames and NO_x chemistry are two prominent examples. The work of Frenklach *et al.* (1984) and Miller and Bowman (1989) constitute seminal breakthroughs and have been recognized as such immediately by the combustion community. Consider the unprecedented quantity and quality of the questions submitted for the Frenklach paper at the Twentieth Symposium; combustion scientists knew what was at stake. This doesn't mean that there is nothing left to do in gas-phase combustion chemistry. Important issues remain unresolved, as is illustrated by the large area under the knowledge accretion curve in future years.
3. Future directions in turbulence and fuel decomposition are uncertain, and with little experience in these areas I dare not hazard a guess. Turbulence is widely viewed as more difficult and complicated than the regime of high-temperature gas phase chemistry. Despite innovative experimental advances and much activity, major

breakthroughs have not been forthcoming. We often hear that “more research is needed”, which is a frustrating state of affairs. Even more discouraging may be the prospects for understanding and predicting the time and temperature evolution of gaseous fuels from condensed phase decomposition processes. Although much has been learned about the gas-phase pyrolysis of hydrocarbons, results on the chemical and thermal breakdown of pure liquids and solids are scarce. Only for a very few condensed phase fuels (such as PMMA) burning in specific configurations can we predict the mass burning rate and fire spread. This area is at least 10–20 years behind the other two and may never catch up.

MEASURING ATOMS AND MOLECULES—CHALLENGES FOR THE LASER JOCKS

When pulsed dye lasers became widely available in the early 1970's and people touted their wonderful spatial and temporal resolution for flame studies, combustion diagnostics offered the promise of exciting advances. It is disappointing that meaningful results have come slowly in the early years. One can argue that we've learned far more combustion chemistry via molecular beam sampling studies than from optical measurements. For example, Phil Westmoreland (1986) obtained data for 212 species in a premixed acetylene/oxygen flame, including over 20 radicals! However, molecular beam sampling has been restricted largely to low-pressure premixed flames, and these constitute only a small subset of the combustion conditions of interest. Accurate measurements of radical species, which are the most rigorous tests of proposed chemical mechanisms, have been rarely made in atmospheric-pressure flames using sampling methods (Miller and Taylor, 1987). As researchers have investigated increasingly more complex combustion environments, laser-based measurements have continued to improve and have become more widespread. Although Hanson's 1986 symposium review of combustion diagnostics was the last time this topic was highlighted at the biannual International Combustion Institute meeting, laser results are being incorporated into a rapidly growing fraction of the accepted papers.

Quantitative measurements are the most difficult to make but are also the most valuable. To quote Lord Kelvin (Wm. Thomson):

“When you can measure what you are speaking about and express it in numbers, you know something about it, but when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind. It may be the beginning of knowledge, but you have scarcely, in your thoughts, advanced to the stage of science, whatever the matter may be.”

In our attempts to express experimental results in numbers, we should also add uncertainty estimates and carefully specify our initial conditions. Does anyone really know what the temperature, velocity, and species concentration fields are right at their burner surface? These are the first questions from a modeler.

Today, laser-induced fluorescence (LIF) is the most widely employed and useful combustion diagnostic, despite the fact that LIF is inherently not a quantitative method and relatively few species fluoresce. Hence considerable efforts are being expended to

improve LIF measurements by devising quenching-independent strategies, measuring quenching cross sections, and developing a variety of calibration procedures. In addition, there is great interest in new approaches for probing additional species, with a growing emphasis on obtaining quantitative information. Degenerate wave mixing, laser-induced incandescence, and tunable diode laser spectroscopy are all making important contributions. The field of laser diagnostics is dynamic and evolving rapidly.

Despite the utility and need for laser-based flame measurements, optical techniques have significant disadvantages, including expense, perturbations (e.g., photochemically producing the species one is trying to measure), and analysis difficulties (such as unknown quenching corrections for fluorescence measurements, varying lineshapes, and complex energy transfer processes). Researchers who understand their equipment the best also obtain the most reliable results—by far. As a consequence, a given approach developed in one laboratory is typically not easily disseminated and used elsewhere. Unfortunately, the practitioner, who is usually best aware of the pitfalls and range of applicability of a given technique, may not use his or her expertise to address important combustion problems. Then the entire effort spent in developing the method is wasted. Future support from the combustion community will increasingly follow only those laser diagnosticians who also tackle significant questions head on, carefully choosing a given flame system and analyzing their results in detail. This is a tall order and often can best be achieved only through collaborative efforts, but it is the only way to go beyond simply accumulating data. Our own experience has shown that if we don't make measurements with a given approach that we've developed, it is likely that no one else will. Once we've obtained species, temperature, and velocity profiles, it's up to us to carry out as much analysis as possible.

Laser-based measurements have been reported in flames for the past twenty years, yet obvious and important issues have not been addressed. For instance, increasing attention is now being devoted to understanding the strong coupling between gas phase chemical reactions and turbulent mixing. One approach for including chemical reactions in computational models of turbulent diffusion flames is to utilize libraries of strained laminar flame calculations which incorporate detailed reaction mechanisms. Results of such computations for one-dimensional CH_4 /air diffusion flames have been widely published as a function of the overall strain rate. However, no experimental results of how radical concentrations vary with the strain rate have been reported. Is there not enough gloss or glory in these measurements? There is no excuse for this omission. Likewise, it is remarkable that only recently have quantitative imaging measurements been made in steady, laminar flames (Smooke *et al.*, 1992). Instead, most of the imaging effort has been dissipated on generating false-color pictures of turbulent flows with no calibration in simpler flame systems.

Once we've set out to make quantitative flame measurements, we face subtle but significant additional hurdles. Comparisons of experimental data against flame computations tend to over-emphasize the good news (profiles agree!) and stumble on the bad news, even though it may be more interesting. Important differences go unexplained. For example, where is the follow up to the paper of Westmoreland *et al.* (1986), which compared their detailed experimental species profiles against the predictions of four published chemical mechanisms for acetylene combustion? Serious areas of disagreement were revealed, yet the hoped-for response from the modelers and further comparison against

this comprehensive dataset has not been forthcoming. Sometimes we simply don't know why an important difference exists, but at other times we hesitate to declare a winner or a loser. In our own work (Norton *et al.*, 1992) we have found discrepancies between experimental results and flame structure computations and have not known where the error lies. Once the comparisons are made and the issues raised, that's too often the end.

ACADEMIC CHEMISTS WILL EMBRACE COMBUSTION

This article began with two quotes from a conversation which occurred three years ago. To this point the discussion has focussed upon amplifying the thoughts of Speaker 1. What about Speaker 2? Was he criticizing chemists for burying themselves in minutiae, or was he applauding chemists for their willingness to delve into the most complex details? Twenty-five years ago even combustion scientists regarded the area of high-temperature chemistry as a hopeless tangle, particularly for the chemical growth reactions leading to soot formation:

“To recognize all details of the reactions causing rapid particle growth seems almost impossible, since there are too many parallel steps leading to hundreds of intermediates, most of which are not known as chemical individuals” (Homann, 1967).

While we may indeed never know all the individual reactions involved in soot formation, our perceptions have changed greatly in recent years. More detailed experimental measurements have led to greater understanding rather than greater bewilderment. For chemical growth processes a small and tractable number of routes dominate, not dozens of parallel pathways. Computational capabilities have advanced rapidly to the point where one can now incorporate simplified chemistry into time-varying flowfields which include even soot formation and radiation transport (Kaplan *et al.*, 1994). In the past, academic chemistry departments have eschewed combustion as a quagmire unsuitable for the training of their students. These attitudes are being transformed, albeit slowly; what once looked like a mess is now much more understandable. As such areas as molecular beam reaction dynamics, cluster spectroscopy, and photodissociation processes play their remaining cards as research topics, physical chemists will turn to the rich diversity offered by combustion as fertile ground for study. The interplay of chemical reactions, fluid flow, transport processes, and energy transfer is ready to be unravelled if the chemists and fluid mechancians can find a common ground.

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