SFPE Classic Paper Review: Diffusion-Controlled Ignition of Cellulosic Materials by Intense Radiant Energy by Stanley B. Martin

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INTRODUCTION

In 1964, at the Tenth International Symposium on Combustion held at Cambridge University, during the first ever full session solely dedicated to Fire Research at a Combustion Symposium, Stan Martin presented an exemplary paper (titled as above) on the topic of pilotless/ spontaneous ignition of cellulosic solids exposed to intense thermal radiant heating. The session opened with Stan's paper and the proceedings were released [1] in 1965.

The centerpiece of Stan Martin's paper was its Figure 1, reproduced here, containing a map of various sorts of ignitions resulting from various irradiances, i.e., radiant exposure intensities, H (kW/m^2), imposed on the surface of a cellulosic solid of carefully controlled thickness, L (m), and various physical and chemical properties. This map is the culmination of almost a decade long research effort by its author and his coworkers at the US Naval Radiological Defense Laboratory (NRDL) in San Francisco, CA USA.

The abscissa in this remarkable graph is the *irradiance parameter* defined as HL/K, where K is the specimen thermal conductivity (kW/(m K)). The ordinate is the *fluence parameter*, which is defined as $Q(\rho cL)$. The quantity ρc in the denominator here is the volumetric heat capacity (kJ/(m^3 K)) of the specimen solid. The quantity Q is the exposure dose, defined as the integral of irradiance, H, with respect to time, t. Martin preferred to call Q by the name 'fluence.' Its units are (kJ/m^2). In all the experiments underlying Figure 1, irradiance (from a carbon arc source)

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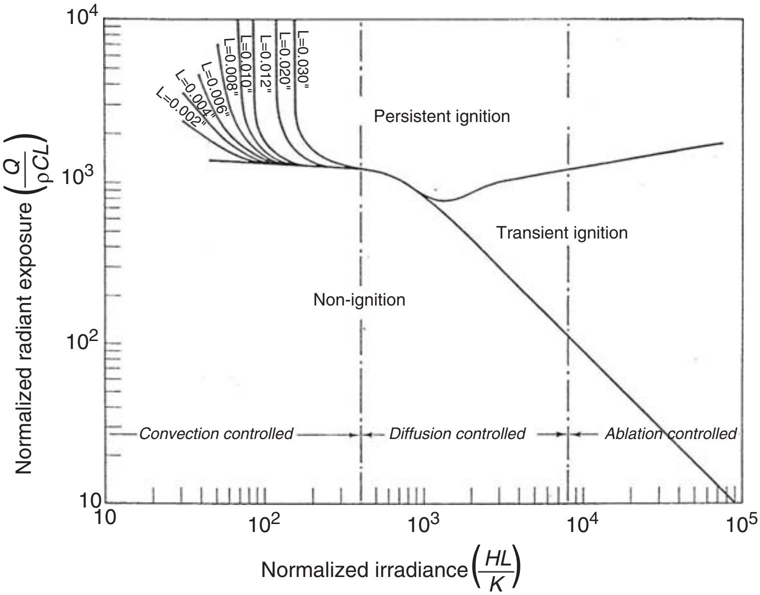

Figure 1. *Ignition behavior of cellulose, showing areas controlled by convective cooling, diffusion of heat into the solid, and ablation of the exposed surface. Reproduced with kind permission by the Combustion Institute [1].*

is a step function in time so that $Q = H \times t$. The fluence parameter thus is $Ht/(\rho cL)$. Both the irradiance parameter and the fluence parameter have units of temperature. They later were shown [2] to be correct and meaningful quantities, attesting to the depth of physical understanding Martin had mustered towards arriving at the ignition map. A ratio of the fluence parameter to the irradiance parameter is $Kt/(\rho cL^2)$. This quantity can be recognized as the *Fourier modulus*, ubiquitous in transient conduction problems.

HISTORICAL PERSPECTIVE

Upon serving in the US Army and mapping occupied areas in the Pacific Theater, Stanley Buel Martin studied physical chemistry at San Jose State University, graduating in 1951. He joined the newly established NRDL in 1952. His research at the lab involved the following projects: developing instrumentation to measure thermal radiation at nuclear tests; building and calibrating high-intensity carbon arc thermal radiation sources; and measuring the time to ignition of cellulosic solids as dependent upon the intensity of radiant exposure. By 1955, the year in which the National Academy of Sciences – Committee on Fire Research was established [3], Martin and his collaborators had honed the technique of ignition measurement to such a fine art that their measured ignition thresholds of drapes, typing paper, dry rotted wood and leaves were included in the newer printing of Glasstone's *Effects of Nuclear Weapons* [4]. Only three other researchers in the world were then measuring times to radiant ignition of cellulosic solids: Hottel of Massachussetts Institute of Technology; Akita at the University of Tokyo; and Simms at Borehamwood Laboratory in the UK.

Even more importantly, by 1956, the NRDL group had conducted systematic and extensive ignition time measurements [5,6], which Martin was attempting to correlate into a coherent framework. In 1961, he coauthored with Broido (of the US Forest Service) a paper [7] on the ignition behavior of cellulose doped with potassium bicarbonate, $KHCO_3$. The results are presented on a fluence, Q, to ignition versus irradiance, H, map. Glowing, transient and sustained ignition regimes are identified as dependent upon the dopant loading. From the graph for transient ignition of untreated cellulose, a quantitative relationship is obtained, namely that ignition is seen to occur when $QH(\equiv H^2 t) \geq 1 \times 10^5\,(\text{kW/m}^2)^2\,\text{s}$. This result is very much the same as the transient ignition threshold line of slope -1 in Figure 1, indicating that the time to transient ignition is inversely proportional to the square of the irradiance, in excellent accord with transient conduction solutions for the temperature of the exposed surface of a very thick slab.

In 1964, Martin [8] published a map, which is in all respects the same as in Figure 1 except that the x-axis is not the irradiance parameter but rather the square root of the Fourier modulus defined above. It is this version that attracted the attention of Emmons [9,10] who placed Martin's map among the then four most important fundamental problems of a free burning fire.

MECHANISMS

Note that the map in Figure 1 is delineated into regions of low, medium, and high irradiance parameter. According to Martin, the heating and ignition phenomena in these three regions are governed respectively by 'convection' (loss), 'diffusion' (i.e., conduction), and (surface) 'ablation.'

Convection Control

Due to absorption of a fraction of the irradiance, the solid surface becomes hotter gradually. As this occurs, the surface suffers substantial loss of heat to the surrounding gas phase by transient natural convection, such loss dominating in the determination of time to ignition, if ignition occurs at all. Thus Martin labels the entire left-third of the figure, where the radiance parameter is low, as 'convection controlled.'

In the lower left region of this left-third, the consequence of low radiance, low fluence and large convective loss is such that very little heat is conducted into the solid to cause pyrolysis, leave alone ignition.

In the upper left region, the radiance is low and the specimen thickness is small. The thin solid is heated and pyrolyzed so slowly that a flammable mixture hardly forms in the gas phase to be ignited so as to result in a flame. Instead, the char undergoes glowing ignition followed by complete consumption. This is the only region of the map in which the specimen thickness matters. Analytical description [2] indicates that the thickness parameter on the curves in this region takes on the nondimensional form of a Biot number, hL/K, where h is the transient natural convective heat (loss) transfer coefficient with units of $(\mathrm{kW}/(\mathrm{m}^2\,\mathrm{K}))$. In the limit of Biot number tending to zero, the fluence parameter for ignition becomes a constant near about 1300 K, independent of the irradiance parameter.

Diffusion Control

As the irradiance parameter is increased, reflection at the irradiated surface and conduction into the interior of the thicker solid dominate to make convective loss less important. This makes conduction into the solid govern the heating behavior in the middle-third of the figure where the irradiance parameter is moderate and is labeled as 'diffusion controlled.'

At very low fluence values in this middle-third region, conduction serves merely to drain the absorbed energy into the interior of the solid. This drainage precludes the raising of the solid near the surface to a temperature sufficiently high to commence pyrolysis. No ignition occurs. This failure to produce ignition due to conductive draining occurs also at moderate fluence values near the lower radiance boundary of the diffusion-controlled region.

If the radiance is larger towards the right boundary of the diffusion-controlled region; however, at moderate fluence values, solid layers near the surface do attain high enough temperatures to permit pyrolysis while continuing conductive drain to warm up the solid's interior. Under these conditions, flaming ignition is possible but the production of combustible gases is not profuse enough to sustain the flame. The flame ceases. The result is what Martin calls 'transient ignition.'

Sustained or persistent ignition is possible only in the upper-most region of the diffusion controlled middle-third of the figure. In this region, heating and pyrolysis of the solid are advanced enough to assure a continued supply of pyrolyzates to sustain the flame initiated by the ignition event. A high fluence parameter may appear to be the single sufficient condition to obtain sustained ignition. Sauer [11] thought that attainment of a minimum char depth assures a pyrolysis rate copious enough to sustain ignition. Attainment of a minimum solid mean temperature across its depth has also been argued [2] to be a reasonable criterion for sustained ignition.

Ablation Control

Very thick solids of low thermal conductivity exposed to a very large irradiance pertain to the right-third of the map, the region labeled 'ablation controlled.' At low fluence parameter values, the specified conditions are likely to heat a surface layer to a high temperature at which ablation phenomena arise to consume, sublime or spall the surface away. In a wide range of moderate fluence parameter values, transient ignition prevails. At high fluence values, sustained ignition is encountered again.

CLOSING PERSONAL REMARKS

Study of a fire science problem, whether experimental or theoretical, should always be founded soundly on first principles; and, it should involve a sufficiently detailed scrutiny of the associated physicochemical phenomena. Finally, study results have to be useful for improving practical fire safety. If these qualifications are all met, the study can be deemed 'good.'

A good study naturally brings to light a number of sub-problems which are limiting cases and extensions of the original problem and which are usually not recognized *a priori*. Delineating the various sub-problems and the domains of physical (and/or chemical) property conditions within which they arise is quite useful. One way of exhibiting such a delineation is through a two-dimensional map with the most meaningful and important properties serving as the abscissa and ordinate. Such a map shows the family of sub-problems and their relative standing in a broader and generalizable perspective. This elevates the quality of the study from 'good' to 'excellent' or even 'exemplary.' In this sense, within the related fields of thermodynamics, fluid mechanics, heat and mass transfer, and combustion and fire, the author (allowing for some subjectivity) can count fewer than a dozen existing archival papers, which meet the distinction of being 'exemplary.' Thus, use of the word 'exemplary' in the first paragraph of this article is not only deliberate but also very appropriate.

In addition to the topic of spontaneous ignition described here, Stan Martin made important contributions to a long list of other fire science problems. Pyrolysis of cellulosic and synthetic solid combustibles,

Stanley B Martin. From the Martin family photo album. Reproduced with kind permission by the Martin family.

flame-proofing of materials, fire suppression, room fire flashover, fire product toxicity testing protocol, instrumented fire tests of full-scale wood structures, modeling of blast–fire interactions, simulation of mass fires and Pasquill dispersion in plumes are but some of the topics on this list.

I met Stan in 1964 in Cambridge, England. In the years 1973–1975, I worked under his management in the Fire Research Group at Stanford Research Institute. Our collaborations continued for over thirty years. Stan passed away in October 2006 leaving behind four wonderful grown children. I am fortunate to have been given the honor of writing this tribute to a friend and colleague. Few tasks in life have been more fulfilling and gratifying.

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