

# Ignition: A Century of Research and an Assessment of Our Current Status\*

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**ABSTRACT:** Ignition has been systematically, scientifically studied for about a century now. But the development of knowledge in this area has been uneven, and while an advanced understanding has been reached in some areas, knowledge is scant in others. A review of the literature of the field indicates that the following are some of the notable areas where engineering calculation methods are poor or lacking: hot-surface ignition of liquids; ignition of liquid sprays or aerosols; ignition of solids from hot bodies (hot solids or liquids); ignition of solids by small flames; glowing ignition of solids, especially of lignocellulosic materials; almost all aspects of the ignition of dust clouds; and electrical fires. It is also noted that, despite a century's research, there have been very few theories developed in the ignition field that have engineering utility. The vast majority of theoretical development efforts have produced unwieldy computational models that would require a plethora of generally unavailable input data, along with the use of computer codes that are proprietary to the individual author and not available to the research community. Thus, laboratory testing is almost invariably required, and theories are typically only used as a means of interpolating or extrapolating data.

**KEY WORDS:** ignition, solids, liquids, gases, dust clouds, electricity, research.

## INTRODUCTION

**I**N 2003, SFPE published the *Ignition Handbook* [1]. This was the first time that a comprehensive review of the entire field of ignition was undertaken. A number of interesting conclusions emerged from this work and this article examines some of these highlights. Emphasis is placed on examining the state of the art areas where systematic knowledge, including theories and predictive methods, are available, versus areas where a need for research exists and the knowledge base is poor or fragmented.

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## Early History of Ignition Research

The earliest recorded information on ignition research comes from the Romans, who used wood for the construction of structures and ships and found a need to limit wood's ignitability. Consequently, they invented fire-retardant treatments for wood, as described by Browne [2]. Perhaps the next highlight is the work of Count Ivan Tschernischev, who was charged with studying the self-heating propensity of materials after a particularly disastrous loss of a ship belonging to the Russian Admiralty. He conducted systematic experiments during 1781 and published his study in 1782 [3]. Sir Humphry Davy invented the miner's safety lamp in 1815, as a means of preventing lamps from igniting methane in coal mines. His research [4] has laid the foundation for all later studies of flame arrestors and flame quenching distances. The problem of ship fires due to self-heating continued to be vexing, and in 1882, Thomas Rowan published an entire book [5] devoted to the topic of self-heating of coal in ships' holds.

The nineteenth century did not see much work done in fire safety engineering, but it was a century of remarkable advances in chemistry, and it was the work of the nineteenth century chemists that established the foundations of quantitative research in the ignition area. The history of chemistry is not within the scope of this article, but some of the highlights can be mentioned, comprising the earliest studies directly related to ignition:

- Mallard and Le Chatelier [6] published the first study on flammability limits of gases in 1880.
- van't Hoff [7] laid the theoretical basis for understanding autoignition of gases in 1883.
- Hill [8] published the first quantitative study on the ignition temperature of wood in 1887.

But, apart from such very few early studies, the history of ignition research has been a twentieth century endeavor. Thus, this article will review some of the highlights and attempt to establish – in broad outline – what is and what is not known at the present time, as discovered during twentieth-century research.

## Research Topics in Ignition

The broadest subdivision of ignition topics is:

- Ignition properties of ignitable materials;
- Characteristics of ignition sources;

- Self-heating (since in this case, the ignitable material and the ignition source are one and the same).

Thus, each of these will be addressed in turn, and after that, address some topics that do not neatly fall into this division.

## IGNITABLE MATERIALS

Owing to the fact that three states of matter are encountered, and behavior is different in each one, the study of ignitable materials must be divided into gases, liquids, and solids.

### Gases

In the ignition research field, the topic of gases has been of highest interest from the 1880s through the 1940s. Thus, with the exception of some early work on self-heating of solids, the topic of gases was the earliest subject of concerted research. This is not surprising, since, in all branches of physics and chemistry, gases are usually easier to study than are liquids or solids. But part of this also had a practical motivation. In the US, UK, and other countries, during the nineteenth and early twentieth centuries, coal mining was an exceedingly dangerous occupation, and one of the major hazards was the possibility of a coal mine explosion. Thus, much of the research was motivated by the need to reduce loss of life in coal mine explosions. Consequently, the institutions which emerged as pre-eminent in this research were the Bureau of Mines in the US, and the Safety in Mines Research Board in the UK.

Since the researchers were most often chemists, a part of the research was published in chemistry journals, but almost none in engineering journals. The chemistry-journal papers, however, tended to be summaries, with actual detailed research being published only in agency reports. This era ended with an outstanding monument – the publication in 1951 of the first edition of Lewis and von Elbe's book, *Combustion, Flames and Explosions of Gases* [9]. Although the last edition was published in 1987, the book remains a unique resource – the only major combustion textbook which emphasizes phenomenological observations and experimental work, rather than mathematical theory.

Although the Bureau of Mines continued to exist until 1996, after about 1950, research on ignition of gases, especially with engineering applications, decreased precipitously. In Germany, however, research at Physikalisch-Technische Bundesanstalt continues to this day, but most of their findings are published in reports that are unavailable in US libraries.

Research at universities, of course, continues worldwide, but most of this is purely theoretical and does not help solve engineering problems. The situation, however, is not as dire as this might imply. Indeed, for practical fire-safety purposes, it might be claimed that all that is needed is already known! The area where lack of knowledge turns out to be important is in the chemical manufacturing industry. Thus, the majority of the studies being done today on practical aspects of the ignition of gases comes from the chemical engineering community and typically involves questions not addressed in the pre-1950 research, e.g., unstable gases, or behavior of gases at very high pressures.

It must be emphasized that knowledge of the ignition of gases today remains essentially an empirical science – to find out the autoignition temperature (AIT) or flammability limits, for example, one must perform an experiment. Theory is useful primarily as an adjunct to empirical data, specifically, as a means to extrapolate data to conditions not encompassed in the experimental work. Calculations from first principles have essentially no use to the engineer today – for some simpler systems, it is possible to perform elaborate chemical kinetics calculations which may yield an AIT value close to that found experimentally. But doing the calculations will require a major effort by a PhD researcher, while a technician can determine the AIT experimentally in one day's work. Furthermore, the computer software needed to use such models has invariably been proprietary. Thus, even if users would wish to make use of an existing theory, they would generally have to start by re-developing the required software.

## Liquids

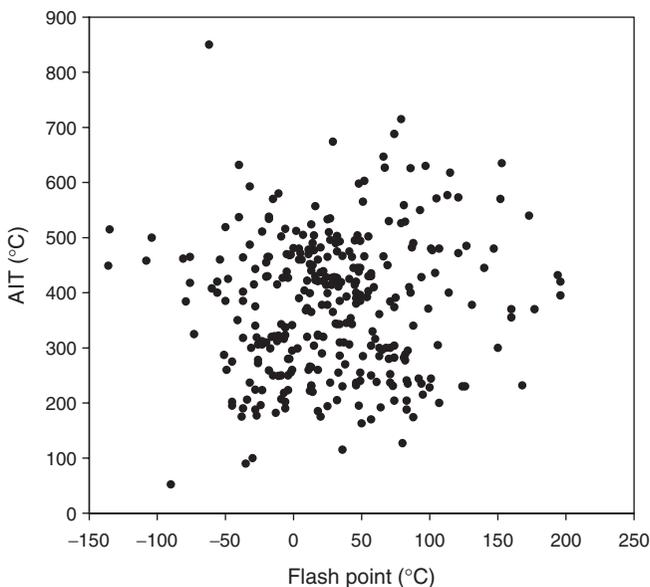
Research on the ignition of liquids and gases overlaps very significantly. This is due to two reasons:

1. When a liquid burns, it is actually the vapors that burn; consequently, concepts such as AIT would have no meaning when applied to the liquid, unless the translation is automatically made that it is really the vapor of the liquid (i.e., a gas) that is of interest.
2. The majority of the test apparatuses, which have been developed for determining the AIT of gases, actually consist of devices where the substance is injected in liquid form and allowed to vaporize.

Thus, research on the AIT or flammability of liquids, *per se*, is not needed. The primary topic of interest concerning the ignition of liquids is their flash point. This is a concept which is innately tied to the liquid phase and has no meaning in a gas (flash points reported for gases actually refer to the

substance brought down to a temperature sufficiently below ambient to liquefy; only then can the flash point be measured). Research into flash points of liquids has generally been exceedingly empirical and surprisingly old. The UK Parliament passed the Petroleum Act in 1862, which endeavored to restrict fuels having a flash point below 37.7°C (100°F). This precipitated a veritable flood of gentlemen-scholars inventing flash point apparatuses [10,11]. It is improper to refer to this work as ‘science,’ however, since these were inventions that did not seem to benefit from any significant application of physics or chemistry to the problem. The situation calmed down in the twentieth century and there have been much fewer such devices invented after 1900.

Flash points have generally not been of much interest to the mining-research institutions, or to the universities. Consequently, in the twentieth century, most of the work on flash point research was carried on in the chemical manufacturing industry or the paint industry. The latter was particularly prolific and their *Journal of Paint Technology* documents much of the twentieth century research in this field. An important concept concerning the ignition of liquids is that there is no relation between the AIT and the flash point, as shown in Figure 1. The AIT is a measure of the chemical reactivity of the substance, while the flash point primarily reflects the volatility – and these two molecular properties are not related.



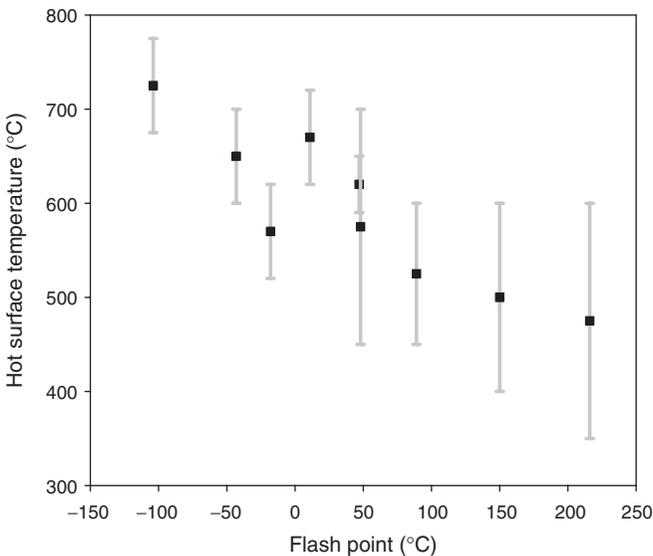
**Figure 1.** *Gases and vapors: the non-correlation between flash point and AIT.*

Two problems on the ignition of liquids have been the subject of research during the second half of the twentieth century without being satisfactorily solved:

- Ignition of aerosols (mists, fogs, sprays);
- Hot-surface ignition.

Both these problems are of considerable industrial importance and are also important in transportation, i.e., airplanes and road vehicles. Considerable research on the ignition of aerosols was carried out by John H. Burgoyne at Imperial College during 1949–1957 and this body of work still remains the main resource. More recently, the ignition of high-flash-point liquid aerosols has been of interest, and this new research has been coming from Physikalisch-Technische Bundesanstalt.

Hot-surface ignition of liquids has been studied since the 1930s, but the present state of knowledge is still very limited. One interesting correlation emerged during the preparation of [1]. Figure 2 shows that higher-flash-point liquids are, in fact, easier to ignite on a hot surface. This is understood to be a volatility effect – a lower-flash-point liquid, when spilled onto a hot surface, will create a large zone of vapor too rich to burn next to the hot surface. But for a less volatile fuel, the concentration may drop



**Figure 2.** The relation between flash point and hot-surface ignition temperature for some liquids used in the transportation industry.

below the upper flammability limit (UFL) close enough to the hot surface that sufficient temperature still exists to ignite the fuel. Only one research group attempted to model this phenomenon theoretically, but their theory could not predict the experimental findings.

The hot-surface temperature needed for ignition of a liquid is normally substantially higher than the AIT, so it is acceptable to use the AIT as a conservative bound. But this can lead to excessive economic penalty, so in industry it is often assumed that the hot-surface ignition temperature is 200°C above the AIT. The hot-surface ignition temperature, however, depends on the ‘enclosedness’ of the hot surface, and a hot surface which is highly enclosed will end up resembling the heated flask used for AIT determinations. Thus, if this geometry is encountered in practice, it is not safe to use a value above the AIT.

While the overwhelming majority of liquid ignitions occur due to volatilization of the liquid and combustion of the vapors, some liquids are unstable or reactive and can show exothermicity in the liquid phase itself. This, in fact, is an important cause for explosions in the chemical manufacturing industry. The reactions are typically decomposition, polymerization, or isomerization. Much rarer are heterogeneous oxidation-type, liquid–liquid reactions, which can also lead to explosions.

As for gases, while numerous PhD degrees have been earned for the development of ignition theories of liquids, the theories developed have generally not been helpful towards solving engineering problems. Indeed, unlike for gases, there are few theories that are of any help in making data extrapolations.

## **Solids**

It is convenient to subdivide solids into three types, since both the theories and the test methods are different for each: pyrolyzing solids, elements (typically metals), and dust clouds.

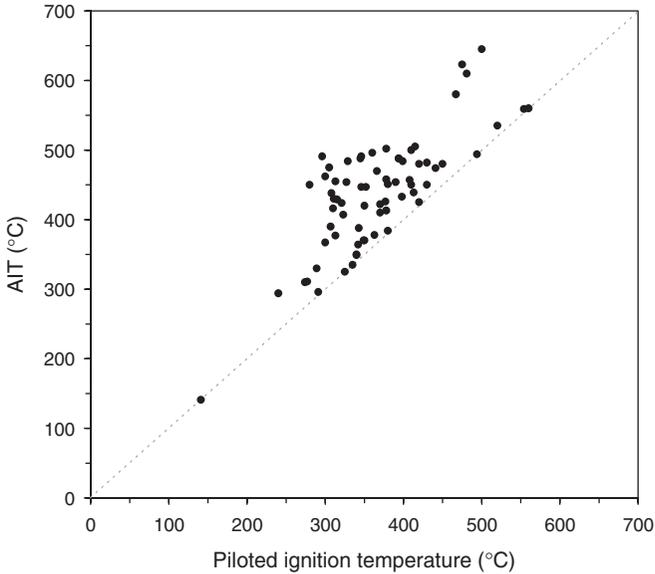
### *Pyrolyzing solids*

These are the common, everyday solids – wood, plastics, agricultural products, vegetation, etc. Pyrolyzing solids most commonly burn in a flaming mode: the fuel molecules break down, produce a gas, and it is this gas that burns, not the solid directly. A certain fraction of pyrolyzing solids can also ignite and burn in a glowing mode. For these materials (which invariably are ones that do not melt), sufficient oxidation can take place directly on the surface of the solid, so that glowing ignition and combustion is possible. Wood and other cellulosic and lignocellulosic materials are the primary examples.

Research on ignition of pyrolyzing solids was negligible until about 1950. During the 1950s and 1960s, some research began to be done by military agencies in the US and by the Fire Research Station (FRS) in the UK. After about 1970, the 'plastics era' motivated more concerted research. The first attempts to provide some scientific understanding on the ignition of pyrolyzing solids were specific to wood as the material. For convenience, it is useful to separate theories into 'fundamental' and 'engineering' theories in this field. The earliest 'engineering' treatments were by Bamford et al. [12] in 1946 and by Lawson and Simms [13] at FRS in 1952. The solid-ignition problem, in fact, is exceedingly complicated, since chemistry in both the solid and gas need to be taken into account. Furthermore, for most geometries of interest, a 1-D representation cannot properly represent the events in the gas phase, so a 3-D approach is needed. Thus, a 'fundamental' approach was not feasible until the modern era of computers. Successful models of this kind have, in fact, been rather recent, e.g., those of Yuen [14] in 1998 or Tsai [15] in 2001. These have been shown to accurately reproduce experimental data, but are not models of engineering utility, i.e., the effort to develop such a model and to obtain the plethora of input values needed for it is vastly greater than that required to obtain data by running standard laboratory ignition tests.

Since there is a need for ignition data for pyrolyzing solids, both test methods and 'engineering' theories were concertedly developed since 1950. The theory that is of most interest for engineering work is one where the heat flux imposed on the specimen is the input variable and ignition time is the output. Of such theories, the most fruitful one is generally considered to be that of Janssens [16]. His method is basically a scheme for theory-based extrapolation or interpolation of experimental data. The experimental data themselves during the last two decades have most commonly come from laboratory calorimeters (e.g., ASTM E 1354, developed at NIST [17,18] in the 1980s). A variety of other test methods exist for this purpose, however, as do alternate means of data analysis.

Over the years, research has demonstrated that, for most materials under most circumstances, the ignition temperature, i.e., the temperature of the specimen's surface at the moment of ignition, is relatively independent of exposure conditions. Consequently, for the whole of twentieth century (even before this relative invariance was justified!), ignition temperatures of solids were being measured and reported. But surprisingly, only a single test method for measuring the ignition temperature of solids has ever been published by ASTM. The sole method is the Setchkin Furnace, ASTM D 1929 [19], developed in 1949 [20]. This method has numerous faults, including a poorly designed pilot and the intrinsic problem that it measures the furnace temperature, not the specimen temperature at ignition.



**Figure 3.** Solids: the correlation between piloted ignition temperature and AIT for various plastics.

Nonetheless, with this ‘best-available’ tool in hand, it is interesting to compare the relationship between reported values for piloted ignition temperature and AIT. Figure 3 shows the results for a series of plastics where data are available [1]. The results can be interpreted as indicating that the AIT will generally be from 0 to 100°C above the value of the piloted ignition temperature, but that the actual increment is random within that range. The relative meaning of the two quantities, however, is not as distinct as is the relation between AIT and flash point for liquids. For solids, the AIT does not solely indicate the chemical reactivity, as it does for gases. Materials less prone to volatilizing will produce less pyrolysates at a given temperature, and this will require that a higher temperature be attained before a sufficient concentration can be developed. Until this temperature is reached, reactivity cannot be assessed. Chemical reactivity, then, might be viewed as inversely related to the increment by which the AIT exceeds the piloted ignition temperature. The results of Figure 3 indicate that this increment varies only over a modest range.

Probably more research efforts have gone into studying the ignition of wood than all other pyrolyzing solids put together. It is also one of the materials which can ignite either in a flaming mode or in a glowing mode. A recently published review article [21] on the ignition of wood has revealed

for the first time some important data trends, the most important being that the ignition temperature is a constant only in the medium-to-high heat flux regime. For heat fluxes close to the minimum needed for ignition, the ignition temperature is not a constant, but rather increases rapidly with increasing heat flux. Even with this new analysis, however, the situation is not satisfactory, since much data scattering exists, even under seemingly ideal circumstances. In addition, the ignition of wood is complicated since, not only can it ignite in either flaming or glowing mode due to short-term, external heating, but it is also a material susceptible to self-heating. The latter mode of ignition [22] can be encountered when a device such as a hot pipe provides long-term, low-temperature<sup>1</sup> heating.

### *Elements*

An element cannot pyrolyze since heat cannot cause chemical change in an element. Consequently, a solid comprised of a pure element will most likely ignite in a glowing mode due to direct oxidation at the surface. In some cases, if the element can sufficiently vaporize, then flaming combustion can also be possible. Most of the ignitable elements of interest are metals (e.g., aluminum, magnesium, zirconium). But some non-metal elements (e.g., boron, graphitic carbon, sulfur) ignite and burn in a similar manner, thus this class of solids is more suitably referred to as elements, rather than as metals.

Ignition of metals is relatively rare and most commonly a problem in certain industries and in the military. Theories specific to elements are needed to understand their ignition and combustion due to the dominant role of surface reactions. One important issue the theories have to address is the nature of the metal oxide that is formed on the surface – behavior is different if it cracks, compared to when it stays in place. Research on the ignition of metals has been done almost exclusively by the military and by the rocket-propulsion researchers; Russian researchers have also been particularly active in this area, with most of the published studies dating from the 1960s and 70s. Newer research work has tended to focus on accidental ignitions in high-pressure oxygen piping systems. This area, of course, is even more specialized and the ignition of elements in high-pressure oxygen streams does not necessarily correlate to ignition in the open atmosphere.

Despite the work of some exceptionally talented researchers, the current status here is similar to other ignition fields – theories exist, but these do not generally enable engineering problems to be solved without recourse to

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<sup>1</sup>Low-temperature' being low in the sense of being much lower than the ignition temperature associated with ignition due to short-term heating.

specific testing. Even testing is difficult because, with the exception of the high-pressure oxygen area, standard test methods do not exist.

### *Dust clouds*

Dust clouds are composed of solid particles, often comprising a common, pyrolyzing solid. Examples include wood flour, corn dust, and dusts of various plastics and pharmaceuticals. Coal dust explosions have, of course, historically been very important, and here the nature of the solid is complex – the volatile content of coal can vary widely and coal particles can burn either in a pyrolyzing mode or by surface oxidation.

Because of the nature of the aerosol, no theories or test methods intended for solid substances have applicability to dust clouds. Instead, there is a much higher similarity in their ignition and combustion to that of gases, but obviously the modeling problem is vastly more complicated than for gases. Because of this, there has been negligible development of theories for dust clouds, and there are none which would enable useful engineering calculations to be made on the basis of some ‘fundamental’ properties.

As for gases, AIT and flammability limits are important properties for dust clouds. But AIT is of lesser interest since actual dust cloud explosions normally occur due to piloting (e.g., a static electricity spark), not because the environment exceeded the AIT. Consequently, the most important ignition property of dust clouds has, in practice, been the lower flammability limit (LFL), sometimes referred to as MEC (minimum explosible concentration). For gases, the LFL is commonly reported in volume units, but for dust clouds it is necessarily in concentration units ( $\text{g m}^{-3}$ ).

Despite the existence of numerous test methods sanctioned by ASTM, ISO, and DIN, the status of dust cloud LFL measurement technology can only be described as poor and primitive, since these tests routinely report LFL values as low as  $20 \text{ g m}^{-3}$ . The misleading nature of this can readily be realized when it is recognized that the two organic gases showing the lowest LFL values are acetylene at  $26.6 \text{ g m}^{-3}$  and 1,2-propadiene at  $27.8 \text{ g m}^{-3}$ . Obviously, an aerosol of a solid is not easier to ignite than the most easily ignitable of gases and, in fact, research showed that the errors are serious indeed. For example, Lesikar et al. [23] measured one type of dust which had a published LFL of  $25\text{--}50 \text{ g m}^{-3}$  and found that the true value was  $290 \text{ g m}^{-3}$ . In most cases, the problem with the test methods has been non-uniformity of concentration in the apparatus – the LFL is reported on the assumption that the dust is uniformly mixed, but the actual concentration at the vicinity of the igniter may be much higher than the average value.

From the US point of view, the research situation in this field has been especially problematic since the literature can be nearly inaccessible.

The leading institutions doing the research have been German, Norwegian, and Swiss and much of their published output is either solely in in-house reports or in proceedings of conferences of which there may not be a single copy in a US library.

## CHARACTERISTICS OF IGNITION SOURCES

Apart from self-heating substances, the question ‘Can this ignition source ignite that substance?’ is of topmost importance in the ignition field. But it turns out that this is not an easy question to answer, since the simplest strategy (determine the minimum ignition energy (MIE) required for the substance and compare that to the energy available from the ignition source) is usually inappropriate. Instead, it is usually essential to know how the energy is being delivered, not just its totality. The ‘how,’ in turn, can be expressed as four different characteristics of an ignition source which can determine the ignition process:

- The temperature;
- The total energy supplied;
- The rate at which it is supplied, or the time period over which it is delivered; and
- The area over which it is delivered.

But this formalism, while conceptually useful, is not sufficient to help solve quantitative problems today. Instead, in [1], it proved necessary to consider the individual characteristics of ignition sources for each different class of ignition sources; consequently, ignition sources had to be grouped into broad functional categories:

- (a) High ambient temperatures (what is ‘high’ depends on the substance, of course)
- (b) Hot solids, liquids, or gases (contact with)
- (c) Shock, impact, pressure, vibration (i.e., mechanical forces)
- (d) Flames or remote burning objects
- (e) Electric current, static electricity, electromagnetic waves, particulate radiation
- (f) Light energy, lenses, and mirrors
- (g) Aerodynamic heating.

Not all of these categories, of course, are of equal importance – (a), (b), (d), and (e) are pervasively important, while the other three occur only in specialized situations.

## **High Ambient Temperatures**

Any ignitable substance will ignite if it is inserted into a sufficiently high-temperature environment. This underlies the study of ignitions of all kinds and can only be properly studied with a specific substance in mind. The concept of 'ignition temperature' of course is based on such testing and on the further assumption that this temperature does not vary too much if certain other changes (e.g., size of specimen) are made in the environment.

## **Hot Solids, Liquids, or Gases**

Hot liquids are a very rare cause of ignition, while hot (but not flaming) gases occur in specialized industrial situations, most commonly in the design of the equipment for use in flammable atmospheres. Hot solids, however, are a relatively common source of ignition. In all cases, the present research situation is very poor. Obviously, the size of the hot solid is an important variable, and some theories have been produced to take this into account, for both gaseous and solid ignitable substances. But these theories are so limited that they will hardly ever encompass a situation of practical interest. For example, no theory has ever been offered which would attempt to predict the conditions under which a hot, circular, metallic disk applied onto the surface of a wood specimen will cause its ignition.

## **Shock, Impact, Pressure, Vibration**

Ignition due to high pressure is most readily observed in the case of a diesel engine, but this is not within the scope of accidental ignitions. Otherwise, these mechanisms only occur in rare cases or specialized industries.

## **Flames or Remote Burning Objects**

Flames or heating from a remote burning object is a very common source of ignition and is the way a fire spreads throughout a building. Significant progress in quantifying the heat fluxes from flames has been made over the last three decades. But the *response* of materials to non-uniform heating from a flame has not been explored at all. For example, the most commonly used flame tests in the US are the UL 94 series of tests [24]. The test method itself was first published in 1972, but initial work at UL dates back to 1941. Yet, there has not been a single paper in the literature which attempts to model the ignition process that takes place when one of the flames specified

in that test is applied onto a specimen. There have been a number of papers seeking a correlation between the UL 94 results and those from some other test, but generally, and unsurprisingly, a good correlation was not found. The UL 94 is simply one of hundreds of small-scale flame tests which have been promulgated by various agencies around the world. Theoreticians have not made headway with these other tests, either. The reason is not hard to understand – unlike the ignition of a large specimen from a uniform radiant heat flux, modeling the ignition of a small sample which is highly non-uniformly heated, and which can melt, shrink, twist, retract, and exhibit other gross geometry changes upon exposure will obviously be difficult. Yet, the UL 94 test is a real-scale (not even scaled-down) representation of some types of flames which ignitable materials may encounter in real life. Thus, understanding the ignition process would be highly valuable.

### **Electric Current, Static Electricity, Electromagnetic Waves, Particulate Radiation**

Electromagnetic waves and particulate radiation (e.g., from nuclear weapons) are very specialized ignition sources, but electric current is exceedingly common as an ignition source and static electricity is common in certain industries. During the preparation of [1], it became clear that, despite this importance, research in the US on electrically caused fires has been limited, fragmented, and generally poor and unsatisfactory. Unraveling of the issues involved in the early-1970s fires due to the aluminum wiring fiasco [1] has been about the only sizable US research endeavor in this field. The current electrical-fires research status, however, is not as bad as this might imply, since research at least has been persistently conducted in Japan for the last several decades. Japanese research has led to an understanding of such aspects as the ‘last-strand’ ignitions of stranded cords, glowing connections with copper wiring, and the role of deliquescence in the ignition of PVC wiring [25]. Much of this Japanese research output has been presented in English for the first time in [1]. Nonetheless, it is a very serious concern that, to this day, there is no research group which has the competence, mission, or funding to do significant research in the US. The vast majority of standards in the US, pertinent to electrical devices and appliances, are promulgated by Underwriters Laboratories (UL). Thus, it is of special concern that, apart from a very few projects funded by Federal agencies, there has been no significant UL research publications in this area. It cannot be determined if the UL standards are being developed without the benefit of research, or whether research is being conducted but kept secret. In either case, however,

since peer-reviewed publication is the cornerstone of scientific credibility, the situation is unsatisfactory.

### **Light Energy, Lenses and Mirrors; Aerodynamic Heating**

These are rare and highly specialized ignition sources and not much research has been done on them; however, ignition from focused solar radiation is occasionally a problem, and guidance is actually available [1].

## **SELF-HEATING**

Self-heating is simply a chemical reaction which is significantly exothermic. Solids, liquids, and gases from a wide variety of chemical families can be susceptible to such exothermicity. In practice, however, self-heating has been of most concern for certain groups of granular or porous solids, e.g., coal or haystacks, where there has been a long history of accidental fires. As mentioned above, some of the earliest-recorded scientific ignition studies were on the topic of self-heating. But, while the problem has been of major practical interest for a few hundred years, quantitative studies are much more recent. Some early insights were reached by Hugo Miede in 1907 [26], but the first theory that was fully worked out was by Nikolai Semenov in 1928 [27]. His theory was useful for gases and liquids, but not particularly suited for solids. A suitable theory for solids was presented by another Russian researcher, David Frank-Kamenetskii in the 1940s [28]. It only became useful, however, when Philip Thomas [29,30] refined it at the British Fire Research Station (FRS) around 1960. In the same time period, Philip Bowes, also at FRS, developed a practical scheme for obtaining bench-scale self-heating data by means of oven-cube testing. A compilation of his studies appeared much later in a book form [31].

Since the modified Frank–Kamenetskii (F-K) theory can be implemented simply in a spreadsheet and the laboratory tests can be performed at a modest cost, in subsequent years it became quite common to predict self-heating of various granular or porous substances by using the F-K theory and the FRS experimental procedures. More recently, however, it has been realized that substances which can be successfully (i.e., accurately) treated by this strategy are outnumbered by ones where the theory is not applicable. Substances which have been studied and found to have a more complicated behavior that cannot be successfully treated by the F-K theory include [1]:

- bagasse (due to pivotal role of moisture flow)
- benzoyl peroxide (due to multiple reactions and effects of phase change)
- calcium hypochlorite (due to two different reaction regimes)

- coal (due to the strong role of oxygen and moisture flow; also since the problem time constants are typically so long that a full time-dependent solution must be sought, rather than being able to rely on steady-state results)
- fertilizers (due to multiple reactions, high variations in thermal conductivity, moisture flow, and melting)
- haystacks (due to biological heating by micro-organisms)
- liquid-soaked pipe insulation (in cases where the fluid is of high volatility and low exothermicity)
- sodium dithionite (due to two exotherms)
- synthetic dyestuffs, certain types (due to complex reactions)
- synthetic rubber, SBR type (due to presence of both endothermic and exothermic reactions).

It should be observed that even the ‘classical’ problematic substances, coal and haystack, appear on this list.

Apart from coal and haystacks, another commodity where large numbers of spontaneous combustion fires have occurred comprises cloths soaked in wood-finishing preparations based on ‘drying’ oils. The chemistry of drying oils is quite complex and a treatment based on F-K theory and currently available laboratory data does not capture the trends, since such an exercise predicts that roughly a 300-mm cube of material would be needed in a room-temperature environment, whereas a 25 g quantity has been empirically shown to suffice [1]. Another category of practical fires are the ones originating in wood members that have been heated for months or years by a steam pipe or similar hot object [22]. The process involves self-heating of wood, but, again, the simplified theory does not apply.

The nature of the self-heating problem is that there are basically two practical questions: (1) will this material ignite; and, if the answer is Yes, (2) how long will this take. For the second question, there are no reliable methods for engineering purposes. A number of theoretical treatments have been suggested but their results differ by several orders of magnitude and none has emerged as being the correct one.

## CONCLUSIONS

Systematic research on ignition dates back to roughly 100 years, even though some scattered scientific findings were available much earlier. During this span of one century, our phenomenological knowledge of ignition has increased enormously, that is to say, the majority of the phenomena can now at least be understood on a qualitative level. Quantitative knowledge today remains largely test-based. With some

exceptions, there are no 'simple, universal physicochemical constants' which would allow prediction of ignition phenomena for engineering purposes. In the academic arena, during the last 20 or 30 years, huge advances have been made in computational fluid mechanics (CFD), including calculations which incorporate chemical reactions. Research based on this approach has produced dozens of PhD dissertations on ignition, but the computational effort involved is still huge, and, consequently such computations are rarely made for practical fire safety purposes. Furthermore, validation is often limited for even the most advanced of such schemes, so that it is not clear how much trust could be placed in the computed results.

If one accepts that testing, rather than fundamental modeling, will be done to address ignition questions, then the status is more positive. The means of treating flammable gas explosions were already developed approximately 50 years ago. Problems concerning the ignition of liquids often reduce themselves to treating the volatilized vapor, so the treatment becomes identical. However, some aspects of the ignition of liquids are still poorly known. These include the ignition of aerosols, sprays, and foams, and all kinds of ignitions by hot surfaces. The response of solids to radiant heating has been systematically studied during the last 30 or 40 years, and some very useful – although empirical – treatments are now available. For ignition of solids by other mechanisms, research has been very scant. This includes ignition by hot bodies, convective heating, and glowing or smoldering ignition. Self-heating of granular or porous solids has been studied since around 1930, but quite concertedly during the last half-century. An idealized theory exists, along with test procedures specifically couched in its terms. But the theory is only useful for fairly 'ideal' solids and many substances – perhaps the majority – do not meet the assumptions of the theory. In addition, prediction of the time of spontaneous combustion with these substances (as opposed to whether or not it will occur) has had too many theories, and these diverge so widely that it is generally difficult to rely on any of them.

The ignition of metals is interesting to only a few industries, most saliently, the nuclear industry. Research on this specialized topic was active during the 1960s and 70s, with very little work being done currently. Consequently, available techniques may not be adequate. Dust clouds have an ignition response which is much more similar to gases than to bulk solids. Here, concerted research has been going on since the 1970s. Because dust cloud problems also are important only to a limited number of industries, the research has tended to be highly test-oriented – very few studies have been undertaken that are more fundamental in nature. In addition, there are serious problems with some of the commonly used test methods, so that the numerical data produced by them tend to be systematically inaccurate.

Generally, there has been much more research into the response of materials, with characterization of ignition sources receiving only limited attention. A crucial area where ignition source characteristics need to be carefully understood is electrical fires. There was only limited research in this area prior to 1970. Since that time, research has progressed well in Japan, but little has been done in the US. As a result, treatment of electrically caused ignitions has been largely empirical, without the benefit of a scientific methodology. Reference [1] is the first English-language presentation of much of this Japanese research. This would form a good basis for starting some US research, but it is not clear if this will happen.

The author's observation is that, over the next century, the largest opportunities in the ignition field will be for the replacement of some of the test-oriented approaches by computational methods. It should not be impossible to envision that, say 50 years from now, CFD calculations might become as easily made as are spreadsheet calculations today. After all, an interactive spreadsheet calculation in 1955 would have been exceedingly costly and resource-intensive. The basis for computational predictions, however, has to be that the physics and chemistry of the problem are well enough understood. At the moment, this is not true across-the-board in the ignition field, and many areas exist where computations could be made, but the results would be of unknown reliability, due to lack of underlying research. It may be noted that laboratory research in fire dynamics peaked during the 1980s and has been shrinking more recently. The situation in the ignition sector of fire dynamics simply reflects the broader field.

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