

*In 2001, prior to the completion of the **Ignition Handbook**, the following paper was published, giving some interim findings: Babrauskas, V., Pyrophoric Carbon...The Jury is Still Out, *Fire and Arson Investigator* **51:2**, 12-14 (Jan. 2001).*

*Due to the interim nature of this initial publication, below is a revised presentation of this topic which takes into account the final findings, as published in the **Ignition Handbook**. The Handbook is a peer-reviewed publication and was published under the auspices of the Society of Fire Protection Engineers in 2003.*

'Pyrophoric Carbon' and Long-term, Low-temperature Ignition of Wood

by Vytenis Babrauskas, Ph.D.

Summary

Recently, claims have been made that scientific research has disproven the concepts of 'pyrophoric carbon' or 'pyrophoric char.' Because of this, it has been claimed that wood exposed to long-term, low-temperature heat sources cannot exhibit spontaneous combustion, if the heat sources are below about 150°C (about 300°F). It will be shown that these claims only arise because an oversimplified theory was used, which is not capable of quantifying important phenomena in the problem. It will also be shown that the experimental research in support of those conclusions did not, in fact, speak to the issue. Finally, it will be shown that (a) practical guidance is available concerning conditions that are hazardous, with respect to long-term, low-temperature ignition of wood, but that (b) additional research is desirable in order to obtain an understanding of the physicochemical details of this phenomenon. The available practical guidance—i.e., the fires that have been documented to have occurred when wood members were exposed to heating sources at 77°C (170°F) or higher—forms a reliable, scientific basis for concluding that an ignition hazard exists if a heat source at 77°C or higher is applied to a wood member for a protracted period of time.

Background—The scientific concepts of ignition

Ignitions of combustible substances are generally divided into two types:

1. due to external heating
2. due to internal heating (self-heating).

There are situations of overlap, but this division proves convenient both in the scientific world and in practice. Most ignitions encountered are due to external heating. If a match ignites paper, or a halogen lamp ignites a curtain, the source is external. Fire investigators are also well familiar with internal heating. When a pile of linseed-oil soaked cloths bursts into flame, the cause is due to internal heating. Internal heating is more complicated than external heating, since factors such as air flow or exact details of the oxidation chemistry, which are of minor importance in external ignitions, become of major concern.

There had earlier been much disagreement about the minimum temperature needed for ignition of wood due to external heating. A recent study¹, however, systematically examined the results from more than a century's worth of research on this topic and concluded that—if wood is heated under the minimum heating conditions that will suffice for it to ignite—it will ignite at a temperature of approximately 250°C (482°F). If wood is exposed to an environment where heating conditions are greater than the minimum ones that are required, the actual temperature of ignition rises; thus the 250°C value is a suitable limit for design or hazard analysis purposes.

If a wood member ignited upon being heated for minutes, or up to a few hours, then it can be concluded that it ignited due to external heating. However, if wood is exposed for months or years to a temperature lower than 250°C, it can still ignite, because, on this time scale, self-heating plays a role. The recently-published **Ignition Handbook**² contains a collection of data on the temperatures that were involved in various real-life incidents where wood members ignited after exposure for months-to-years-long time periods. A particularly well-documented incident described in the Handbook of this phenomenon is shown in Figure 1. The Handbook also describes that the incident involving the lowest documented temperature at which a fire was reported involved a hot-water pipe operating at 77°C (170°F).



(a) Ignition of wood floor/ceiling assembly from a hot-water supply pipe (left pipe in the photo)
(Courtesy Ken Swan)



(b) Close-up of above
(Courtesy Ken Swan)

Figure 1. Fire caused by contact of a supply pipe from a hot-water heating system. The pipe penetrated a floor assembly comprising a 38.1 mm (1.5") wall plate on top of a 15.9 mm (5/8") OSB subfloor; the furnace was producing water at a temperature of 88 – 93°C.

It is important to note that since the physical and chemical mechanisms involved in ignitions due to external heating, and those due to self-heating are different, no specific relation can be assumed to exist between the 250°C value and the 77°C value.

A theory for the self-heating of substances was first developed by the Russian researchers Nikolai Semenov and David Frank-Kamenetskii from 1928 through the 1940s. The theory is generally called the “F-K theory” in honor of Frank-Kamenetskii. The theory was subsequently refined by British researchers, especially Philip Thomas, and came into fairly wide use by the 1960s. To understand some of the uses of this theory, it is first important to understand some basic terms.

Self-heating: an increase in temperature due to exothermicity of internal reactions.

Thermal runaway: self-heating which rapidly accelerates to high temperatures.

Spontaneous combustion: visible smoldering or flaming caused by thermal runaway.

Almost all organic substances (and many inorganic ones) can undergo exothermic reactions, typically, decomposition or oxidation. Since that is the case, it is necessary to understand why these substances are not spontaneously igniting all the time. The answer lies in the difference between self-heating and spontaneous combustion.

Suppose a modest heap is piled up of milk powder, a substance known to exhibit self-heating tendencies. If the pile is not too large, the temperature inside will rise by maybe 10°C, then will slowly drop back down. Suppose now that a very big pile of the milk powder is heaped together. The temperature inside will rise slowly at first, then start to accelerate very rapidly. The material will be the hottest in the inside. It will start to smolder rapidly and the smolder front will advance through the material. Finally, flaming may break out when the smolder front reaches the outside surface. In other cases, the entire pile may be consumed by smoldering, and flaming will not appear.

It has been found that the F-K theory can reasonably represent the events that occur in the pile of milk powder³. The theory, however, is based on extremely simplified chemistry and physics:

- There is only a single chemical reaction that takes place, and this reaction can be represented by an equation of the so-called Arrhenius form.
- All reaction products are the final products, and no further reactions amongst the products need to be considered.
- As much oxygen is available as needed.
- No account is taken of the mass flow of anything.
- Moisture has no role in the process.
- No physical changes, for example, cracking, are considered.

With these simplifications, it may be surprising that the theory can predict anything! But, in fact, there have been some well-publicized successes. On the other hand, it has been found out that the F-K theory does not apply to:

- haystacks (due to biological heating by micro-organisms)
- bagasse piles (due to pivotal role of moisture flow)
- coal (due to complex interrelation between oxygen and moisture)
- fertilizers (due to multiple reactions, high variations in thermal conductivity, moisture flow, and melting)
- numerous other substances², often of ones industrial concern.

The historical problem of low-temperature, long-term ignitions of wood

Around 1900, fires started being reported with steam or hot-water heating pipes where the pipes had been passed through wood members. Ignitions were being observed typically 3 months to 15 years after installation^{4,5}. The installations typically involved hot-water or low-pressure steam, where temperatures should be not much over 100°C (212°F). A small fraction of the incidents evidently involved some boiler malfunctions, and notably high temperatures would be expected. But for the majority, it is clear that these ignitions are not be categorized as external ignitions. It might be noted that investigators making the determinations of the cause in these long-term, low-temperature wood ignitions included Prof. Ira Woolson⁶ (the first US professor of fire science) and Voitto Virtala⁷ (the ‘father’ of fire science in Finland).

Even in the era of 100 years ago, it was evident that such ignitions were, in some sense, different from external-heating ignition and that a different explanation had to be provided. The original explanation that was proposed for these ignitions was put forth by the German scientist Ernst von Schwartz⁸ in 1902. Based upon a theory earlier suggested by the German scientist H. von Ranke as an explanation for haystack fires, the theory claims that low-temperature, long-term heating of wood converts the wood to “pyrophoric carbon,” and that this pyrophoric carbon is much more readily ignitable than is virgin wood.

For most of the 20th century, this theory was taken for granted, but no research was done to quantify or to understand it. Dr. Fred Shafizadeh, professor at University of Montana, and considered to be the world’s leading authority on pyrolysis of wood, started investigating the problem in the late 1970s. Shafizadeh created wood chars under aerobic (having access to air) and anaerobic (inert atmosphere) conditions. He found that char created under anaerobic conditions was highly reactive. The reactivity was an exothermic chemisorption of oxygen onto the char surface. Shafizadeh stated⁹: “This gives credibility to Ranke’s theory of pyrophoric char and his explanation of spontaneous ignition.” Unfortunately, Prof. Shafizadeh died while the research was still in progress.

It has been often reported that 288°C (550°F) is the charring temperature of wood. But this has been based solely on very brief exposures. In fact, it does *not* require high or even medium temperatures for wood to get charred—this has been well documented although less publicized. In 1945 McNaughton¹⁰ reported on a study done at the US Forest Service laboratories, where he exposed tiny (3 mm × 6 mm) sticks of wood for long periods. His results are shown in Table 1.

Table 1 Results of exposure of matchstick-size wood samples for long periods

Temperature	Time (days)	Condition
107°C	1050	light chocolate color
120°C	1235	brittle, dark-chocolate color
140°C	320	lost 45% of weight, became like charcoal
150°C	165	lost 65% of weight, became like charcoal

These results prove that very small pieces of wood, when exposed for a few years to 120 – 150°C temperatures, will turn into char. A number of fires have occurred, however, at temperatures below 120°C, and as low as 77°C. It is also obvious that wood will not ignite due to self-heating unless it has actually charred. Thus, it is important to understand that the McNaughton study only documents the starting-point temperature needed to cause charring for extremely small pieces of wood, much smaller than ones that have been involved in the known fires. The reason that temperatures as low as 77°C were sufficient to char and to ignite wood members is because the members involved were substantially larger than McNaughton's matchstick-sized specimens. Even though there does not currently exist a computational formula which would allow direct prediction of the ignition of such wood members based on a size/temperature relationship, it is well-known in the scientific literature that, for all the substances that have been studied, a lower starting-point temperature suffices if the size of the specimen is increased. Thus, it is not surprising that members which are a 2" × 4" (nominal) size, or larger, have been found to char and to ignite at lower starting-point temperatures than matchstick sized test specimens.

Efforts to disprove long-term, low-temperature ignitions of wood

There have been two efforts in recent times to prove that long-term, low-temperature ignitions of wood cannot occur. In 1984, Philip Bowes, a researcher at the Fire Research Station in the UK, published his conclusions¹¹ that wood members cannot be ignited from steam pipes that are operating at less than 200°C. Bowes did not do any experimental work to address the specific question. Instead, he analyzed existing experimental data in an attempt to find the answer. His basic reasoning steps were the following:

- He showed that wood samples which were pre-charred *in an atmosphere where the oxygen availability was never limited*, and then exposed to *external* radiant heating (in unlimited oxygen), ignited at about the same temperature as did non-pre-charred wood.
- Using available data obtained from tests of small cubes of material in an oven with unlimited access to oxygen, he applied the F-K self-heating theory.
- The theory indicated that a steam pipe would have to be operating at a temperature of about 200°C for runaway conditions to take place.
- Thus, he concluded that all of the reported investigations of fires which were attributed to sub-200°C heat sources had been incompetent, and that the steam or hot-water pipes actually were at temperatures of at least 200°C.

As described in detail in the **Ignition Handbook**², at the present time there is an incontrovertible collection of data to indicate that competent fire investigators have documented fires due to this cause at temperatures much lower than 200°C, and in fact as low as 77°C.

More recently, in 1999, Bernard Cuzzillo published the findings from his dissertation^{12,13}. In his thesis, he claims that he has disproven the existence of pyrophoric carbon (but it is not entirely clear from his writings whether he holds the same position as Bowes, or whether he accepts that long-term, low-temperature ignitions of wood do occur, but that they occur due to some mechanism which does not include oxidation of a reactive char). Cuzzillo based his thesis on three series of experiments that he conducted:

- (1) tests in an oven, with unlimited oxygen, on chips of virgin wood
- (2) tests in an oven, with unlimited oxygen, on chips which had been pre-charred under unlimited oxygen conditions

(3) tests in an oven, with unlimited oxygen, on 89 mm cubes of whole wood.

His tests indicated that:

- there was no significant effect of pre-charring on the behavior of the wood chips
- a wood member of 89 mm size must be exposed to a temperature of around 200°C to go into thermal runaway.

Cuzzillo then used the F-K theory as a tool to extrapolate the data to other sizes. But since an 89 mm (3.5") size is fairly typical for beams through which a steam pipe might imprudently be cut through, there was not a great deal of need for extrapolation.

Analysis

Both Bowes and Cuzzillo succumbed to a similar flaw in logic: Both relied on data collected in test environments dissimilar to the environment of actual fires. Both used extrapolations of, or numerical calculations with, a highly simplistic theory. Calculations with the F-K theory should not even have been necessary, since simple plots of existing data from oven-tested specimens would have shown that the thermal-runaway time scale for, say 90 or 150 mm size specimens is hours, not months or years. This should have suggested to Bowes and Cuzzillo that the F-K theory cannot hope to explain ignitions of modest-sized members that take months or years to occur.

It is important to consider Shafizadeh's view that highly-exothermically-reactive (that is, 'pyrophoric,' although the term is not a well-chosen one, in the opinion of this author) char is formed under conditions where oxygen is excluded from the char generation site. In his textbook, John DeHaan¹⁴ points out that fire cases identified as being due to pyrophoric carbon are especially prone to occur when the wood is sealed under an impervious layer, such as sheet metal. The generation of reactive char occurs initially under conditions where access of oxygen is limited. Subsequently, something happens that makes oxygen more available to the reactive char. DeHaan illustrates this with cases where a metal or tile covering is originally present, then becomes disrupted. It can also be envisioned that the process may well occur in the case of the ordinary steam pipe. Steam pipes and heating ducts play a similar role to a sheet-metal cover, in that they occlude the flow of oxygen for quite a while, until substantial shrinkage or charring of wood occurs. It is known that wood char cracks as heating continues. The time scale of the problem is most likely established not by a simplistic F-K one-step chemistry reaction, but by the char-cracking process. This is, unfortunately, a very poorly understood process, but it may well be playing a crucial role.

Thus, it is entirely likely that Prof. Shafizadeh was right in hypothesizing that long-term ignitions are a 2-step process:

(1) a reactive char gets formed under restricted-oxygen conditions.

(2) the reactive char then ignites. This may occur when further shrinkage takes place and oxygen enters newly-formed cracks. But a number of things are not known about the process:

- The flow of oxygen in depth into a wood member exposed to heat, but having only limited access to air.
- The mechanics of char, that is, being able to predict when and how it cracks.
- The relation between chemical reactivity and formation of cracks.
- The role of moisture in the entire process. Prof. Woolson and a number of later investigators have suggested that cyclic heating appears to be more deleterious than a constant temperature. The reason for this is not currently known, but clearly moisture will be one of the main variables that undergo large changes when thermal cycling occurs.

It may be surprising, but the details how wood char cracks have received only very brief study^{15,16} and the studies do not provide a basis for answering the above questions.

Conclusions

For wood that is exposed to heat sources for no longer than a few hours, the concept of external ignition is applicable. Self-heating plays a negligible role at short durations, and an evaluation of the results from numerous experimental studies of ignition under external-heating conditions shows a mean value of 250°C (482°F) for the ignition temperature obtained under worst-case (minimum heat flux) conditions. For wood exposed to lower temperatures, but for long time periods (months-to-years), self-heating is the dominant phenomenon. The concept of a fixed ("handbook") ignition temperature **does not apply** to a self-heating substance, and the hot-object temperature which will suffice to cause ignition under such circumstances depends strongly on the size of the specimen. For wood building members exposed to such long-term heating conditions, case incidents indicate that ignition is possible at a hot-object temperature as low as 77°C (170°F). It must be emphasized that the hot-object

temperature is the *starting-point* temperature of the self-heating process and that the self-heating process progressively raises the temperature of the wood member, so that when it actually ignites it will be at a temperature that is much higher than the starting-point temperature.

In terms of safe design and safe practices for the installation of heat-producing devices adjacent to wood surfaces, it should not be a new or surprising piece of information that 250°C would represent an extremely hazardous condition and that 77°C, in fact, must not be exceeded if the heating is prolonged. Already in 1959 UL¹⁷ issued this recommendation: “As a limitation on the temperature to which wood may be heated for long periods of time from a standpoint of fire prevention, many authorities indicate that 90°F above room temperature (approximately 80°F) normally prevailing in habitable spaces is a safe maximum and one which incorporates a reasonable margin of safety.” Since $80 + 90 = 170^\circ\text{F}$, the temperature cited in the 1959 UL recommendation is identical to the one derived in the present study. But there is an important difference in that, in our study, the 77°C value has a zero safety factor, whereas the UL value of 77°C, based on much earlier research, was intended to include some positive, but unspecified, safety factor. In any efforts to establish an “allowable” temperature, when considering data on temperatures at which ignition *can* occur, a safety factor must be included to ascertain that ignition *will not* occur, rather than will-just-barely occur.

No researcher, on the basis of applying a theory (especially a theory which is too simplified to capture the actual chemistry and physics of the phenomenon) can disprove the possibility of long-term, low-temperature ignitions of wood, since credible documentation, reported by reliable sources, exists to characterize fires due to this cause. A theory which disagrees with factual observations is obviously to be rejected. The studies of Bowes and Cuzzillo did not improve the theory beyond the already-available F-K theory, which is entirely inadequate to encompass the chemistry and physics involved in the present case. In addition to theory, Cuzzillo also conducted laboratory testing, but since the tests were performed under conditions notably different from those prevailing in real-life, long-term, low-temperature ignitions of wood, these results do not help to quantify the conditions under which such ignitions will occur.

The chemistry, physics, and thermostructural behavior involved in producing spontaneous combustion due to long-term, low-temperature heating of wood are clearly very complicated, interrelated phenomena. It may be many decades before a theory is evolved that can give useful numerical results. However, expanded guidance to investigators could be obtained in a few years by conducting a series of well-designed experiments. The simplest and best strategy might involve the following:

- Conduct real-scale tests (e.g., actual wood members) under realistic test conditions. This means a mockup of a meter or so in size, with maybe a 150 mm (6") thick member being used. These should not be oven tests, but, rather, the wood member must be heated the way it will be in practice—by a hot metal pipe or duct.
- In view of the possible importance of thermal cycling, two types of tests should be run: ones with the pipe at a constant temperature, and ones with temperature cycling.
- A period of 3 years might be a suitable time during which the experiment should be in place and left to run its course.

The US Dept. of Transportation¹⁸ defines: “A pyrophoric material is a liquid or solid that, even in small quantities and without an external ignition source, can ignite within 5 minutes after coming in contact with air.” Thus, applying the term ‘pyrophoric’ as a descriptor of long-term, low-temperature ignition of wood is not appropriate.

Finally, in view of the recent confusion in the Courts¹⁹, it is essential to emphasize that scientific knowledge of a phenomenon does *not* require that a theory or an equation exist for it. It is obviously the desire of all scientists to increase knowledge to the point that reliable computational theories become available. But the fundamental basis of all science is a systematic collection of data. And a collection of observations is sufficient to form a basis for making scientific conclusions. Thus, in the present case, it *is* possible to reliably conclude that any heating device of 77°C or higher, if applied to a wood surface for a protracted period of time, presents a documented ignition hazard.

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