

The author(s) shown below used Federal funds provided by the U.S. Department of Justice and prepared the following final report:

Document Title: Spontaneous Ignition in Fire Investigation

Author: James G. Quintiere, Justin T. Warden, Stephen M. Tamburello, Thomas E. Minnich

Document No.: 239046

Date Received: July 2012

Award Number: 2008-DN-BX-K166

This report has not been published by the U.S. Department of Justice. To provide better customer service, NCJRS has made this Federally-funded grant final report available electronically in addition to traditional paper copies.

Opinions or points of view expressed are those of the author(s) and do not necessarily reflect the official position or policies of the U.S. Department of Justice.

Report Title: Spontaneous Ignition in Fire Investigation

Award Number 2008-DN-BX-K166

Author(s): James G. Quintiere, University of Maryland
Justin T. Warden, University of Maryland
Stephen M. Tamburello, University of Maryland
Thomas E. Minnich, Technical Manager, NCFS

Abstract

The results of this project will provide the investigator with an understanding of spontaneous ignition. It presents a scientific description of spontaneous ignition, and presents the theory of the subject. Three scenarios for ignition are presented: (1) a cold material in hot surroundings, (2) a material on a hot surface, and (3) a hot material in cold surroundings. It defines the properties needed for spontaneous ignition as two parameters P and M . It presents two test methods for measuring these properties. The test requires a specialized oven and its design and operation are described. The Frank-Kamenetskii method is described along with the crossing point method. The latter is simpler, and its use is illustrated in an extensive study on developing the properties of linseed oil on cotton over a range of mass concentration loadings. This is the widest range of results for this common spontaneous ignition medium. Examples are presented on how to use the material, a technique for measuring the heat transfer coefficient of the oven test, and a database of property data was compiled.

Table of Contents

Report Title: Spontaneous Ignition in Fire Investigation	1
Award Number 2008-DN-BX-K166	1
Abstract.....	1
Table of Contents	2
Executive Summary	3
I. Introduction	17
1. Problem Addressed.....	18
2. Literature.....	19
3. Rationale for Research.....	21
II. Methods Used	22
1. Development of the Oven Test	22
2. Measuring Basket Heat Transfer	27
III. Results.....	30
1. Survey Results	30
2. A Qualitative Scientific Description of Spontaneous Ignition	30
2. Analytical Theory to Predict Spontaneous Ignition	38
2.1 Material in a Warm Environment, δ_c	41
2.2 Material on a Hot Surface, δ_c	42
2.3 Hot Material in a Cold Environment, δ_c	44
2.4 Time to Ignition.....	46
3. Measurements for Properties P and M.....	46
3.1 F-K Oven Method	47
3.2 Crossing Point Method.....	49
3.3 Heat Transfer Results for Our Oven	51
4. Example: Warehouse with Wood Fiberboard	54
5. Cotton and Linseed Oil Results	57
6. Tabulation of Properties from the Literature.....	61
IV. Conclusions	65
V. References.....	66
VI. Dissemination of Research Findings.....	67
VII. Nomenclature	68

Executive Summary

Spontaneous ignition is a fire cause that can easily be missed by an investigator. It is likely the cause of many fires that have defied recognition due to its slow and nearly invisible origin. In the investigations of these cases, the phenomenon is difficult to determine due to the destruction of evidence from the fire and lack of information on the symptoms of spontaneous ignition. Spontaneous ignition is a complex process and many investigators may not fully understand the factors that promote it, and how to assess its likelihood. It occurs in solids, liquids, and gases. In the latter, it is more commonly known as “auto-ignition”. Most common to flaming fires events is the involvement of solid configurations in spontaneous ignition. The solid-based fire is the focus of this work. It can occur in well-known media as cotton impregnated with linseed oil, moist haystacks, and least known as buried woody debris, and recycled plastic storage piles. Heat transfer, or the inability to cool a hot material, initiates the process. The process starts as a chemical reaction that is not yet deemed combustion, and the consequence of ignition can be smoldering or flaming. The key variables are the size of the material and nature of the heat transfer, and the particular chemical and physical properties of the material. In fire investigation, it is important for the investigator to recognize the signature of spontaneous ignition, to learn how to estimate if it were possible in the particular fire scenario, and to appreciate how to establish samples for measurements. In addition, it is importance for forensic laboratories to have the capability and understanding to utilize methods to achieve such properties.

Two main goals of this study were considered: (1) Provide investigators with a scientific understanding of spontaneous ignition and its analysis, and (2) Inform forensic laboratories on practical methods for measuring properties needed in analysis of spontaneous ignition. The latter goal was not fully achieved as the focus was on developing the laboratory techniques first. This was part of the subject in two MS theses, and that work took the bulk of the time. However, those theses and this report provide information to potential forensic laboratories that wish to adopt these measurement techniques.

A first step was to learn about the experience of investigators in the field with respect to spontaneous ignition. A survey of over 200 investigators was made that provided information about their experience with spontaneous ignition. In one case, a dwelling filled with garbage to knee-high exhibited the signs of the beginnings of spontaneous ignition, as charring was found in a portion of the garbage. The majority of the survey revealed that most of the incidents believed to have been caused by spontaneous ignition involved linseed oil infused materials, wet hay storage and problems with clothing just taken from a dryer. Other incidents involved potting soil, mulch and a variety of other materials. This project focused on linseed oil and cotton.

In addition, two Master of Science theses studies were undertaken. J. Worden [1] explored methods of measuring the spontaneous ignition properties of cotton impregnated with varying concentrations of linseed oil. S. Tamburello [2] examined the procedures for predicting the possibility of spontaneous ignition for several fire scenarios, and also compiling a data set of properties for a range of materials.

Scientific description of spontaneous ignition

A chemical reaction that releases energy is termed exothermic. Any substance that possesses exothermicity by itself or in the presence of air is prone to an unstable condition in which its internal temperature can increase significantly. The substance can be a solid, liquid or gas. The chemical reaction can be a decomposition of the substance, or an oxidation due to, for example, the presence of air. For example, the decomposition of the propellant ammonium perchlorate ($\text{NH}_4 \text{ClO}_4$) is exothermic. A sufficient temperature increase can cause an accelerating reaction front propagating through the material. Gaseous product can be trapped causing large pressure increase or fissures in the material. The reaction front can travel at less than the speed of sound in the material (deflagration) or greater than (detonation); explosive materials fall into this category of exothermically decomposing solids. Wood is even known to have an exothermic decomposition reaction at high temperature. Wood fiberboard is known to have exothermicity. Porous solids in air can oxidize exothermically throughout, and combustion gasses mixed with air can do the same. For the porous solid, the reaction may lead to a high enough temperature to initiate smoldering. The

diffusion or buoyant flow through the porous solid can supply the oxygen to sustain the smoldering. Vertical channels might develop due to flow and pressure effects. Eventually, the smoldering can make a transition to flaming by combusting in the incomplete product gases or fuel gases from decomposition of the solid itself. The term spontaneous ignition here can apply to the initiation of smoldering or flaming. Both will lead to sudden increases in temperature. This “ignition” is also referred to in the literature as “Thermal runaway” or “Thermal explosion” as fire or explosion may occur depending upon the substance and the reaction.

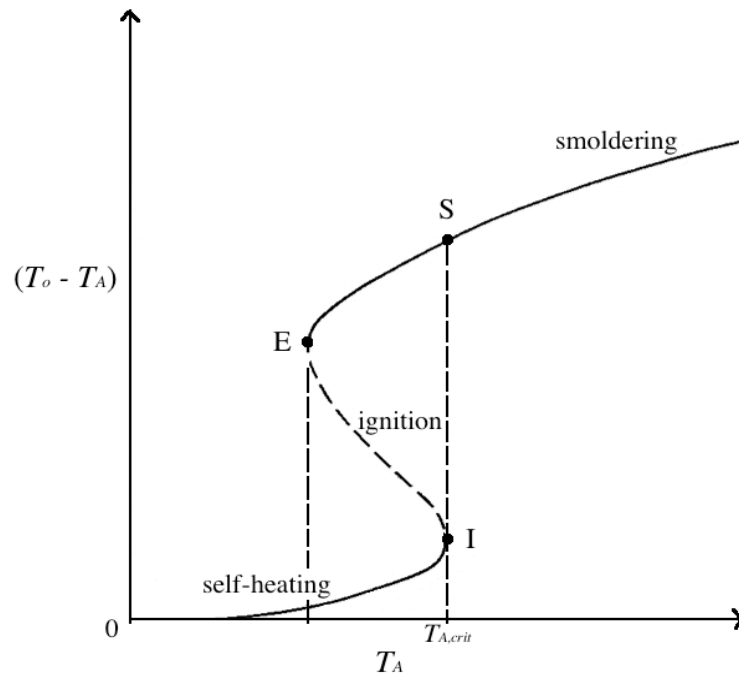
Worden [1] vividly shows the process of ignition in cotton cloth impregnated with linseed oil. With the medium in the form a cube composed of layers of the cloth and subjected to an air temperature in an oven of 48 °C, he recorded the processes. Three states are noted: (1) self-heating in which a chemical reaction giving off heat exists, but the state is not combustion, (2) smoldering, in which a distinct jump in temperature has occurred, and finally (3) flaming. The transition to state 2 is termed spontaneous ignition. It may or may not be followed by flaming.

For the first 50 minutes in exposure to 48 °C the material is in state 1. The core center of the material exceeds the oven temperature at about 25 minutes. During this 50-minutes period the process is termed self-heating and is not combustion. At 50 minutes a sudden rise of the core temperature marks ignition to smoldering where it is maintained at about 100 minutes to nearly 200 minutes at around 425 ° C. So smoldering is initiated at 50 minutes and then takes another 50 minutes to reach a fairly steady state. At about 190 minutes, there is another sharp rise in temperature to over 700 °C. This indicates the transition of the smoldering process to flaming. It is most likely due to the continued oxidation of the char by the infiltration of air into the core. The occurrence of a void space allows for more air with increasing velocity that now promotes flaming. As the smoldering progressed, it depletes the material. The infiltration of air is essential for this medium to maintain its oxidation. Natural convection or buoyancy drives air through the material, and pressurized pockets can occur. This effects lead to voids that allow more air to enter, and promote the transition to flaming.

This process for the cotton with linseed oil is indicative of spontaneous ignition in general. In this case the oven temperature and the cube size were sufficient to cause ignition in about 50 minutes. The chemical reaction initially was a low level reaction and not deemed combustion. But eventually, the core temperature increased and promoted a faster chemical reaction. At about 50 minutes ignition occurred that drove the reaction even faster and this culminated in fully developed sustained smoldering. The chemical reaction associated with smoldering is now clearly combustion. However, this reaction is very incomplete in terms of its products. The later flaming state is more complete, and has a much higher energy output. As the center of the cubic has the largest distance through which to lose heat, it traps the chemical energy, and the core receives that highest temperature and degree of chemical degradation. This internal damage indicative of the process promoting spontaneous ignition.

Porous oxidizing or exothermically decomposing solids are the substances considered from here. But it should be recognized that gases and liquids can undergo the same process, and the explanations given here for the porous solids also would apply. The principle theoretical basis of the analysis for spontaneous ignition is simple, but highly mathematical in its nature. Here, this complex mathematical presentation will be avoided, but equations cannot be eliminated as a scientific method for quantitative results are the goal. The original theory on spontaneous ignition was put forth by Frank-Kamenetskii (F-K) in 1938 [3] and forms the basis for much of the analysis done and discussed here, as well as the measurement method for characterizing materials. In addition to the two MS these referenced here, there are several excellent treatises that describe many aspects of the subject [4-7]. These and other literature have been investigated in the course of this study. The simple theory, while powerful in its ability to make practical predictions, does ignore many factors such as the diffusion of oxygen through the porous material, moisture that can promote biological energy, and competing chemical reactions in mixtures such as cotton and linseed oil, as both oxidize.

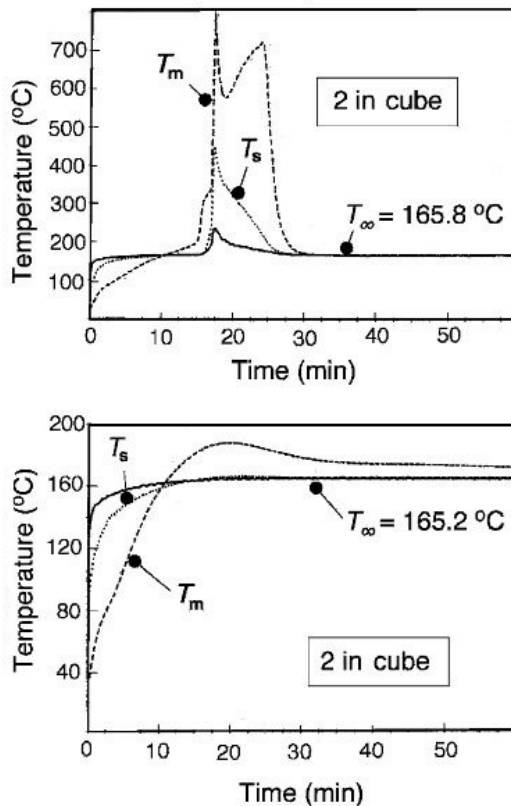
A graphical description of the process of achieving spontaneous ignition is represented in the figure below:



It shows the core temperature, T_o , rise over the environment or oven air temperature, T_A . As the air temperature is increased the early oxidation process results in a slight increase of the core temperature. So for this material, in its particular geometric configuration, up to point I, there is only a slight possible temperature increase. For 0 to I, the curve represents the various steady state temperatures in which the reaction continues and the core is slightly elevated. This range of possibilities is termed subcritical, and represents what is commonly called “self-heating”. Nothing dramatic happens. Of course, in reality this process can never be steady because the chemical reaction will cause the material to be depleted, and then will stop. Here, this is considered to happen later. Now the nature of the chemical reaction and the ability of the material to lose heat make the self-heating process unstable. This instability occurs because the chemical reaction is a very sensitive function of temperature, and increases sharply as the temperature increases. If the heat loss cannot keep up with the increase in chemical energy, the temperature will continue to rise. This feedback between an increase in the chemical reaction rate and the increase in temperature can lead to an instability and “thermal runaway” to a new state of equilibrium. This

instability is indicated by the jump in the core temperature rise from I to S. S, and the upper curve, represent the smoldering process where the chemical reaction of self-heating has now moved to that of smoldering. This is a new chemical reaction that is now classed as combustion. Any environment air temperature greater than the critical value associated with state I is termed “supercritical”, and below is “subcritical”. The ability to determine the critical state at I is the first step to assessing the possibility of spontaneous ignition.

The goal in testing is to find the minimum air or oven temperature to just cause the jump at I. This can be a tedious process, and at time difficult to accurately discern. However, the figure below shows that the critical temperature is between 165.2 and 165.8 °C. This is a very precise finding.



Analytical methods to predict spontaneous ignition

The F-K theory with one-dimensional heat conduction and a chemical source term forms the basis of mathematical and experimental analyses. In a one-dimensional model a specific dimension such as thickness or radius will be key, and each problem defines this variable specifically. In general it will be designated as r , but it has specific meaning to each problem. The next variable of importance is the temperature that is driving the initial heat transfer, and here will be called T_R , a reference temperature. This could be the temperature of the environment, the temperature of a hot surface adjacent to the material in question, or the temperature of the interior of the material following some processing. Three scenarios have been depicted:

- A cold material in warm surroundings
- A cold material in contact with a hot surface
- A hot material exposed to a cold environment.

While these cases are not exclusive, they do represent many scenarios of interest. Other scenarios of interest, such as heating by radiation, would need to be developed or sought in the literature. However, for these three cases, the governing equations have been solved and the literature contains results that lend themselves to analysis, and an estimate of the conditions needed for spontaneous ignition. Here, only the condition “if” spontaneous ignition is possible will be identified.

The F-K theory leads to a dimensionless parameter that governs whether ignition is possible. This is known as a Damkohler number given the symbol, δ . It represents the ratio of the chemical energy produced to the heat lost by conduction. Generally, if this number exceeds about 1, the condition is supercritical. However, the specific analyses for each of the scenarios given above result in values of the critical Damkohler number, δ_c . While the value for δ depends on the size (r), heating (T_R) and chemical and physical properties of the material for F-K theory, it can be represented as $\delta = \frac{r^2}{T_R^2} \exp\left(M - \frac{P}{T_R}\right)$. Here M and P represent material properties. Specifically, $P = \frac{E}{R}$ with the units of temperature (K) and R as the universal gas constant [8.314×10^{-3} kJ/mol-K], and E known as the activation energy, in units of kJ/mol. The activation energy represents the energy needed to initiate the

chemical reaction. The lower it is, the easier to initiate. Typically values for self-heating reactions range from about 60 to 140 kJ/mol. The parameter M represents a collection of physical and chemical properties in the form: $\exp(M) = \frac{E}{R} \frac{\rho A Q}{\lambda}$ where in this presentation it has units of $(\text{K}/\text{mm})^2$. The other parameters include the density of the material (ρ), the heat of combustion (Q), the thermal conductivity (λ), and another chemical rate term (A). While specialized apparatus may be capable for measuring each of these properties, it is common in the study of spontaneous ignition to determine just the P and M properties from direct measurements on the material. This is particularly needed since the material usually has the structure of a porous array, as a pile in layers or particles, with air filling the void spaces. Hence it is necessary to characterize the properties of the array, not the individual solid. A measurement process will be discussed later, but for now results for the three scenarios will be summarily presented. More details are found in references [1-7].

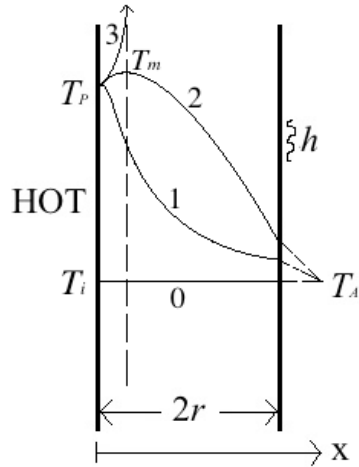
The analytical process is to identify the ideal scenario that best matches your problem of interest. Then, assuming P and M are known for your material, the Damkohler number can be determined for your size and heating condition. This means δ in Eq. (1) is calculated. Then it is necessary to consult the literature (or solve the governing equations) to determine the critical value δ_c for your scenario. If $\delta < \delta_c$ the problem is subcritical and ignition is not possible, but if $\delta > \delta_c$ the problem is supercritical and ignition is possible. The following three sections will describe how the critical value can be determined for each of the three scenarios considered here. They all will depend on both conduction through the material and on heating from the material to the environment. This environmental heat transfer can be composed of both convection and radiation. It requires knowledge of heat transfer to fully appreciate and evaluate. Suffice that it is represented as another dimensionless group called a Biot number given by the symbol α . The Biot number is the ratio of the convective and radiative heat transfer to conduction in the material. Specifically, $\alpha = hr/\lambda$. In the literature, and for a first approximation, α is often considered to be large (or infinite). It will show up in the following presentations on how to find δ_c .

Material in a Warm Environment, δ_c

This scenario represents a pile of material in a particular shape and size exposed to an environment at temperature, T_R . The pile can in the shape of a sphere, infinite cylinder, slab or cube. Graphical results are given on how to determine δ_c for a particular shape. We shall show results for a slab of thickness $2r$ and a cylinder and sphere of radius r . However, a cold object in hot surrounding involves the heat transfer conditions between the air and the surrounding by both convection and radiation. This heat transfer effect introduces another dimensionless parameter known the Biot number (α). Due the difficulty in estimating the Bi number, commonly results for δ_c are given for α as infinite, for example a cube for side $2r$ and α large has a value of 2.52. There are refinements in determining δ_c to account for depletion of material due to the chemical reaction and these might be pursued [2-7]. However, the accuracy of prediction is imperfect in extrapolating to real scenarios, and such refinements might be omitted. One can only hope for indications of the prospects for spontaneous ignition, not a perfect theory. Yet these techniques are powerful tools for the investigator. An example of a particular event is computed in the body of the report that illustrates the expected level of accuracy in the results.

Material on a Hot Surface, δ_c

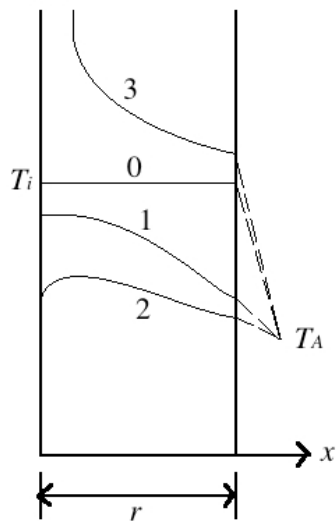
Here the process is illustrated in the figure below in which the hot surface is at T_P and there is heat transfer to the surroundings at T_A . Curve 1 would result in a straight line if the material were inert (unreactive). For a reactive material, curve 2 shows the subcritical state, and curve 3 the critical state of “thermal runaway”. The tendency for ignition increases as the hot surface increases, and its difference with the surroundings is small.



- Curve 0: Initial State; $T_i = T_A$
- Curve 1: Unsteady heating
- Curve 2: Steady condition; $\delta < \delta_c$
- Curve 3: Thermal runaways; $\delta \geq \delta_c$

Hot Material in a Cold Environment, δ_c

This case is depicted in the figure below in which a slab of half-thickness r is initially subjected to a uniform temperature T_i (taken as the reference temperature T_R in the Damkohler number), while the environmental temperature is T_A . This initial temperature could have been the result of processing or heating, e.g. clothes taken from a dryer.



- Curve 0: initial condition
- Curve 1: cooling
- Curve 2: steady result, $\delta < \delta_c$
- Curve 3: ignition event, $\delta \geq \delta_c$

The critical value of δ decreases as the initial temperature increases. Results are given for the slab, cylinder and sphere.

The above three scenarios only allow the determination if spontaneous ignition is possible. For a given problem, if the Damkohler number computed is

greater than the critical value computed in one of the three scenarios, then ignition will occur. A formula to estimate the time to ignite is given and the time directly depends on the size dimension and inversely on the Damkohler number.

Material Properties

The previous discussion gave methods for determining δ_c , but properties for the material are needed to complete this analysis. Obtaining the properties with sufficient accuracy to represent the material in the real spontaneous ignition scenario is not trivial. In many cases, the sample tested in the laboratory may not exactly be the same as that in the field. Moreover, the need to preserve the character of the porous matrix representative of the material is a must. This is why tiny samples representing the solid may not be sufficient for testing. Such testing might be accomplished by TGA/DSC devices, yet larger samples are preferred as more representative. Hence the usual method of choice is based on the F-K theory using larger samples representative of the real scenario.

F-K Oven Method

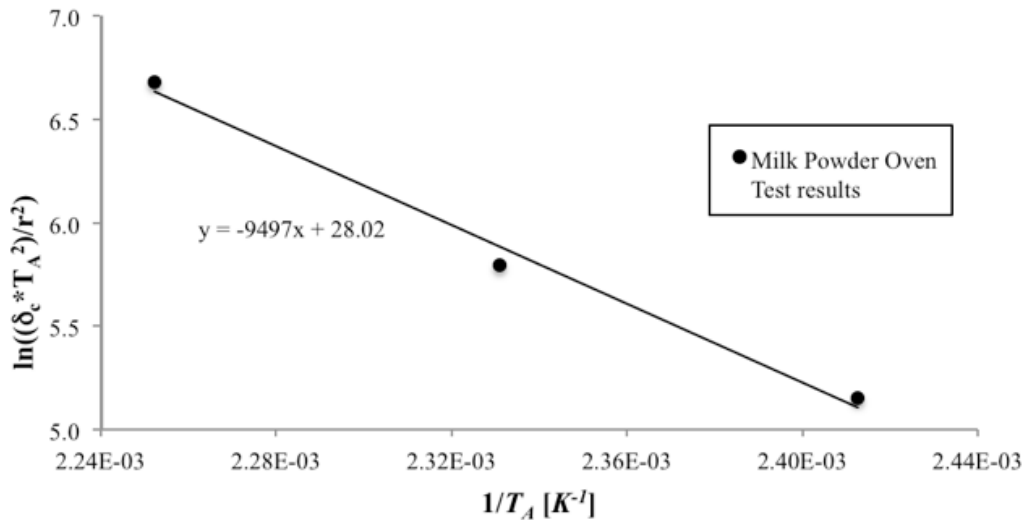
The F-K test basis is oven testing with specific shape samples in a wire basket suspended in an oven. This test method corresponds to the first scenario discussed, i. e. a cold material in a hot environment. The oven temperature is set and the sample is inserted with the center temperature continuously monitored. Worden describes this test with safety considerations in some detail [1]. The test is repeated until the critical temperature is found for a given sample size, usually a cube. It is a tedious process that can take days to carry out. However once a minimum of three critical values have been found an analysis can be conducted.

The procedure is to plot the left hand side of the equation below against $1/T_R$.

$$\ln \left[\delta_c \left(\frac{T_R}{r} \right)^2 \right] = -\frac{P}{T_R} + M$$

The Biot number must be known for the oven condition and a method and data to accomplish this is presented by Tamburello [2] and later discussed. An example of

this process is illustrated in the figure below:



Values found for P and M are respectively, 9497 K and 28.02. Note this is based on $\exp(M)$ having units of $(K/mm)^2$.

The F-K oven method is tedious, as it requires repeated tests to best establish the critical temperature. The point of ignition can also be problematic to recognize, as it is not always a sharp rise in temperature. So some judgement is needed. While this is the method of choice for establishing good values for P and M , it is time consuming. Another element of the F-K method is the need to know the heat transfer characteristics of the oven. It is desirable to use a convective oven with good circulation to produce high velocities around the sample to give high convective heat transfer. The radiation exchange between the basket and the walls of the oven must also be determined. All of this is needed to establish the Biot number for the oven operating condition. In addition, the Biot number needs the thermal conductivity for the material as well, and this task is not trivial, and is usually estimated. However, for the heat transfer characteristics of the stainless steel oven used in this study, Tamborello [2] established the convective heat transfer coefficient as a function of oven velocity and basket size. He developed a technique for measuring the overall convective-radiative heat transfer coefficient. It used a transient method with the

basket in the oven serving as a calorimeter. The rate of temperature rise of the basket after suddenly being immerse in the oven allowed the determination of the heat transfer coefficient. This will discussed in more detail.

Crossing Point Method

Using the same process as the F-K oven method, a short cut can be taken to obtain data for the property evaluation by doing essentially several oven temperature levels for one basket size. This method was first explored by Jones et al [9] and Chen et al [10]. The method requires the determination of the point at which the core temperature equals (crosses) the oven temperature [9] or the sample surface temperature [10]. At this point it is assumed that there is no heat transfer between the sample and the oven. This is an approximation. While the surface temperature criterion is better, its measurement is troublesome. The oven crossing point is easier to use and Warden pursued data for linseed oil and cotton by that means.

The theory upon which the method is based considers, at the crossing point, that the sample has a uniform temperature equal to that of the core. The governing equation is $\rho c \frac{dT}{dt} = Q \rho A e^{-E/RT}$. This equation can be rearranged to introduce M

and the thermal diffusivity, a , directly: $\ln\left(\frac{dT_o}{dt}\right) = \left[M + \ln\left(\frac{a}{P}\right) \right] - \frac{P}{T_o}$. By determining

the slope of the core temperature rise at the time when the core temperature equals the oven temperature, data can be assembled for a given basket size at different oven temperatures. Then these data can be plotted according to the previous equation against $1/T_o$. The results give M and P , provided the thermal diffusivity of the material can be estimated. Warden [1] illustrates this method and gives first time results for linseed oil with cotton cloth over a range of oil loadings. The table below gives a portion of his results. The results form the ingredients of P and M , as he was able to probe more deeply by his analysis. This is discussed further.

Results for Linseed Oil and Cotton

Basket Size and Concentration	E (kJ/mol)	QA (W/kg)	λ (W/m-K)	a (m ² /s)
10cm - 80%	11.73	3.59E+05	0.130	2.25E-07
7.5cm - 77%	15.76	2.63E+06	0.127	2.38E-07
5cm - 75%	16.97	5.30E+06	0.125	2.28E-07
5cm - 50%	27.40	2.27E+08	0.104	5.22E-07
5cm - 33.3%	42.37	2.60E+10	0.089	6.33E-07
Gross and Robertson 16.6%	88	4.7E+13	0.046	1.06E-07

Tabulation of Properties from the Literature

Tamburello [2] tabulates values for P and M as found in the literature. He lists nearly 40 entries. Many are the same generic material with variations in their P and M values. Thus data for generic materials are not definitive, and this indicates that testing is needed in each case. Nevertheless, the database does provide some quantitative guidance on the values measured for materials prone to spontaneous ignition.

Closing Remarks

This study sought to bring the science and test methodology for spontaneous ignition to the fire investigator. Three scenarios were illustrated for making calculations to establish whether spontaneous ignition is possible. An approximate formula was given to estimate the time to achieve spontaneous ignition. Two methods, using an oven and samples in cubical baskets were described. The crossing point method is the simplest and is recommended for a first consideration in obtaining property data. This method was used to determine the properties of linseed oil on cotton, and showed increasing tendency for spontaneous ignition with increasing concentration.

I. Introduction

Spontaneous ignition is a fire cause that can easily be missed by an investigator. It is likely the cause of many fires that have defied recognition due to its slow and nearly invisible origin. In the investigations of these cases, the phenomenon is difficult to determine due to the destruction of evidence from the fire and lack of information on the symptoms of spontaneous ignition. Spontaneous ignition is a complex process and many investigators may not fully understand the factors that promote it, and how to assess its likelihood. The theory of spontaneous is advanced, as it involves an understanding of higher mathematics and chemistry. It is not an easy subject to fully appreciate as a student of fire. It is likely more difficult for the average fire investigator. It occurs in solids, liquids, and gases. In the latter, it is more commonly known as “auto-ignition”, and standard tests exist. Such a test usually involves the heating of a flammable mixture of the gas with air in a spherical vessel. The result depends on the size of the vessel, with lower auto-ignition temperatures found for bigger vessels. A common source of auto-ignition of a flammable gas mixture is a hot surface. This process is distinctly different than the heating of the same gas in spherical vessel. Consequently the temperature of the hot surface to cause ignition of the gas mixture can be nearly double that measured in the spherical vessel test. This is indicative of the complex nature of spontaneous ignition, especially in quantitatively understanding heat transfer and reaction chemistry.

Most common to accidental flaming fire events is the involvement of solid configurations in spontaneous ignition. The solid-based fire is the focus of this work. It can occur in well-known media as cotton impregnated with linseed oil, moist haystacks, and least known as buried woody debris, and recycled plastic storage piles. The media must be porous to enable oxygen to infiltrate and cause oxidation, or decompose exothermically. Heat transfer, or the inability to cool a material initiates the process for an array undergoing oxidation or exothermic decomposition. The process starts as a chemical reaction that is not yet deemed combustion, and the consequence of ignition can be smoldering or flaming. The key variables are the size of the material and nature of the heat transfer, and the particular chemical and physical properties of the material. In fire investigation, it is important for the

investigator to recognize the signature of spontaneous ignition, to learn how to estimate if it were possible in the particular fire scenario, and to appreciate how to establish samples for measurements. In addition, it is importance for forensic laboratories to have the capability and understanding to utilize methods to achieve such properties.

1. Problem Addressed

The principal goal of this study was to review the subject of spontaneous ignition in solid arrays and provide a treatise on subject useful in fire investigation. The specific goals are listed below:

- Provide investigators with a scientific understanding of spontaneous ignition and its analysis, and
- Inform forensic laboratories on practical methods for measuring properties needed in analysis of spontaneous ignition.

As the subject is complex, a description of the science is needed in its simplest form. Still it is likely that an engineering knowledge is needed to fully grasp the analytical aspects of the subject. However, the key points should be accessible to the average investigator.

Much of the subject is not presented in a quantitative manner for the investigator, and the investigator can be at a loss for how to seek analysis. Also testing is empirical and some old standard methods only give suggestive answers. In the science of spontaneous ignition, methods exist and should be translated to forensic procedures for more quantitative analyses.

Data for such quantitative testing is dispersed throughout the literature, and a database on materials that have contributed to spontaneous ignition can be a useful reference to the investigator.

In short, the science of spontaneous ignition needs to be translated into fire investigation.

2. Literature

The specific literature reviewed and used in this subject is contained in two Master of Science theses. The first by Justin Warden [1] addressed the design and operation of an oven for testing samples in order to obtain quantitative data for analysis. This study illustrates how to establish the measurement procedure and how to operate with safety. Such testing involves the placement of cubical baskets containing the material under a controlled oven temperature. The measurement of the center temperature of the material in the basket indicates the exothermiscity of the material. A nonreactive material's temperature will just rise to approach the oven temperature; a reactive material will exceed the oven temperature. If it dramatically exceeds the oven temperature "ignition" is said to have occurred. Finding the lowest ("critical") temperature for a given material size and configuration to just cause ignition is a key measurement to begin to determine quantitative property data. Warden examined this method and a simpler alternative known as the crossing point measurement. His work specifically examined linseed oil on cotton cloth with varying degrees of oil by weight. He determined property data needed to predict the behavior of this oil cloth array in general. We will describe those results later.

The second thesis by Stephen Tamburello [2] addressed the theory of spontaneous ignition, the general methodology for determining properties by the critical temperature data, and compiled key property data for many materials. He also used a method to measure the heat transfer characteristics of the various size cubical baskets in the oven test. Knowledge of the heat transfer is a critical factor in using the critical oven test method, as previous investigators appear to have just estimated this factor.

The general theory of spontaneous ignition comes from Frank-Kamenetskii [3]. His theory addresses a balance between the energy production rate from the chemical reaction (oxidation or decomposition) and heat transfer. Data for the chemical reaction must come from experiments such as the oven test method. The procedure in analysis is to solve the steady problem with these balancing terms. The problem can be posed for many configurations, but the ones fully studied are three that we will review here: (1) a material in a warm environment, (2) a material on a hot

surface, and (3) a warm material suddenly exposed to a cool environment. The mathematics of these problems is complex, and they require special analytical approaches or numerical solutions. By the solution of the steady problem, a critical value for special parameter in the solution representing the size of the material and its thermochemical properties is found. At this critical value the solution no longer exists, and this implies that the solution is now unsteady and that the onset to ignition will occur. This critical parameter is known as the Damkohler number. Any value of the Damkohler number larger than its critical value means the material will go to spontaneous ignition. So the Frank-Kamenetskii (F-K) theory gives the bases for establishing the critical Damkohler number for a given configuration as indicated in 1-3 above. The critical temperature in the oven test occurs at the critical Damkohler number for the cubical basket. Consequently, oven test data with this theory form a basis for measuring the key needed properties of a particular material.

One of the most complete texts, if not the sole text, on spontaneous ignition, was written by Bowes [4]. This text is filled with mathematical analyses for many configurations, the considerations of variations from the simple F-K theory, and examples of tests and data for many materials. It is likely the definitive text in the field. However, it is difficult for the novice to negotiate the book, and hopefully our presentation herein will sharpen the focus for the reader. Another recent book by Babrauskas [5] on ignition in general contains similar material on spontaneous ignition as Bowes, and may be an easier read for the student. Babrauskas also compiled property data and information on many materials, as taken for the literature. We have mostly relied on Bowes and Babrauskas in assembling our data base information on material properties.

Two other sources of information on how to address spontaneous ignition can be found in different editions of the Society of Fire Protection Engineering Handbook. These authors, Beever [6] and Gray [7] have worked in the field and provided a good outline of the subject.

A recent study by Kamiya et al [8] examined the case of spontaneous ignition in plastic waste sites. This study examined a novel warning device to alert people at the waste site on the possible onset of spontaneous ignition. It should be emphasized

that before the event of ignition, the material is still chemically reacting and producing energy. While the chemical process is generally oxidative, it is not combustion in the sense of that chemical process that follows ignition. This pre-combustion process is generally denoted as “self-heating”. While the self-heating process is proceeding before ignition, although low in chemical activity, it can produce telltale signs. The chemical by-products of self-heating usually produce odorous gases. Indeed, in this recent study of plastic waste [8], the scientists developed an odor sensor could warn of the possible onset of spontaneous ignition in the storage areas. Odor is not uncommon as a precursor to spontaneous ignition.

While the oven test method based on the F-K theory and a determination of the critical temperature is most common, it is tedious involving many runs. Studies by Jones [9] and Chen [10] have examined a shortcut. Warden applied this shortcut approach to the study of linseed oil and cotton. The method merely involves analysis of the point where the oven cubical basket center temperature crosses the fixed oven temperature. It is known as the “crossing point” method. Its application to the linseed oil and cotton study will be described in detail later.

3. Rationale for Research

The approach in addressing this issue of translating the science of spontaneous ignition to the investigator involved several steps. Firstly the process of spontaneous ignition of solid arrays is described in qualitative terms. This should give the investigator the essence of the phenomenon and a sensitivity to its prospect for a given fire scenario.

Secondly, we try to relate the math and science of establishing the basis for assessing the possibility of spontaneous ignition, and the time that it might take to occur. This is not an easy task as it involves formulas and graphs that might not suit the non-engineer investigator. We have attempted to make its presentation as simple as possible, but it is still in engineering terms.

Thirdly, we present the classic oven method, and the short-cut method of Jones [9]. This should be a guide for forensic laboratories to pursue this approach in the analysis of materials suspected of spontaneous ignition. Data derived from such tested can allow the investigator to make a calculation for the real fire scenario, and

establish a quantitative basis for a determination. Such extrapolation for test data provides information but it is approximate and subject to challenge. However, it is the only way to make a scientific determination. It provides key input over the circumstantial evidence of the scenario.

Then we describe results we found for the varying mass loading of linseed oil on cotton cloth. This material is one of the most profound sources of spontaneous ignition, and no other presentation has examined the range of loadings before.

Finally, we list properties needed for spontaneous ignition as compiled from the literature, and put into a unified format.

II. Methods Used

A survey of members of the International Association of Arson Investigators was made to ascertain their experience with respect to spontaneous ignition causation of fires. They were asked to list their experience with spontaneous ignition and the materials involved. Responses were received from 200.

The mathematical results presented here was digested from the literature and then put into the simplest form possible for translation to the investigative field.

The oven test method was designed based on principals laid out in Bowes [4], and developed by Warden [1] in our laboratory. A special technique was developed to measure the heat transfer characteristics of the oven baskets by Tamburello [2]. A description of these apparatuses and processes are described fully in [1,2]. However, they will be summarized here.

1. Development of the Oven Test

The oven used for testing was a Memmert UFE500 115V Forced Air Controlled Convection (Fig. 1). The dimensions of the inside of the oven were 56cm wide by 48cm tall by 40cm deep with an approximately 15cm diameter fan on the back wall, shown in Figure 2. The temperature of the oven was accurate to $\pm 5^{\circ}\text{C}$ and during all of the tests the fan speed was set to the highest setting to assure forced convection.



Figure 1: The Memmert UFE500 Forced Controlled Convection Oven

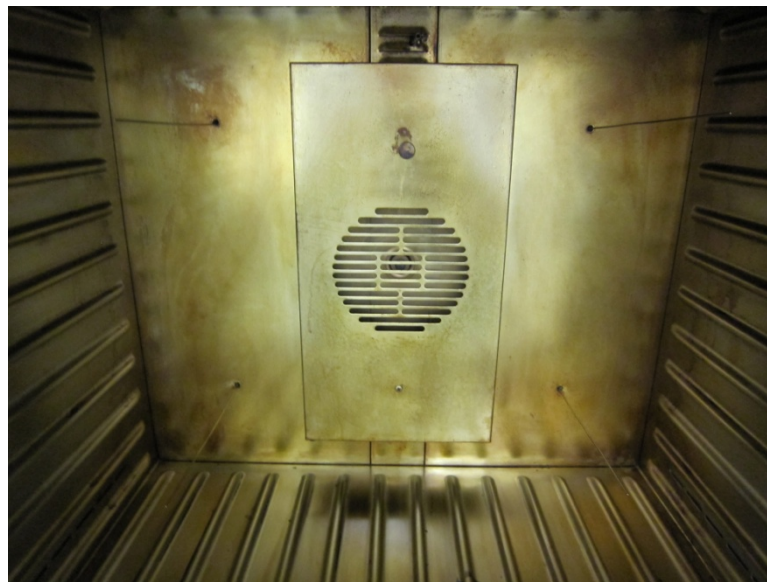


Figure 2: Inside of Oven Showing Thermocouple Placement

Four ungrounded 1/16" diameter stainless steel sheath type K thermocouples were installed in each of the four corners of the oven. Each thermocouple was positioned 4" from the left or right nearest wall and 4" from either the top or the bottom walls of the oven. They extended into the oven 8" from the back wall that left the tip of the thermocouples at the center of the oven depth shown in Figure 2. They give a

measure of the uniformity of temperature in the oven. With the high fan setting this uniformity was good.

There was also a hanging rod installed above the fan that gave each sample a place to hang during its test, shown in Figure 3.



Figure 3: Hanging Rod Installed Above Fan in Oven

The oven test subjects materials to heating in the form of a cube. The cube must be contained in a porous cubical basket to facilitate the containment. The baskets were made from 60-mesh stainless steel having 0.25mm diameter holes. The porosity of the basket is essential because air is needed to be able to freely flow into the material array. In our case layers of cotton cloth cut into squares were placed into the basket. In general any media could fill the basket. Problematic materials are those that melt. In small baskets the critical oven temperature at ignition is higher than for larger arrays, so the material is likely to melt on the exterior of the cube. For such materials, this melting that destroys the integrity of the cube shape might be avoided by using larger baskets. A range of basket sizes is necessary for general oven testing because each basket size provides a data point. These data when processes require the determination of a slope from a plot and therefore at least three points or

basket sizes are needed, preferably more. We made five basket sizes: 2.5, 5, 7.5, 10 and 15 cm sides. These baskets all had tiny holes near the top where a small metal hanging wire could be inserted and secured so the baskets could hang centered in the oven.

For the standard F-K oven test method, as well as the crossing-point method, along with the oven temperature, the center temperature of the cube is needed, and usually the surface temperature of the basket is measured. Figure 4 shows the basket configuration with linseed oil saturated cotton cloth sheets. Figure 5 shows the placement of the thermocouples within and on the basket, showing two surface thermocouples.

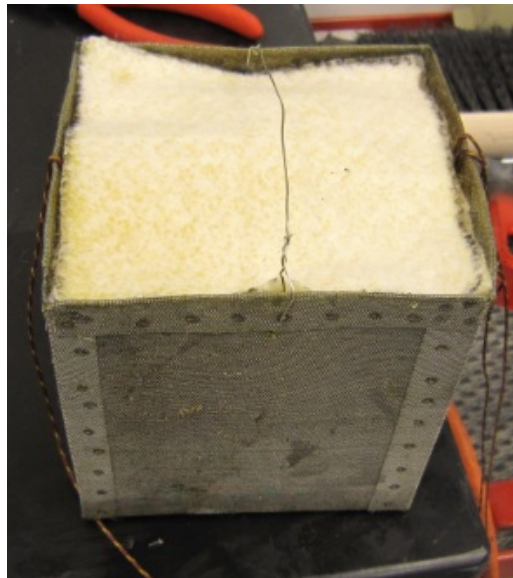


Figure 4: Prepared Sample Ready to be placed in Oven

The material used in our testing was 100% cotton batting cloth impregnated with linseed oil. Klean-Strip Boiled Linseed Oil was used. Linseed oil was applied to the specified amount of squares by one out of two different methods. Our goal was to maintain uniformity of the oil concentration over the cloth.



Figure 5: Thermocouple Placement In the Center and On the Surface of the Sample

The first method of linseed oil application was used for high weight concentrations; namely, the 5cm (75% concentration), 7.5cm (77% concentration) and 10cm (80% concentration) tests. This method used of a pan of linseed oil into which the cloth squares were laid flat and totally saturated. The squares were then wrung out one by one with a roller assembly, and weighed afterwards to confirm a consistent concentration. The second method of application for lower concentrations of oil used sprayer that would evenly apply the linseed oil onto the squares one by one. This method was used for the 5cm (50% concentration) and 5cm (33.3% concentration) tests. Again, each square was weighed to assure the correct linseed oil to cotton concentration was met. Finally, for both methods of application, the entire cubical stack of saturated cloth squares was weighed one last time to double check the concentration. While these methods were tedious, they insured uniform concentrations and consistency throughout the testing.

During testing, the temperatures were recorded continuously using a Fluke 2645A NetDAQ system connected to a computer through an Ethernet cable. Also a safe automatic shutdown system was designed and implemented into the testing procedure. While explosion during such testing is unknown to us and not reported in

the literature, there is a hazardous potential when self-heating during the oven test produces enough vapor to form a flammable mixture. With the onset of ignition, these gases could ignite and cause an over-pressure within the oven. The safety shutdown was designed to shut off the oven, and stop the oxidation process by the sudden purging of the oven with nitrogen. A prescribed center temperature set point of the sample controlled the activation of the shutdown and purge. This system is described more fully by Warden [1].

Other safety issues to consider is the removal of the oven gases generated during self-heating from the laboratory. Therefore the oven must be located under an effective exhaust hood. Another is the disposal of the samples tested. As they can lead to spontaneous ignition, they must not be collected in large arrays that foster such ignition. We disposed of the linseed oil cotton samples into a metal garbage can with a metal lid was filled half way full of water. This disposal also applied to many rags, towels, gloves etc. used to help contain and clean the linseed oil from the lab area.

It must be realized that this type of F-K oven testing seeking the critical temperature for ignition can take hours to facilitate. So for much of the time the testing may not be monitored by a person. The safety considerations considered here become more important under such circumstances.

2. Measuring Basket Heat Transfer

The F-K method of testing requires one to know the heat transfer characteristics of the basket in the oven. This is essential in deriving the critical Damkohler number from the theory, as it depends on knowledge of the heat transfer coefficient. A high heat transfer coefficient is desirable, and that is facilitated by a high fan speed in the oven. We developed a method for measuring the heat transfer coefficient for our baskets and oven that can be used by others. Tamburello [2] describes the full details of the method. Here we summarize the method.

The basket is suddenly immersed in a hot oven, and its temperature over time is recorded. The inside of the basket is filled with low density insulation to maintain

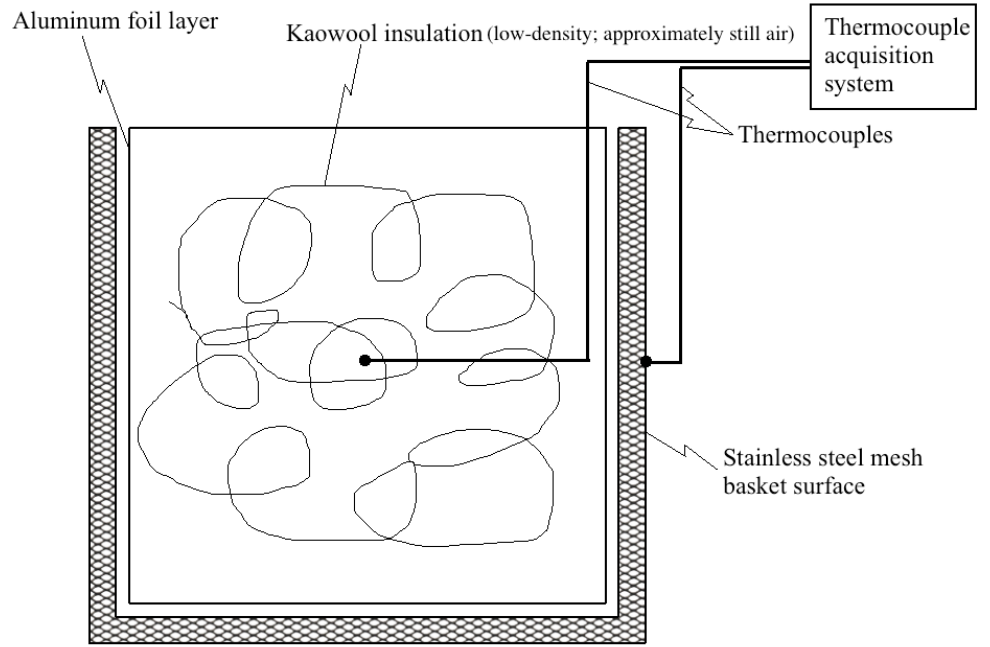


Figure 6. Basket Configuration for Measuring the Heat Transfer Coefficient

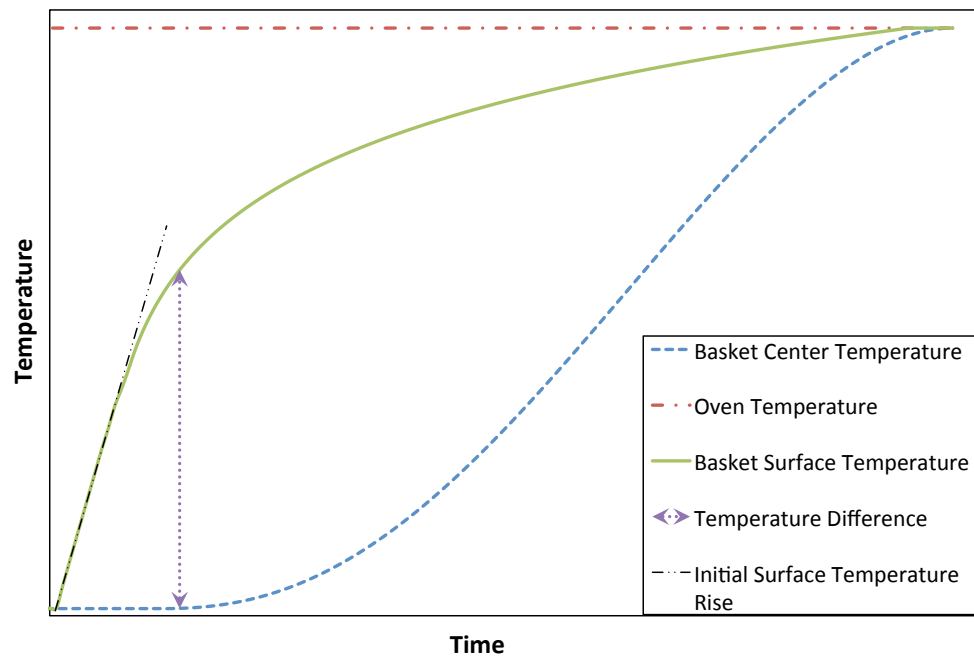


Figure 7: A depiction of the basket surface, basket center, and oven temperatures

still air, and the basket is lined with thin aluminum foil to prevent air being forced through the pores of the basket. These steps insure that the external overall heat transfer coefficient is being measured. The test configuration is shown in Figure 6. The surface temperature of the basket rises sharply after immersion. Its rate of rise gives the value of the overall heat transfer coefficient. The process is depicted in Figure 7 in which the rate of rise is taken at the time of immersion.

The equation giving the heat transfer coefficient is

$$h = \frac{mc}{S} \frac{\left(\frac{dT}{dt}\right)}{(T_A - T_i)} \quad (1)$$

T_A is the oven temperature, T_i is the initial temperature, $\frac{dT}{dt}$ is the rate of temperature rise of the basket surface, mc is the total heat capacity of the aluminum foil and the stainless steel basket, and S is the exterior stainless steel surface area. This method gave good results.

This overall heat transfer coefficient is needed in the F-K analysis. It should be realized that the overall heat transfer coefficient is the sum of both convection and radiation. Both of these can be estimated by theory, and that would provide an alternative to the result given in Eq. (1). The radiative heat transfer coefficient can be expressed as

$$h_{rad} = \frac{\sigma(T_S^2 + T_A^2)(T_S + T_A)}{\frac{1 - \epsilon_S}{\epsilon_S} + F_{12} + \left(\frac{1 - \epsilon_O}{\epsilon_O}\right)\left(\frac{A_{basket}}{A_{oven}}\right)} \quad (2)$$

where σ is the Stefan-Boltzmann constant ($5.67 \times 10^{-8} \text{ W / m}^2 \text{ K}$), ϵ_S is the emissivity of the basket surface, ϵ_O is the emissivity of the oven surface, F_{12} is the view factor (1.0 for parallel plates, as applicable here), and A_{oven} is the internal surface area of the oven. Several tests were run using the procedure based on Eq. (1) with aluminum foil covering the external surface of the basket and the internal surfaces of the oven. This foil emissivity is very low (about 0.04) so that the contribution would be very

small by radiation according to Eq. (2). In this case the results of Eq. (1) yields nearly the pure convection coefficient. Tamburello [2] applied these techniques in order to full characterize the oven heat transfer, and therefore separate out the convective and radiative components. He also used theoretical analyses to show its accuracy to the experimental results. This process laid out a technique out to fully characterize the oven heat transfer. Its results will be described in the next section.

III. Results

This section contains the results of this study. We begin by response from investigators, and then proceed to the substance of the two theses [1, 2]. The theses will be appended to this report and more detail can be found therein. However, this report contains the full scope and principal elements of that work.

1. Survey Results

The majority of the survey revealed that most of the incidents believed to have been caused by spontaneous ignition involved linseed oil infused materials, wet hay storage and problems with clothing just taken from a dryer. Other incidents involved potting soil, mulch and a variety of other materials. No statistical analysis of the data were done. In one case, a dwelling filled with garbage to knee-high exhibited the signs of the beginnings of spontaneous ignition, as charring was found in a portion of the garbage.

The survey and lack of complete data in the literature on linseed oil saturated materials led to our choice of that as a test material. The cases considered for analysis include the situation of a hot material, such as the clothing from a dryer, as one scenario.

2. A Qualitative Scientific Description of Spontaneous Ignition

A chemical reaction that releases energy is termed exothermic. Any substance that possesses exothermicity by itself or in the presence of air is prone to an unstable condition in which its internal temperature can increase significantly. The substance

can be a solid, liquid or gas. The chemical reaction can be a decomposition of the substance, or an oxidation due to, for example, the presence of air. For example, the decomposition of the propellant ammonium perchlorate ($\text{NH}_4 \text{ClO}_4$) is exothermic. A sufficient temperature increase can cause an accelerating reaction front propagating through the material. Gaseous products can be trapped causing large pressure increase or fissures in the material. The reaction front can travel at less than the speed of sound in the material (deflagration) or greater than sonic speed (detonation); explosive materials fall into this category of exothermically decomposing solids. Wood is even known to have an exothermic decomposition reaction at high temperature. Wood fiberboard is known to have exothermicity. In the testing by the F-K method, the mechanism of the particular chemical reaction is not revealed. Only will its attributes be determined. So whether the exothermicity comes from decomposition, oxidation or both is not apparent without more detailed chemical probing.

Porous solids in air can oxidize exothermically throughout, and combustion gasses mixed with air can do the same. For the porous solid, the reaction may lead to a high enough temperature to initiate smoldering. The diffusion or buoyant flow through the porous solid can supply the oxygen to sustain the smoldering. Vertical flow channels might develop and pressure effects might influence the flow pattern. Such effects are not considered in the theoretical analyses to follow. Eventually such airflow patterns may cause the smoldering to make a transition to flaming. This gas phase combustion of the incomplete product gases or fuel gases from decomposition of the solid itself is the basis of flaming.

In general, the term spontaneous ignition here can apply to the initiation of smoldering or flaming. Both will lead to sudden increases in temperature in the tests. This “ignition” is also referred to in the literature as “Thermal runaway” or “Thermal explosion” as fire or explosion may occur depending upon the substance and the reaction.

An example of the smoldering and flaming processes involved in spontaneous ignition can be illustrated by tests with cotton and linseed oil (Figure 2), here in a cubical basket. Worden [1] vividly shows the consequences of ignition of this

combination exposed to a slightly elevated temperature in an oven. Figure 8 shows the results of heating at an oven temperature of 48 °C. The curve labeled ignition, smoldering and flaming is the center temperature of the cotton

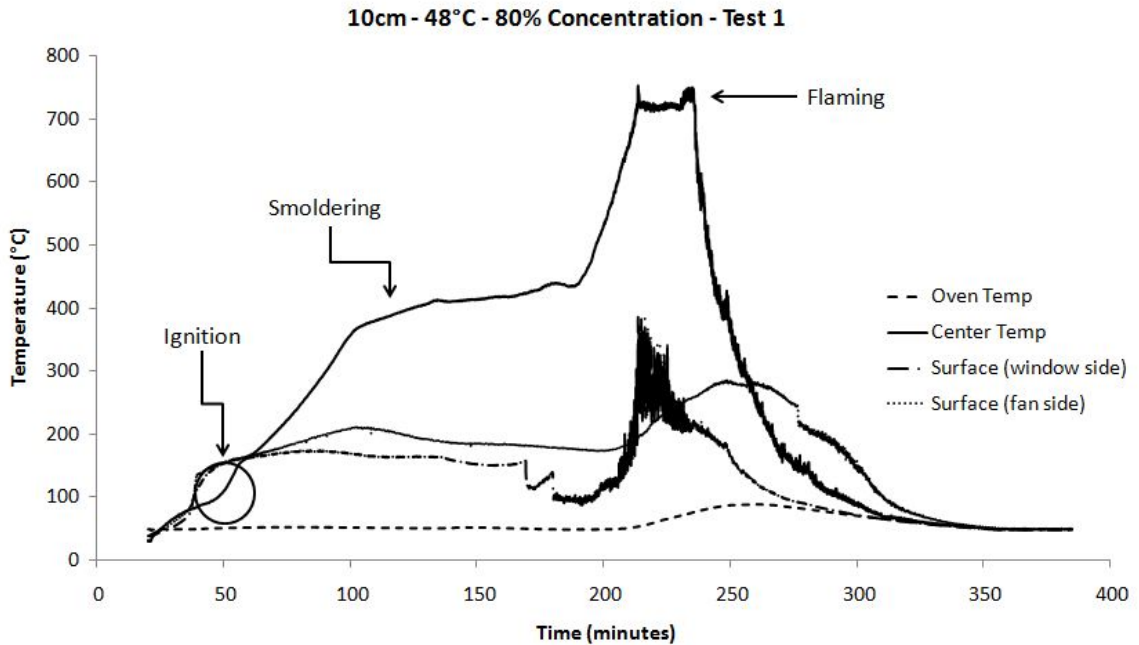


Figure 8. The Three States of a Typical Test: ignition, smoldering and flaming

with linseed oil. That curve shows three states of the process. First, at about 50 minutes (at the circle), the center temperature starts to rapidly climb where it crosses the temperature of the cube surface, already experiencing exothermic behavior, as it began to exceed the oven temperature at about 25 minutes. This sudden and rise of the core temperature marks ignition to smoldering where it is maintained at about 100 minutes to nearly 200 minutes at around 425 ° C. This period is characterized as steady smoldering. Figure 9 is a photograph of this smoldering process for another heating case in which flaming did not occur. Clearly, the self-heating process is greatest at the center of the material. This is a signature of that process and marks the potential to ignition. Hence, in any fire investigation in which material is thermally damaged in its core, spontaneous ignition is a lurking possibility. In such a fire scene,

some material may have gone to ignition and trigger the fire, while other of the same material may not have made the transition to ignition.

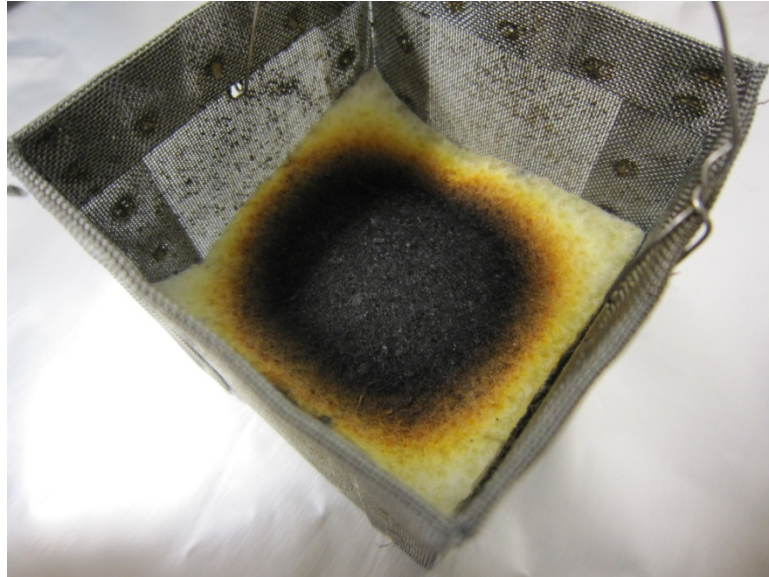


Figure 9. Charred core representative of smoldering or just self-heating

Let us continue to examine Figure 8. At about 190 minutes, there is another sharp rise in temperature to over 700 °C. This is an example of the transition of the smoldering process to flaming. It is most likely due to the continued oxidation of the char by the infiltration of air into the core. The occurrence of a void space allows for more air with increasing velocity that now promotes flaming. Figure 10 shows the void space that occurs. Thus, unless flaming occurs after spontaneous ignition, there will be no fire. With a fire the material will be consumed and the signature of spontaneous ignition lost. Only by understanding the circumstances of the fire scenario, or by having unconsumed similar material will the prospect of spontaneous ignition be apparent.

This process for the cotton with linseed oil is indicative of spontaneous ignition. In this case the oven temperature and the cube size were sufficient to cause ignition in about 50 minutes. The chemical reaction initially was at a low level reaction and not deemed combustion. But eventually, the core temperature increased and promoted a faster chemical reaction. At about 50 minutes ignition occurred that drove the reaction even faster and this culminated in fully developed sustained

smoldering. The chemical reaction associated with smolder in now clearly combustion. However, this reaction is very incomplete in terms of its products of combustion. The later flaming state is more complete, and has a much higher energy output. As the center of the cubic has the largest distance through which to lose heat, it traps the chemical energy, and the core receives that highest chemical degradation. This internal damage is indictive of the process promoting spontaneous ignition.



Figure 10. Void space occurs and enhances flaming

Porous oxidizing or exothermically decomposing solids will be the substances considered from here. But it should be recognized that gases and liquids can undergo the same process, and the explanations given here for the porous solids also would apply. The principle theoretical basis of the analysis for spontaneous ignition is simple, but highly mathematical in its nature. Here, this full mathematical presentation will be avoided. The theory was put forth by Frank-Kamenetskii (F-K) in 1938 [3] and forms the basis for much of the analysis done and discussed here, as well as the measurement method for characterizing materials. In addition to the two MS theses referenced here, there are several excellent treatises that describe many aspects of the subject [4-7]. These and other literature have been investigated in the course of this study. The simple theory, while powerful in its ability to make practical predictions, does ignore many factors such as the diffusion of oxygen

through the porous material, moisture that can promote biological energy, and competing chemical reactions in mixtures such as cotton and linseed oil, as both oxidize.

Figure 11 represents a graphical description of the process. This depicts the core temperature, T_o , rise over the environment air temperature, T_A on the vertical axes and the air temperature alone on the horizontal axes. As the air temperature, or in a test the oven temperature, is increased the early oxidation process results in a slight increase of the core temperature. So for this material, in its particular geometric configuration, up to point I, there is only a slight possible temperature increase. For 0 to I, the curve represents the various steady state temperatures in which the reaction continues and the core is slightly elevated. This range of possibilities is termed subcritical, and represents what is commonly called “self-heating”. Nothing dramatic happens. Of course, in reality this process can never be steady because the chemical reaction will cause the material to be depleted, and then the reaction will stop. Here, this is considered to happen later. Now the nature of the chemical reaction and the ability of the material to lose heat make the self-heating process unstable. This instability occurs because the chemical reaction is a very sensitive function of temperature, and its rate increases sharply as the temperature increases. If the heat loss cannot keep up with the increase in chemical energy, the temperature will continue to rise. This feedback between an increase in the chemical reaction rate and the increase in temperature can lead to an instability and “thermal runaway” to a new state of equilibrium. This instability is indicated by the jump in the core temperature rise from I to S. S and the upper curve represents the smoldering process where the chemical reaction of self-heating has now moved to that of smoldering. This is a new chemical reaction that is now classed as combustion. Any environment air temperature greater than the critical value associated with state I is termed “supercritical”, and below is “subcritical”. The ability to determine the critical state at I is the first step to assessing the possibility of spontaneous ignition. This is the basis of mathematical theories applied to a particular configuration.

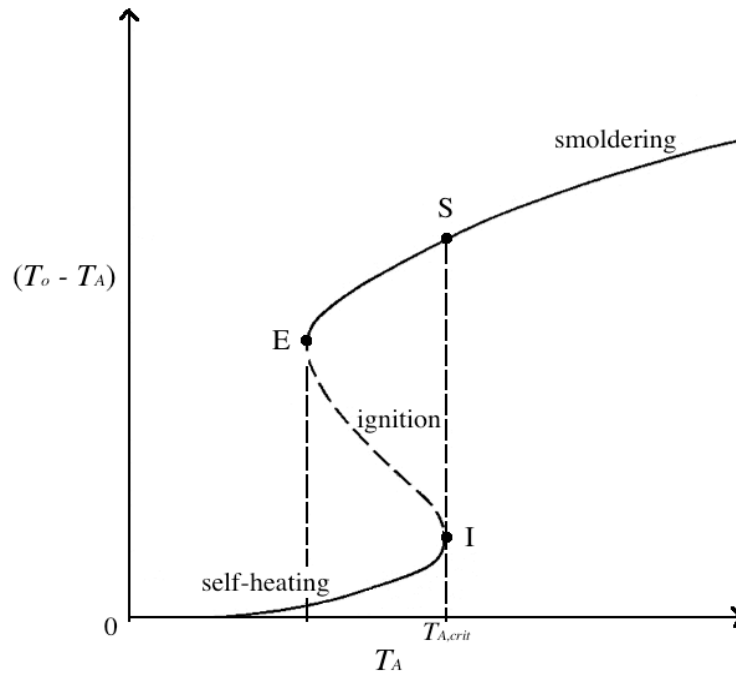


Figure 11. Graphical illustration of spontaneous ignition

Figure 12 shows actual data for a material in a hot air oven environment that is at first 165.2 °C, where the process is subcritical and the core temperature, T_m , increases to about 180 °C, then decays due to depletion of the material in the self-heating reaction. But with the air environmental temperature at 165.8 °C, the process is supercritical and the core temperature actually achieves flaming as it jumps to well over 700 °C. Here the process of the intermediate combustion state of smoldering is short lived apparently commencing at about 300 °C in the figure. The oven temperature to just cause the runaway process to ignition is the critical temperature. The critical temperature for this material and its configuration is between 165.2 and 165.8 °C. Notice that even in the subcritical state (165.2 °C), the core temperature exceeds the oven temperature. For an unreactive material, the core temperature would never exceed the oven temperature. Thus a characteristic of self-heating is an interior temperature in excess of its

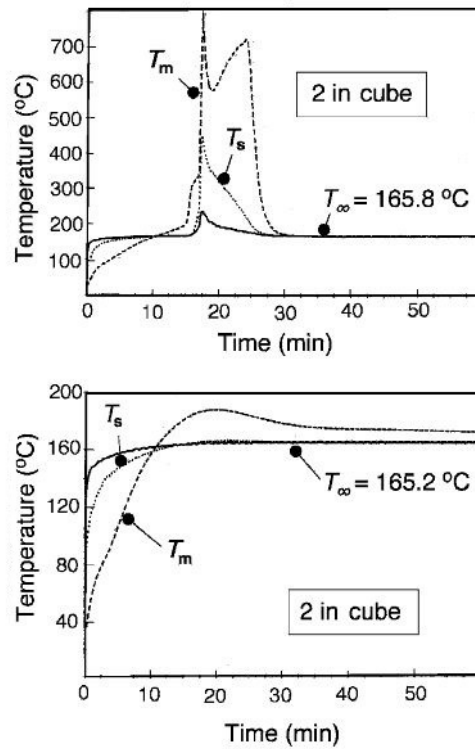


Figure 12. Sub- and supercritical conditions in spontaneous ignition

environment. Sometimes this can occur due to first heating from the environment, or from processes that leave the core warmer than the environment and unable to fully cool. The latter is the hot clothes removed from the dryer scenario.

While it is mathematically possible to predict the critical condition for spontaneous ignition, more information is needed to predict the time for spontaneous ignition to occur. For supercritical states, there will be a decreasing time for ignition as T_A increases away from its critical value in Figure 11. It should be noted that the time for ignition could range from seconds to weeks. While the self-heating process is proceeding before ignition, although low in chemical activity, it can produce telltale signs. Indeed, a recent study by Sugawa et al [8], demonstrated that an odor sensor could warn of the possible onset of spontaneous ignition in storage areas of recycled plastic waste. Odor is not uncommon as a precursor to spontaneous ignition, and should be considered as an element of useful information in an investigation.

Moreover, as the process of self-heating can last for hours and even days, odor is significant.

The mathematical basis for the prediction of spontaneous ignition is commonly the F-K theory that balances the chemical reaction energy of self-heating with the heat loss capability of the material. Most often the material is represented by a one-dimensional heat loss, a specific geometry, and specific configuration of heat transfer. The common configurations studied will be presented. The mathematical details will not be presented, only the principal equations and graphs needed to execute the process.

2. Analytical Theory to Predict Spontaneous Ignition

Much of the analyses can be found in Bowes [4] and we have drawn from that source for the results presented here. Those analyses can be described as mathematically intense and require some study to digest their essence. The following has been developed to cut through the density of Bowes and give the simplest presentation without sacrificing his results.

The F-K theory is based on one-dimensional heat conduction with a source term representing the energy of self-heating. The nature of the one-dimensional problem introduces a size dimension, e.g. thickness, diameter, etc. This dimension, particular to the problem, will be called r . In considering the theory for a given problem, the nature of r has to be precisely recognized. The next important variable is the temperature that is driving the initial heat transfer, and here it will be called T_R , a reference temperature. Again, the nature of this temperature must be strictly recognized. Both r and T_R will show up in formulas and their interpretation must be correct for a given problem.

Three problem formulations have been selected as they represent key fire scenarios in spontaneous ignition. They are listed as follows:

- A cold material in warm surroundings
- A cold material in contact with a hot surface
- A hot material exposed to a cold environment.

While these cases are not exclusive, they do represent many scenarios of interest. Other scenarios of interest, such as heating by radiation, would need to be developed or sought in the literature. However, for these three cases, the governing equations have been solved and the literature contains results that lend themselves to analysis to give an estimate of the conditions needed for spontaneous ignition. These problems only address the condition “if” spontaneous ignition is possible. They give a result that allows the determination of the critical temperature for a given size configuration. The critical temperature will be given in terms of the “reference temperature, T_R . This could be the temperature of the environment, the temperature of a hot surface adjacent to the material in question, or the temperature of the interior of the material following some processing.

The F-K theory leads to a dimensionless parameter that governs whether ignition is possible. This comes from the solution of the conduction equation with chemical heating. The dimensionless parameter is known as the Damkohler number, and is given the symbol, δ . (As notation is going to be continually introduced, the reader can refer to section VII of this report for a complete description of terminology. However, most of the terminology will be introduced when it is first used.) The Damkohler number represents the ratio of the chemical energy produced to the heat lost by conduction. Generally, if this number exceeds about 1, the condition is supercritical and ignition will occur. The value of δ at the critical condition is found from solving the mathematics for the varying scenarios. This is the value where as δ increases it reaches a value for the problem at which a steady solution is no longer possible. This is the jump condition in the general representation of the problem shown in Figure 11. For each of the three scenarios given above, specific values of the critical Damkohler number, δ_c , will be given. The value for δ depends on the size (r) of the material, heating (T_R), and chemical and physical properties of the material for F-K theory. The simplest way it can be represented is

$$\delta = \frac{r^2}{T_R^2} \exp\left(M - \frac{P}{T_R}\right) \quad (3)$$

where here M and P represent material properties. Specifically, $P = \frac{E}{R}$ having the units of temperature (K) and R as the universal gas constant [8.314×10^{-3} kJ/mol-K], and E known as the activation energy, in units of kJ/mol. The activation energy represents the energy needed to initiate the chemical reaction. The lower it is, the easier to initiate. Typically values of the activation energy for self-heating reactions range from about 60 to 140 kJ/mol. The parameter M represents a collection of physical and chemical properties in the form: $\exp(M) = \frac{E}{R} \frac{\rho A Q}{\lambda}$ where in this presentation it has units of (K/mm)². The other parameters include the density of the material (ρ), the heat of combustion (Q), the thermal conductivity (λ), and another chemical rate term (A) – known as the pre-exponential factor. While specialized apparatus may be capable for measuring each of these properties, it is common in the study of spontaneous ignition to determine just the P and M from direct measurements of the material. This is particularly needed since the material usually has the structure of a porous array, as a pile in layers or particles, with air filling the void spaces. Hence it is necessary to characterize the properties of the array, not the individual solid. A measurement process will be discussed later, but for now results for the three scenarios will be summarily presented. More details are found in references [1-7].

The analytical process is to identify the ideal scenario that best matches your problem of interest. Then, assuming P and M are known for your material, the Damkohler number can be determined for your size and heating condition. This means δ in Eq. (3) is calculated. Then it is necessary to consult the literature (or solve the governing equations) to determine the critical value δ_c for your scenario. If $\delta < \delta_c$, the problem is subcritical and ignition is not possible; but if $\delta > \delta_c$, the problem is supercritical and ignition is possible. The following three sub-sections will describe how the critical value can be determined for each of the three scenarios considered here. They all will depend on both conduction through the material and on heating from the material to the environment. This environmental heat transfer can be composed of both convection and radiation. It is the reason why attention

was given to establishing the heat transfer condition in the oven. The heat transfer coefficient must be computed for the specific scenario of interest. The heat transfer between the environment and the material is represented as another dimensionless group called the Biot number given by the symbol α . It represents the ratio of radiation/convection heat transfer to conduction. In the literature, and for a first approximation, α is often considered to be large (or infinite). It will show up in the following presentations on how to find δ_c . In other words, δ_c for a given problem will depend on α . The definition of α is

$$\alpha = \frac{hr}{\lambda} \tag{4}$$

The Biot number can be problematic as the thermal conductivity of the material must be known, and this is not accurately determined. Usually the effect of the Biot number is estimated.

Each of the three scenarios will be considered. Here they will be given for three geometries: a slab, a cylinder of infinite length, and a sphere. Results for other shapes can be found in the literature [1-7]. Generally, in an analysis of a particular scenario the shape that might best approximate the conditions of the scenario are used.

2.1 Material in a Warm Environment, δ_c

This scenario represents a pile of material in a particular shape and size exposed to an environment at temperature, T_R . Figure 13 displays δ_c results for a pile in the shape of a sphere, infinite cylinder, or slab. The results increase to an

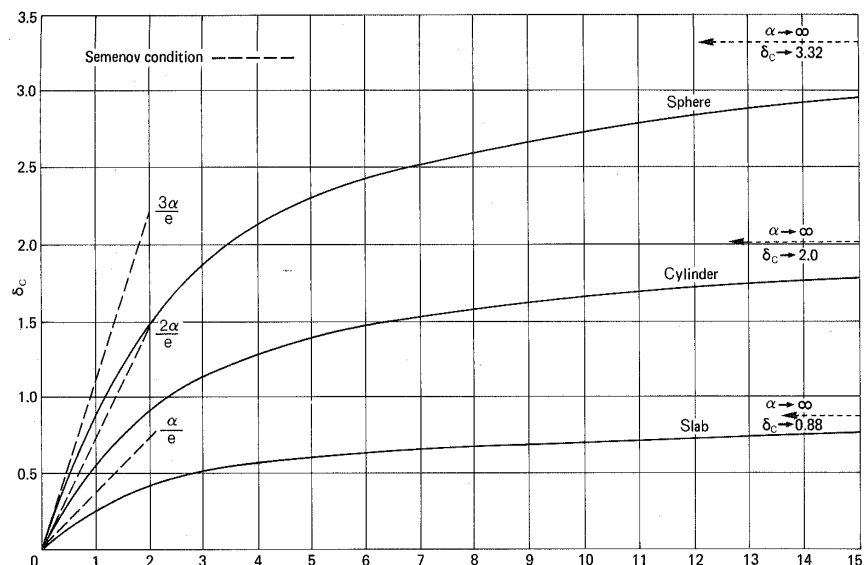


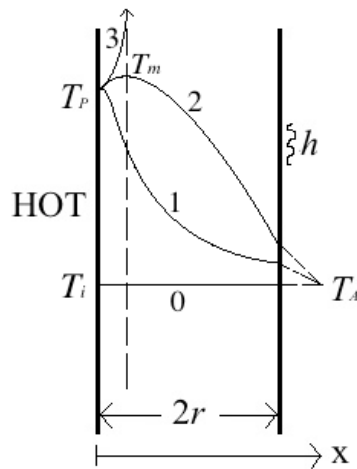
Figure 13. δ_c for a sphere (r as radius), infinite cylinder (r as radius), and slab (r as half-thickness)

asymptote as the Biot number (α) increases. The critical values are of order of magnitude one, with the slab most susceptible to ignition as it has the lowest value. Values for other shapes can be found in the literature, for example a cube for side $2r$ and α large has a value of 2.52. There are refinements in determining δ_c to account for depletion of material due to the chemical reaction and these might be pursued [2-7]. However, the accuracy of prediction is imperfect in extrapolating to real scenarios, and such refinements might be omitted. One can only hope for indications of the prospects for spontaneous ignition, not a perfect theory. Yet these techniques are powerful tools for the investigator because they give a quantitative result. For example, if conditions are in air at 35 °C and properties P and M are known for the material, the analysis might give a critical size from Eq. (3) as 10 m. If the size in the actual scenario was only 1 m, then ignition is certainly not possible; however, if the size were 50 m then ignition would clearly be predicted. Of course if the size were 12 m, then some refinement or lack of certainty in the prediction would be present. This is an indication of the value of the calculations. They offer a prediction, but the prediction may not have high accuracy as many factors may govern the real scenario, compared to the theoretical results.

2.2 Material on a Hot Surface, δ_c

Figure 14 displays the temperature distribution in a slab over time when its right side is subjected to a hot surface at temperature $T_p = T_R$, the reference temperature of Eq. (1). Curve 1 would result in a straight line if the material were inert (unreactive). For a reactive material, curve 2 shows the subcritical state, and curve 3 the critical state of “thermal runaway”. Here the slab characteristic dimension, r , is the half-thickness. Figure 15 displays the critical values of δ_c for this

case. The parameter $\theta_A \equiv \frac{P}{T_R} \left(\frac{T_A - T_R}{T_R} \right)$ is negative here as $T_R > T_A$. (Incidentally, the temperature in these formulas must be in absolute terms, K.) The tendency for ignition increases as the hot surface increases, and its difference with the surroundings is small. But a slab in a hot environment would be more susceptible.



- Curve 0: Initial State; $T_i = T_A$
- Curve 1: Unsteady heating
- Curve 2: Steady condition; $\delta < \delta_c$
- Curve 3: Thermal runaways; $\delta \geq \delta_c$

Figure 14. Temperature distribution in a material on a hot surface

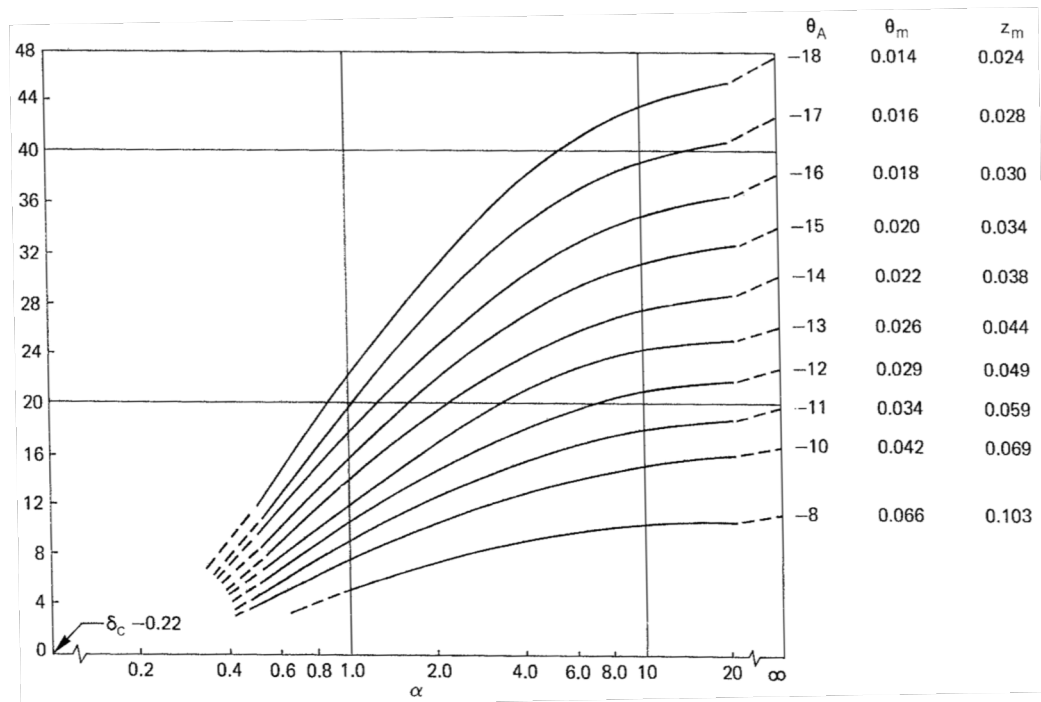


Figure 15. δ_c for a slab of thickness $2r$ on a hot surface at temperature T_R

2.3 Hot Material in a Cold Environment, δ_c

This case is depicted in Figure 16 in which a slab of half-thickness r is initially subjected to a uniform temperature T_i (taken as the reference temperature T_R of Eq. (1)), while the environmental temperature is T_A . This initial temperature could have been the result of processing or heating, e.g. clothes taken from a dryer. Figure 17 shows the behavior of a spherical shape of radius, r , in terms of the extent of initial heating given by $\theta_o \equiv \frac{P}{T_i} \left(\frac{T_A - T_i}{T_i} \right)$. The critical value of δ decreases as the initial temperature increases. Values for other shapes can be estimated for large Biot number by the following formula:

$$\delta_c(j) = M_j [\ln(2\theta_o)]^{N_j} \quad \text{when } \alpha \rightarrow \infty, \quad (5)$$

and Table 1 gives values of the constants M_j and N_j .

Table 1: M_j and N_j values for common shapes from Bowes [4]

Shape	M_j	N_j
Slab (j=0)	2.66	1.30
Cylinder (j=1)	7.39	0.83
Sphere (j=2)	12.10	0.60

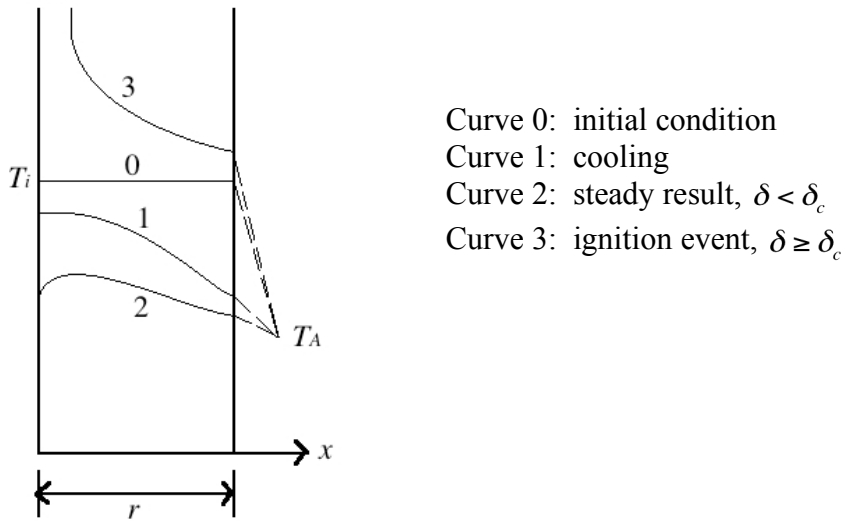


Figure 16. Temperature distribution of an initially hot material

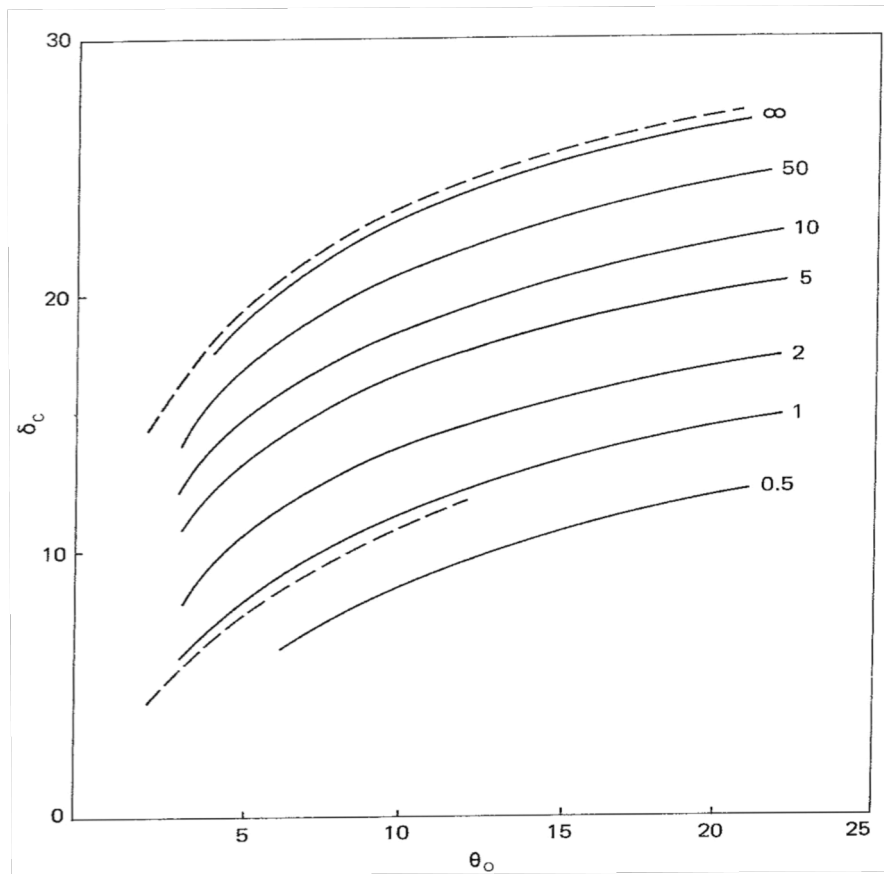


Figure 17. δ_c for a hot sphere in cold surroundings

2.4 Time to Ignition

Analytical methods only give approximate results for estimating the time to ignite when supercritical conditions prevail. A formula for estimation cited in the literature [3,4] is given as

$$t_{ig} \approx \left(\frac{r^2}{a} \right) \frac{C}{\delta \left(\frac{\delta}{\delta_c} - 1 \right)^{1/2}} \quad (6)$$

Here a is the symbol for thermal diffusivity ($k/\rho c$) which might range from 10^{-7} to 10^{-6} m²/s for typical porous materials. It should be noted here that the physical properties of the porous material usually at issue in spontaneous ignition must be determined for the array, and not just the solid component alone. This is the medium of the F-K theory. The value of C is given in the table below for various shapes.

Table 2. C-values in Eq. (6)

Shape	$\alpha \rightarrow 0$	$\alpha \rightarrow \infty$
Slab	1.63	1.53
Cylinder	1.63	1.43
Sphere	1.63	1.32

3. Measurements for Properties P and M

The previous section gave methods for determining δ_c , but properties for the material are need to complete this analysis. Obtaining the properties with sufficient accuracy to represent the material in the real spontaneous ignition evaluation is not trivial. In many cases, the sample tested in the laboratory may not exactly be the same as that in the field. Moreover, the need to preserve the character of the porous matrix representative of the material is a must. This is why tiny samples representing the solid may not be sufficient for testing. Such small scale testing might be accomplished by TGA/DSC devices, yet larger samples are preferred as they are

more representative of the actual scenario. Hence the usual method of choice is based on the F-K theory.

3.1 F-K Oven Method

The F-K test basis is oven testing with specific shape samples in a wire basket suspended in an oven. This test method corresponds to the first scenario discussed, i. e. a cold material in a hot environment. The oven temperature is set and the sample is inserted with the center temperature continuously monitored. Worden describes this test with safety considerations in some detail [1]. The test is repeated until the critical temperature is found for a given sample size, usually a cube. This determination was previously illustrated in Figure 11. It is a tedious process to find the critical condition for a given basket size that can take days to carry out. However once a minimum of three critical values have been found and analysis can be conducted to determine P and M .

Returning to Eq. (3), that equation can be rewritten as

$$\ln \left[\delta_c \left(\frac{T_R}{r} \right)^2 \right] = - \frac{P}{T_R} + M \quad (7)$$

Now the left-hand-side can be determined from the data for T_R and r , corresponding to the critical condition of the test. The value of δ_c for the test configuration can be found from the theory for the particular size and oven conditions, namely α . The Biot number must be known for the oven condition and a method and data to accomplish this is presented by Tamburello [2]. An example of this process is illustrated in Figure 18 by Tamburello [2] and taken from Beever [6] where milk powder was evaluated. The values found for P and M are respectively, 9497 K and 28.02. Note this is based on $\exp(M)$ having units of $(\text{K}/\text{mm})^2$. Here a minimum of three points were used to establish the slope and intercept needed in Eq. (7).

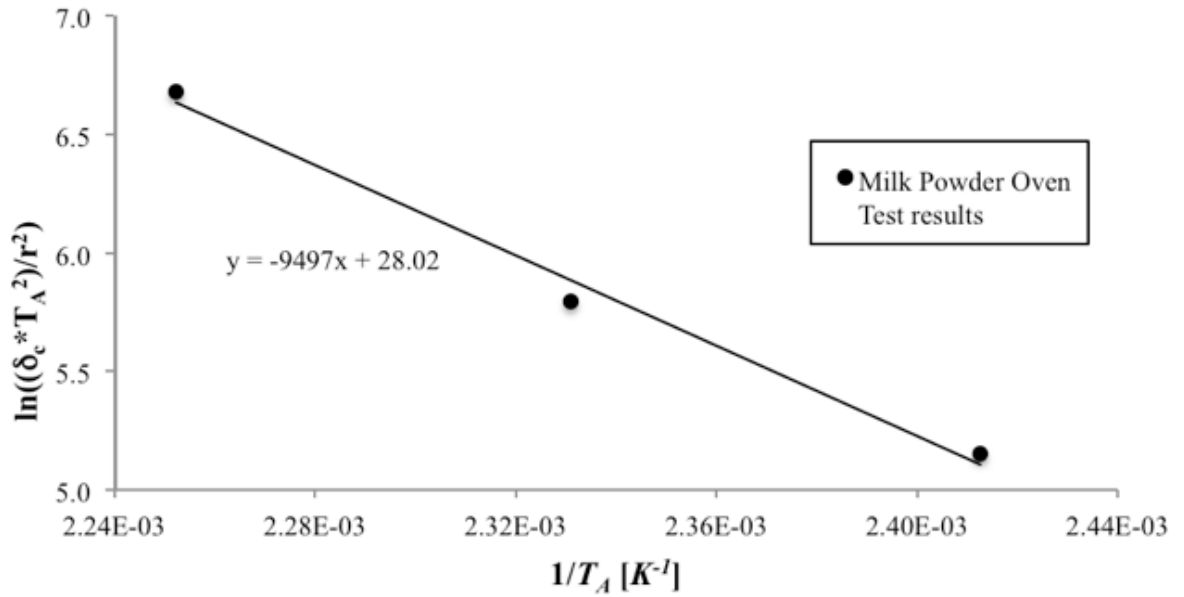


Figure 17. Critical conditions for milk powder using the F-K oven method

In this example the Biot number was taken as infinite. In an actual oven this must be accounted for in determining the critical Damkohler number. In the F-K theory assumptions are typically used, and other factors come into play involving corrections for low activation energy, and depletion of the material in the reaction. Tamburello [2] illustrates how this can generally be done, as prescribed by Bowes [4]. However these correction factors are usually of order 1, and for a first approximation they might be omitted. The Biot number effect is the most significant.

The F-K oven method is tedious, as it requires repeated tests to best establish the critical temperature. The point of ignition can also be problematic to recognize, as it is not always a sharp rise in temperature. So some judgement is needed. While this is the method of choice for establishing good values for P and M , it is time consuming. Another element of the F-K methods is the need to know the heat transfer characteristics of the oven. It is desirable to use a convective oven with good circulation to produce high velocities around the sample to give high convective heat transfer. The radiation exchange between the basket and the walls of the oven must also be determined. All of this is needed to establish the Biot number for the oven operating condition. In addition, the Biot number needs the thermal

conductivity for the material as well, and this task is not trivial, and is usually estimated. However, for the heat transfer characteristics of the stainless steel oven used in this study, Tamburello [2] established the convective heat transfer coefficient as a function of oven velocity and basket size.

3.2 Crossing Point Method

Using the same process as the F-K oven method, a short cut can be taken to obtain data for the property evaluation by doing essentially several oven temperature levels for one basket size. This method was first explored by Jones et al [9] and Chen et al [10]. The method requires the determination of the point at which the core temperature equals (crosses) the oven temperature [9] or the sample surface temperature [10]. At this point it is assumed that there is no heat transfer between the sample and the oven. This is an approximation. While the surface temperature criterion is better, its measurement is troublesome. The oven crossing point is easier. So here the crossing point method will apply to the point where the center core temperature of the sample in the basket first reaches the oven temperature.

The theory upon which the method is based considers, at the crossing point, that the sample has a uniform temperature equal to that of the core. Again this is an approximation. However, it greatly simplifies the analysis. Moreover for samples that easily go to ignition at low temperatures, and a critical temperature cannot practically be found for that size basket, without possibly cooling, it is the method to use. Indeed, we were forced to use this method for the linseed oil cotton samples. The governing equation at the crossing point, assuming uniform temperature in the sample, is

$$\rho c \frac{dT}{dt} = Q \rho A e^{-E/RT} \quad (8)$$

This equation can be rearranged to introduce M and the thermal diffusivity, a . Also taking the natural logarithm gives

$$\ln\left(\frac{dT_o}{dt}\right) = \left[M + \ln\left(\frac{a}{P}\right) \right] - \frac{P}{T_o} \quad (9)$$

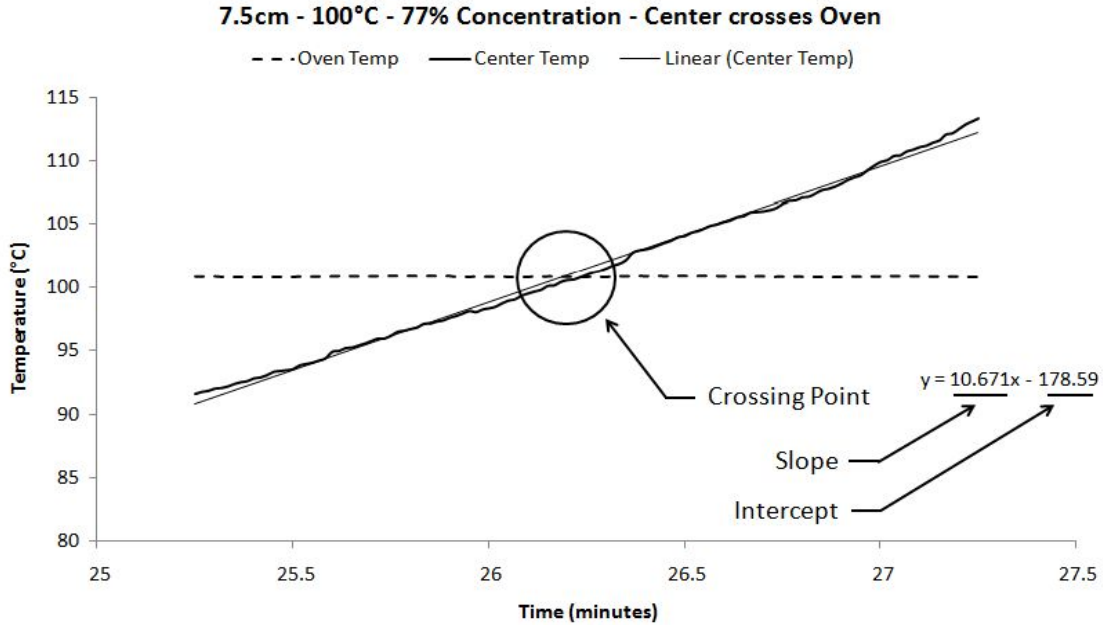


Figure 18. Illustration of the crossing point for cotton with 77 % linseed oil

Here T_o is the core temperature and is equal to the oven temperature at the crossing point. Figure 18 gives an illustration of the center temperature crossing the oven temperature (dashed line). The slope of the core temperature at the crossing point gives the time derivative on the left hand side of Eq. (9). Now if the process is repeated at several oven temperatures, the left-hand-side can be plotted against $1/T_o$ to give the slope (P) and the intercept $[M + \ln(a/P)]$. If a good estimate can be established for the thermal diffusivity (a) of the material, then both M and P can be determined. In any case P can always be determined.

The graph in Figure 19 illustrates data for various oven temperatures and basket sizes developed by Warden [1]. In principle according to the approximation of uniform temperature, there should be no effect of basket size, but an effect is present. The curves have similar slopes varying from 1.5 to 2.1, but differ more in their intercept. This effect is a measure of the accuracy for the method.

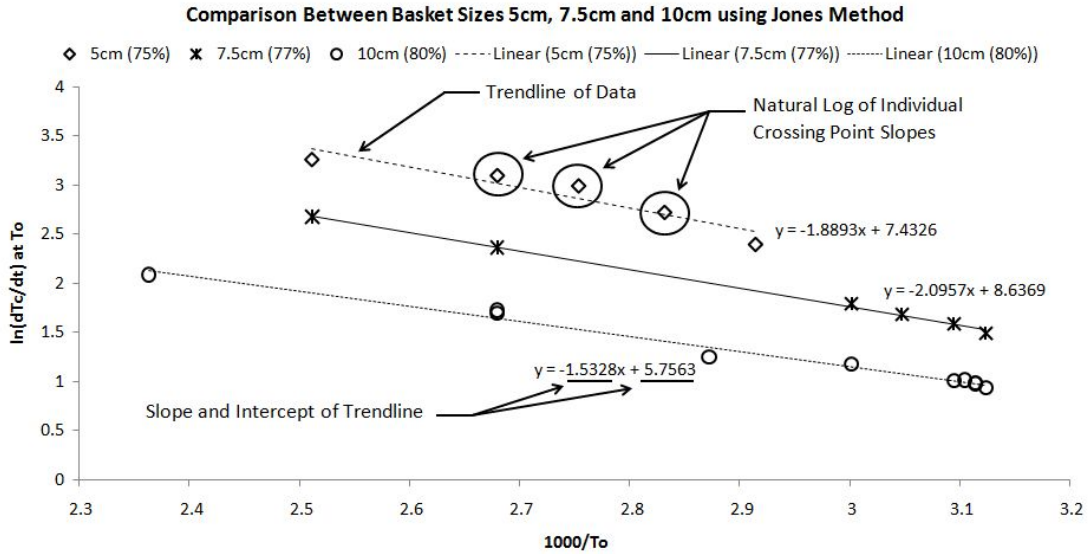


Figure 19. Obtaining properties from the crossing point method [1]

3.3 Heat Transfer Results for Our Oven

The heat transfer coefficient for the oven was measured for five basket sizes based on the side dimension ($2r$): 2.5, 5.0, 7.5, 10.0, and 15.0 cm. The air velocity at the center of the oven was found to be 1.6 m/s with the fan set to maximum speed. Equation (1) was used to compute the overall heat transfer coefficient from immersion tests of placing the basket in a still oven and with the maximum fan speed. These results will be reported primarily for the oven temperature set at 100 °C. The technique of lining the oven interior and the exterior of the baskets with aluminum foil, minimize the radiative heat transfer, and give a approximation to pure convection results. Results will be summarized here, and full details of the experimental method and analyses can be found in Tamburello [2]. Comparisons between the experimental results and theory show favorable agreement [2].

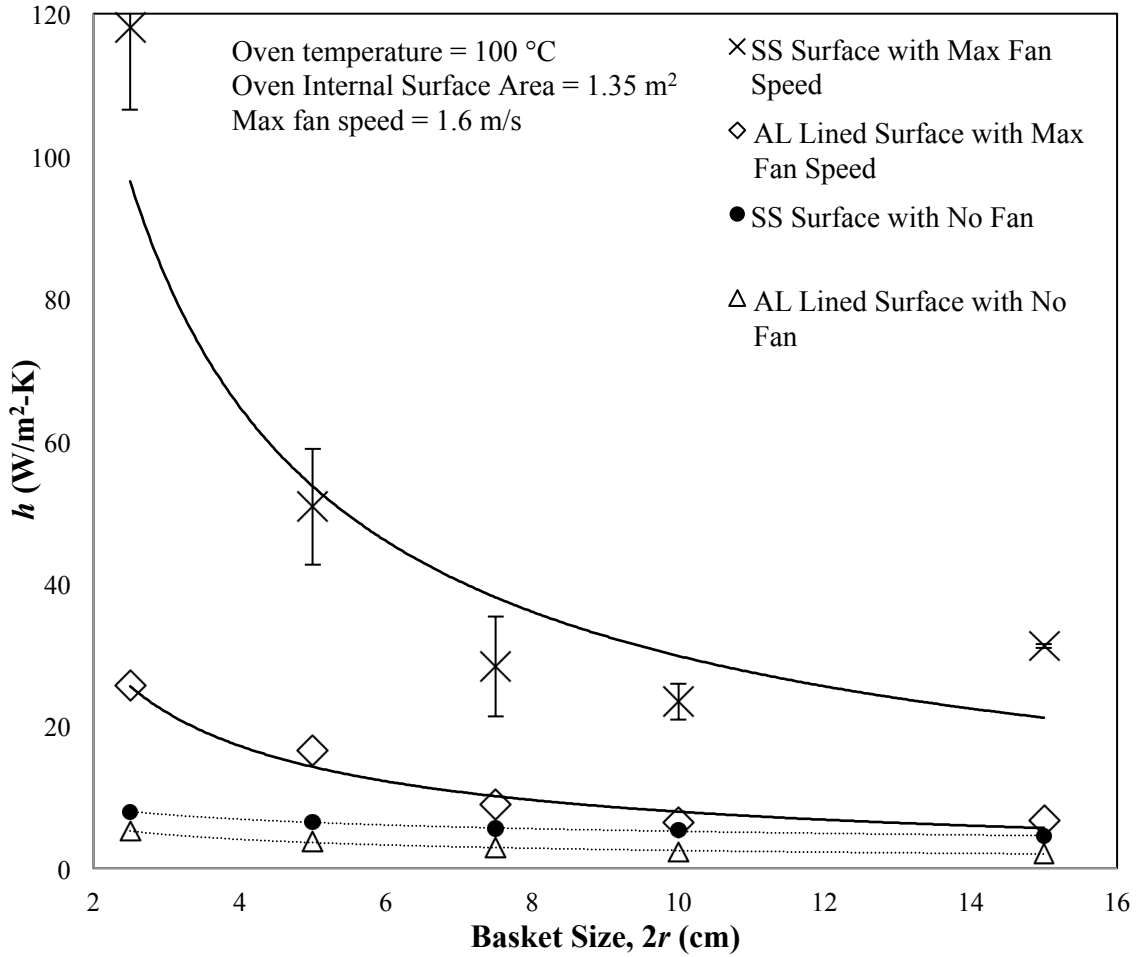


Figure 20: Experimental h values for each configuration and basket size

Figure 20 shows the results for the array of baskets with an oven temperature of 100 °C. The results without the aluminum linings are the values for the oven. The data with the aluminum lining only serve to indicate the effect of radiation on the process. The difference between the curves with and with aluminum is a measure of the radiation contribution to h . It is seen that the radiation is a significant factor in the oven heat transfer for both the natural convection still air case and the maximum fan setting in the oven with a nominal forced speed of 1.6 m/s. These results serve to provide a way to estimate the radiation characteristics of the oven. Tamburello [2] found that the emissivity of the stainless steel baskets and oven interior was approximately 0.36, not much different than values reported in the literature. It should be noted that this holds for our oven in a fairly clean state. Depositions of soot

and tarry product will make this value higher and change the characteristics of the oven.

The importance of knowing the oven heat transfer characteristics is to estimate the Biot number, as this is needed in order to establish the correct value for the critical Damkohler number. For example, if the oven is operating at a high fan condition and the conductivity of the material is 0.5 W/m-K, then for a 10 cm basket ($r = 5$ cm), $a = (23 \text{ W/m}^2\text{-K})(0.05 \text{ m}) / 0.5 \text{ W/m-K} = 2.3$. For the slab in Figure 13, this gives a critical Damkohler number of about 1.6. It is about half the asymptotic value of 3.32 for a infinite. So it is crucial to know the heat transfer characteristics of the oven to obtain accurate results.

A few additional tests were run to examine the effect of a different temperature between 100 and 200 °C. Figure 21 shows these data. The effect appears small, but Eq. (2) suggests that the radiative component will increase with temperature. A way to assess this is to use the theoretical equation (2) for radiation, and assume the results for the aluminum-lined cases in Figure 20 correspond to pure convection. In any case, this method requires results for the oven heat transfer to ultimately obtain accurate property data by the F-K method.

Power law empirical equations are offered to express the relationship between h and r in the range 100-200 °C. For basket sizes $2.5\text{cm} \leq 2r \leq 15\text{cm}$ with the oven operating at the maximum fan speed:

$$h_{tot} \approx 209.7(2r)^{-0.85}$$

and for pure free convection (no fan) heat transfer coefficient is given as

$$h_{tot} = 10.6(2r)^{-0.31}$$

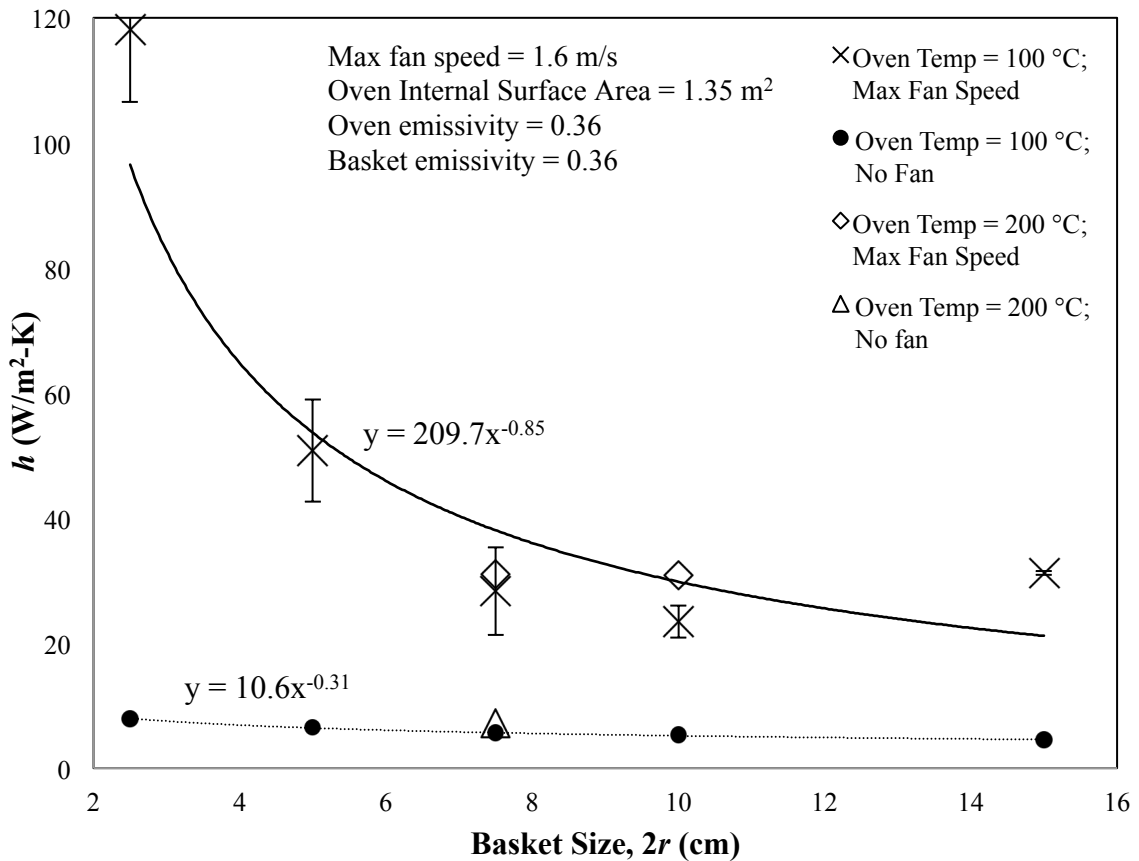


Figure 21: Effect of increasing the oven temperature from 100 °C to 200 °C on h

4. Example: Warehouse with Wood Fiberboard

This example was analyzed by Tamburello [2] in some detail after following Bowes [4] presentation of determining the properties of the fiberboard. The event stimulated work in the US and UK on spontaneous ignition.

On June 2nd, 1951, nine railcars of wood fiberboard were in transit from their manufacturer in the South, to upstate New York. While in the course of switching, only a few miles outside of their destination, one of the freight cars ignited and was left to burn. The remaining cars continued to the Army Warehouse in Voorheesville, NY, where they were unloaded into one pile exceeding 24,000 ft³. On June 17th, two

days after unloading, a fire broke out that destroyed the warehouse and its contents. Spontaneous ignition was determined to have caused the fire.

The F-K method was applied to determine the likelihood of spontaneous ignition as the cause. The description of the fire scenario is vague so many needed parameters have been estimated. The stacking configuration was not specified for the fire scenario, so a cubical shape was analyzed. Also, the investigators suspected that the fire was due to a hot material pile being introduced to a cold environment. This heating configuration as well as the scenario of a cold material in a hot environment will be compared.

Scenario 1. Cold pile in a hot environment. This case was analyzed in which the boards were assumed to initially cool, and the cool material pile was introduced into a hot environment. Summer temperatures inside the warehouse may have reached higher temperatures than the outside air due to lack of warehouse ventilation. For this case, the minimum warehouse temperature require to cause ignition was calculated. The properties of the fiberboard are listed below:

$$P = 12,145 \text{ K}$$

$$M = 34.550 \text{ (} e^M \text{ having units K}^2\text{/mm}^2\text{)}$$

$$\text{Volume} = 24,000 \text{ ft}^3$$

$$\lambda_s = 0.5 \text{ W/mK}$$

For a cube at the described volume, the height would be 28.8 ft and the half cube side dimension, $r = 14.4\text{ft} = 4396\text{mm}$. The convective heat transfer coefficient under natural convection was estimated as $2.4 \text{ W/m}^2\text{K}$. The radiative component was approximately $6.9 \text{ W/m}^2\text{K}$. This gave a Biot number of 818. So the critical Damkohler number for a cube in a hot environment is taken as the large Biot number value of 2.52. Using Eq. (3):

$$\delta = \frac{r^2}{T_R^2} \exp\left(M - \frac{P}{T_R}\right)$$

where T_R for this case is T_A [K]. Substituting for δ and r , with P and M for the fiberboard, gives the critical ambient temperature (CAT, T_A) $106 \text{ }^\circ\text{F}$. Then if the

temperature inside the Army Warehouse were in excess of 106 °F spontaneous ignition would have been likely. Weather history for Albany, NY, located within ten miles of Voorheesville, showed the maximum air temperature for June 16th and June 17th as 79 °F (297 K) on both dates. With the outside air reaching 79 °F, the warehouse would be hotter. But a temperature of 106 °F is likely a stretch. Possibly the material stack could have been larger than the estimated 24,000 ft³. We know spontaneous ignition was the likely cause as a similar fire occurred on one of the freight cars before arriving at the warehouse. Perhaps this is the best such calculations can offer. It is not a perfect answer, but it comes close. In any case, let us examine the second scenario assuming hot material had been loaded from the factory in the South, and that internal higher temperature promoted the process.

Scenario 2. Hot pile in a cold environment. The wood fiberboard may have been hot after being manufactured and stacked without cooling to a safe temperature. This temperature by processing information was approximately 208 °F according to an investigative report. With the addition of the hot temperatures in the South region, the boards may have been self-heating in transit to the Army warehouse. This case was analyzed with an initial material temperature (T_i) of 208 °F (369 K). The air temperature T_A was taken as 79 °F (297 K).

To analyze if spontaneous ignition occurred as a result of a hot material pile being introduced to a colder environment (Section 2.3), the dimensionless center temperature was calculated by $\theta_o = \left(\frac{P}{T_i}\right)\left(\frac{T_i - T_A}{T_i}\right)$ to give 6.4. From Figure 17, the critical Damkohler value of 14.5 is found from the graph. From Eq. (3), using $T_R = T_i$ or 208 °F (369 K), the actual Damkohler for the wood fiberboard stack is found 716. This gives $\delta/\delta_c = 49$ which is much higher than the critical ratio of 1. If the boards were at an initial temperature of 208 °F when stacked, ignition in the Army Warehouse for a cube shape pile size of 24,000 ft³ would be extremely likely. Moreover, if time to ignition is estimated from Eq. (6) for a slab configuration, the time to ignition is computed as 1.6 to 16 hours depending on the precise value of the thermal diffusivity for the stack. The fire broke out two days after unloading, or 48

hours. Again, this is the level of accuracy to be expected. The theory puts results into a range that is of the same order as reality. It predicts hours when indeed it took hours. This is as much as can be expected from this type of analysis. It is about the best that can be done.

5. Cotton and Linseed Oil Results

Worden did an extensive study of cotton soaked with linseed oil using the crossing point method [1]. The F-K oven method at modest temperatures above normal room conditions always gave ignition, so it was not possible to determine the critical temperature without lowering the oven temperature below ambient. He took care in these experiments to uniformly absorb the linseed oil into the cotton by using a roller press or a spray application. He examined concentrations by mass of linseed oil from about 33 to 80 %. His results blended well with other data in the literature at lower concentrations. Figure 22 shows his results for the activation energy and a comparison with other data from the literature. It should be noted that the other data were determined by different methods. The consistency of these data indicates the value of the relatively simple crossing point method.

Worden was able to determine M by estimating the thermal diffusivity of material, and he determined all of the underlying properties as well. He did this by considering the oil and cloth to form a homogenous mixture. He related literature values of cotton cloth and pure linseed oil to mixture values based on the mass fraction, Y_i . For example, the thermal conductivity was represented as

$$\lambda_{mix} = Y_{cotton}\lambda_{cotton} + Y_{linseed}\lambda_{linseed}. \quad (9)$$

Similarly the specific heat was determined. He used values for thermal conductivity for pure cotton cloth as 0.06 W/mK, and 0.147 W/mK (12) for linseed oil. And for the specific heats as 1300 J/kg-K for uncontaminated cotton and 1796 J/kg-K for the pure linseed oil. Table 3 shows his results for all of the properties as found by the weighted values, and by the slope and intercepts of his data by the crossing point method. It is noteworthy that his data, as well as those in the literature by Gross and Robertson and Khattab follow a trend indicating that the activation energy decreases with increasing mass fraction of linseed oil on the cotton. The

value of M also decreases with linseed oil loading, and blends well with the results of Gross and Robertson as shown in Figure 23.

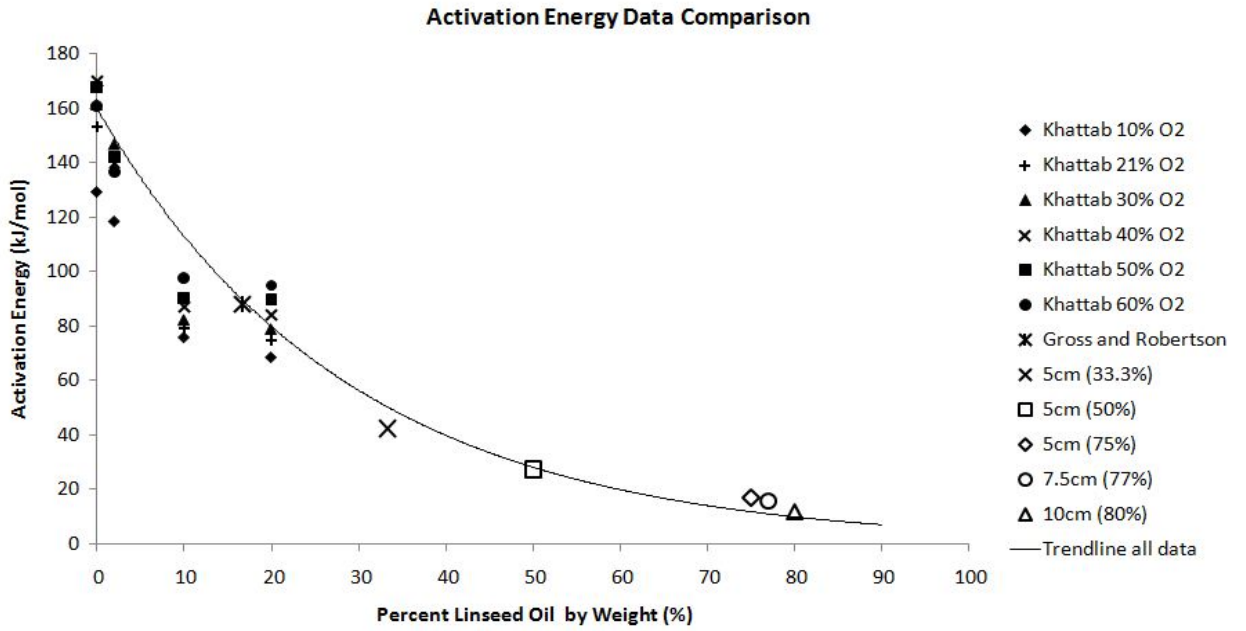


Figure 22. Activation energy of linseed oil on cotton cloth [1]

Table 3. Properties of Linseed oil at various concentrations on cotton cloth

Basket Size and Concentration	E (kJ/mol)	QA (W/kg)	λ (W/m-K)	ρ (kg/m ³)	c (J/kg-K)	a (m ² /s)
10cm - 80%	11.73	3.59E+05	0.130	339	1696.80	2.25E-07
7.5cm - 77%	15.76	2.63E+06	0.127	317	1681.92	2.38E-07
5cm - 75%	16.97	5.30E+06	0.125	329	1672.00	2.28E-07
5cm - 50%	27.40	2.27E+08	0.104	128	1548.00	5.22E-07
5cm - 33.3%	42.37	2.60E+10	0.089	96	1465.24	6.33E-07
Gross and Robertson 16.6%	88	4.7E+13	0.046	309	1400.00	1.06E-07

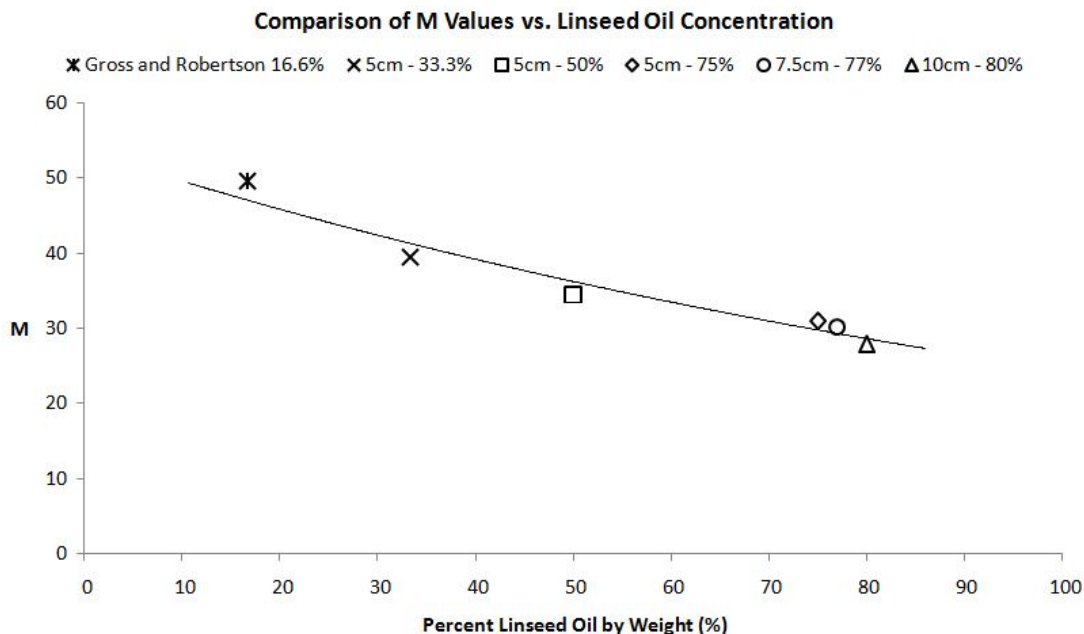


Figure 23: Graph of values of M vs. Concentration of Linseed Oil

It should be noted that these tests were done with the sample inserted just following the application of the oil. It is possible that fully dried linseed oil, or repeated wetting and drying of the same cloth, may give different results. It is recommended that these scenarios might be examined in the future.

Another aspect of Warden results gave the time to ignition or thermal runaway conditions in the oven as a function of mass loading of linseed oil, size of the basket and oven temperature. From the basic equation for the Damkohler number

$$\delta = \frac{r^2}{T_R^2} \exp\left(M - \frac{P}{T_R}\right),$$

it is seen that δ increases with r^2 and, while not so obvious, with T_R as well due to the exponential term. Then by the equation for time to ignition, Eq. (6), we can see the effect of other variables. As d increases the time decreases, it takes longer for ignition the bigger the size, and the diffusivity has an inverse effect on the time. Figures 24 and 25 show results for the time to ignition of the linseed oil impregnated cotton cloth. Figure 24 confirms that smaller baskets ignite faster, and ignition time decreases exponentially with decreasing temperature.

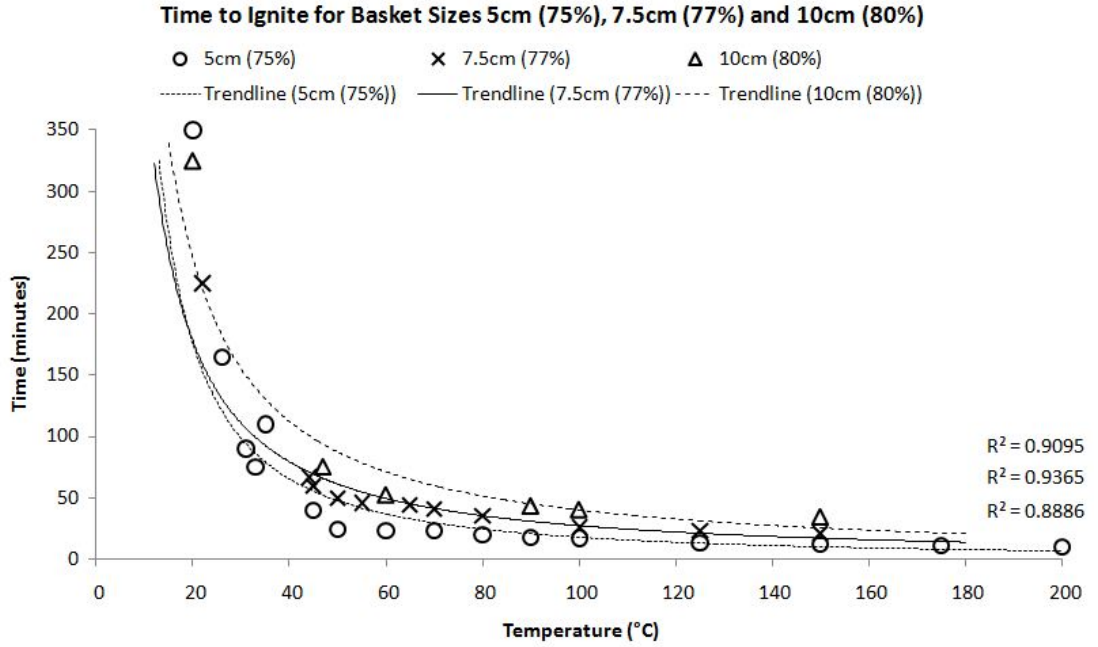


Figure 24: Time to Reach Ignition for 5cm (75%), 7.5cm (77%) and 10cm (80%) Basket Sizes

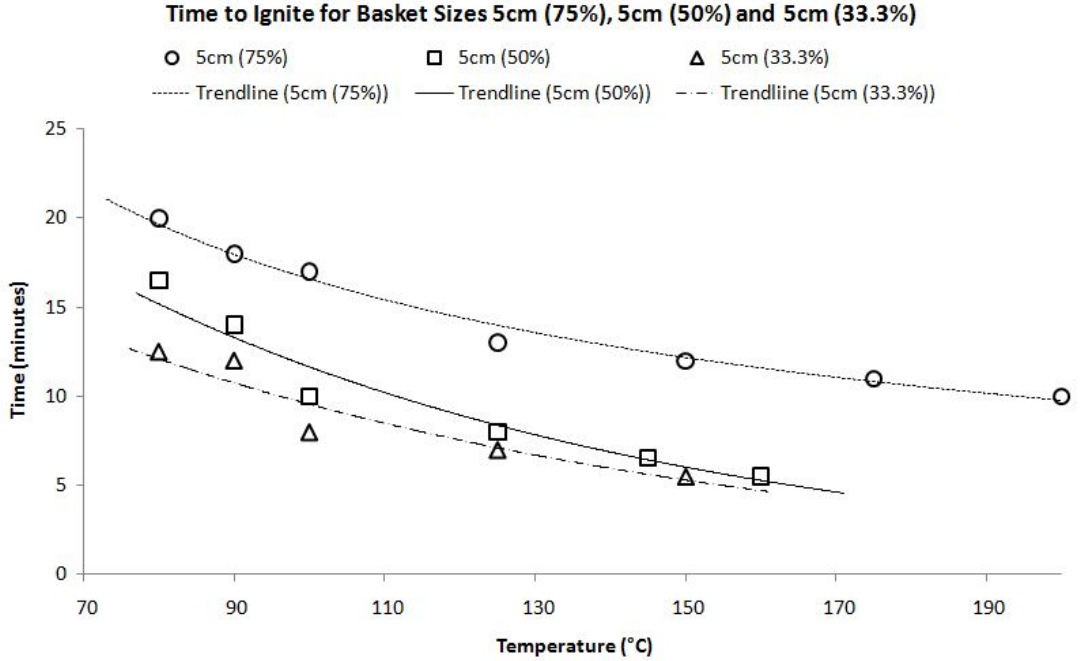


Figure 25: Time to Ignite for 5cm (75%), 5cm (50%) and 5cm (33.3%)

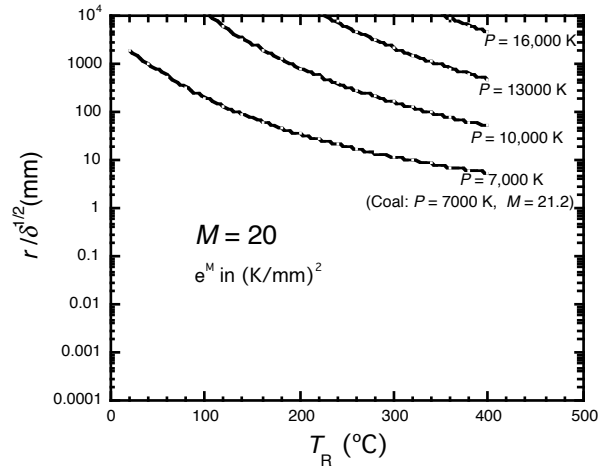
Figure 25 shows more clearly that for the same size, the time to ignite decreases as the loading decreases. This is most likely due to the increase in thermal diffusivity with loading as shown in Table 3. While the time to ignite was not computed from the theory, the theory indicates the trends of the effect of temperature, size and loading on the time to ignite.

6. Tabulation of Properties from the Literature

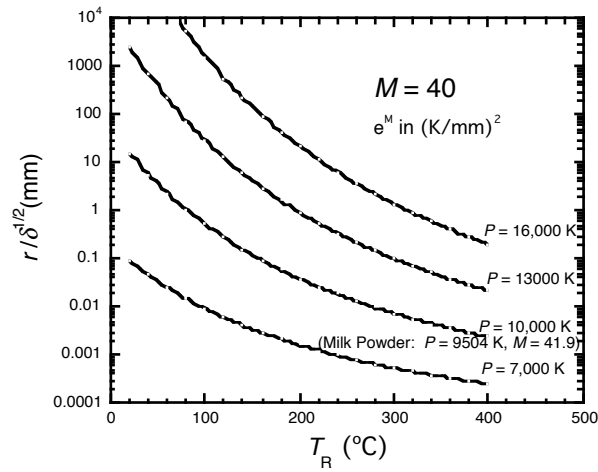
Tamburello [2] tabulates values for P and M as found in the literature and these are given in Table 4. The table contains a variety of materials ranging from ammonium nitrate that exothermically decomposes to cotton that exothermically is oxidizing. The values of M range from 20 to 50 and P from about 7000 to 19000 K.

It is difficult from the array of P and M values in the table to give an easy recognition of which material is better than another. From Eq. (3), $r/\delta^{1/2}$ is plotted as a function of the reference temperature and P and M . This is shown in Figure 26 for values of M from 20, 40 and 60. For a given scenario once a critical δ is found, then the corresponding critical dimension (size) can be found that would cause spontaneous ignition. From the plots in Figure 26, larger values of M tend to give smaller critical sizes. M embodies the reaction rate (pre-exponential term) and the heat of reaction. P represents the activation energy, and the lower is P then the lower is the onset temperature (T_R) for spontaneous ignition for a given size.

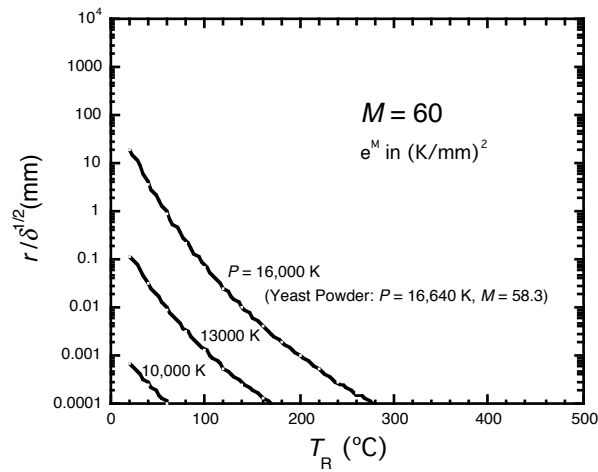
It is also clear from the table that different investigators do not necessarily agree on the values for a given material. This is disturbing, but it may be that the actual material tested or its configuration in terms of arrangement was not the same. Initially it was thought that a compilation of such data would be useful. However, its uncertainty in a new application cries out to do new testing. These trends are seen in the figure. Some real material examples, taken from Table 4 are listed in the plots for illustration.



(a)



(b)



(c)

Figure 26. Trend on critical dimension (r) due to M and P

Table 4. Compilation of Property Data

Material	P (K)	M^*	E (kJ/mol)	Comments	Source
Ammonium Nitrate	17921	43.2	149	fertilizer grade	(Hainer, 1954)
Ammonium Nitrate	16237	42.2	135	fertilizer grade with 7% additional fuel added	(Hainer, 1954)
Animal Feedstuff	8404	26.06	70		(Bowes, 1984)
Bagasse	13000	33.08	108		(Bowes, 1984)
Calcium Hypochlorite	5833	19.5	48.5	hydrated. Values are for low temperature regime	(Gray & Halliburton, 2000)
Calcium Hypochlorite	14793	44.5	123	hydrated. Values are for high temperature regime	(Gray & Halliburton, 2000)
Carbon (Activated)	10007	28.2	83.2	oven-cube tests on powdered activated charcoal over 50-190 °C temperature range	(Nelson, 1992)
Cellulose Insulation	13230	32.8	110	unretarded cellulose from adiabatic furnace test	(Issen, 1980)
Cellulose Insulation	13591	26.5	113	hot-plate method with density of 34 kg/m ³	(Ohlemiller & Rogers, 1980)
Cellulose Insulation	15876	30.1	132	insulation retarded with 20% boric acid using hot-plate method with density of 41 kg/m ³	(Ohlemiller & Rogers, 1980)
Charcoal (Activated)	11666	28.1 - 35.7	97	all types except the 3 minimally hazardous products from oven-cube tests of 10 types	(Cameron & MacDowall, 1972)
Charcoal (Activated)	12700	36.98	106	weathered	(Cameron & MacDowall, 1972)
Coal	8419	25.0	70	bituminous South African with volatile content of 26% over 120-220 °C temperature range	(Tognotti, Petarca, & Zanelli, 1988)
Cork (Dust)	13711	37.2	114	oven basket method	(Hensel, 1988)
Cork (Solid)	9622	23.9	80	calculated directly from E,Q,A, density, and conductivity from values based on small-specimen tests in adiabatic furnace	(Gross & Robertson, 1958)
Cotton	11282	28.6	93.8	based on oven-basket method on cotton fibers of $\rho = 50 \text{ kg/m}^3$	(Gray, Little, & Wake, 1992)
Cotton	17319	41.4	144	calculated directly from E,Q,A, $\rho = 320 \text{ kg/m}^3$, and conductivity from values based on small-specimen tests in adiabatic furnace	(Gross & Robertson, 1958)

* M based on e^M having units K^2/mm^2

Table 4. continued

Material	P (K)	M^*	E (kJ/mol)	Comments	Source
Distiller's Dark Grains	8046	25.3	66.9		(Bowes, 1984)
Eucalyptus Leaves	8539	24.5	71	leaves were at density 140 kg/m ³	(Jones & Raj, 1988)
Fertilizer (12-13-6)	17319	47.9	144	based on oven-basket data for 12-13-6 fertilizer	(Huygen & Perbal, 1965)
Forest Floor Material 1	9862	27.2	82		(Jones et al, 1990)
Forest Floor Material 2	10945	30.2	91		(Jones et al, 1990)
Milk Powder	11678	26.2	97.1	skim milk from temperature range 135 – 170 °C and $\rho = 670 \text{ kg/m}^3$	(Chong, Chen, & Mackerth, 1999)
Milk Powder	9502	34.7	79	skim milk from temperature range 142 – 171 °C	(Beever P. , 1984)
Milk Powder	9538	28.7	79.3	skim milk from temperature range 138 – 173 °C and density 600 kg/m ³	(O'Connor, 1990)
Milk Powder	19292	45.5	160.4	(E seems high) whole milk from temperature range 130 – 145 °C	(Chong, Chen, & Mackerth, 1999)
Milk Powder	9056	20.5	75.3	whole milk from temperature range 145 – 165 °C	(Chong, Chen, & Mackerth, 1999)
Milk Powder	9754	29.4	81.1	milk with 30% fat added from temperature range 130 – 200°C	(J.G. & Synnott, 1988)
Milk Powder	11979	34.2	99.6	milk with 44% fat added from temperature range 135 – 175°C	(Duane & Synnott, 1992)
Mineral Wool	6800	21.6	56.54		(Spokoinyi & Eidukyavicius, 1988)
Plywood (Fire Rated)	11570	35.7	96.2	calculated directly from E,Q,A, density, and conductivity for fire rated plywood	(Loftus, 1985)
Plywood (Plain)	10572	32.9	87.9	calculated directly from E,Q,A, density, and conductivity for plain plywood	(Loftus, 1985)
Rice Husks	12629	32.5	105	small scale oven-cube test with density 140 kg/m ³	(Jones & Raj, 1988)
Spent Brewing Grains	6495	19.9	54		(Walker, 1961)
Wheat Flour	15539	44.2	129.2		(Nelson, 1992)
Yeast Powder	16640	44.5	138		(Bowes, 1984)
* M based on e^M having units K^2/mm^2					

IV. Conclusions

This study sought to bring the science and test methodology for spontaneous ignition to the fire investigator. Three scenarios were illustrated for making calculations to establish whether spontaneous ignition is possible. An approximate formula was given to estimate the time to achieve spontaneous ignition. Two methods, using an oven and samples in cubical baskets were described. The crossing point method is the simplest and is recommended for a first consideration in obtaining property data. This method was used to determine the properties of linseed oil on cotton, and showed increasing tendency for spontaneous ignition with increasing concentration. In addition a database of properties available in the literature has been assembled.

The presentation of the mathematics has been kept to a minimum in order to try to reach the widest range of investigators. Hopefully this report will educate and inform on the principles of spontaneous ignition, and sensitize the investigator to its potential role as the cause and origin of a fire. The results provide also a quantitative framework for making calculations to show that spontaneous is possible and if possible, how long it might take to occur. However, no calculation is possible without specific data for the material. Literature data might give an indication, but its variability might not be sufficient. Therefore, test data must be developed for the material in question. The F-K oven method has been fully described herein, and details include how to design the oven procedure, and its operation. A technique was developed for measuring the needed oven heat transfer characteristics, and that has given good results. However, the F-K method is tedious, and the crossing point was explored. It showed good results for linseed oil and cotton. Indeed, we know of no other comprehensive study of the properties of this medium with varying mass concentration of linseed oil.

Initially we had intended to work with several forensic laboratories on the test methodology. However, the intensity of doing the first cut with novice students did not give the time or the opportunity. It would be useful to see how much of this work is currently done by forensics laboratories in fire. We know the new ATF fire laboratory does not have this capability, but several private laboratories have utilized

it in a need basis. We know of no standard for the F-K method or the crossing point method. If this measurement strategy were to take hold in the fire forensic area, standard test protocols would be needed.

The area of spontaneous ignition is a backwater. While publications on the subject exist in the scientific literature, they are relatively few in number. Early work was done in the UK and US during the 1960's. The US work was at the National Bureau of Standards (now NIST); currently no work is done in the NIST fire program on this subject. Bowes suggests in his treatise on the subject that many fires due to spontaneous ignition may go unrecognized. Yet it is likely more blame is given to electrical ignition causation in a fire than is true. It is hoped that this study might provide the motivation for more study in the field, and more use in fire investigation.

V. References

1. Worden, Justin T., Spontaneous Ignition of Linseed Oil soaked Cotton using the Oven Basket and Crossing Point Methods, Master of Science, Department of Fire Protection Engineering, University of Maryland, College Park, MD, 2011.
2. Tamburello, Stephen Michael, On Determining Spontaneous Ignition in Porous Materials, Master of Science, Department of Fire Protection Engineering, University of Maryland, College Park, MD, 2011.
3. Frank-Kamenetskii, David A, Temperature Distribution in Reaction Vessel and Stationary Theory of Thermal Explosion. *Journal of Physical Chemistry* , 13, 738-755, 1939.
4. Bowes, P. C. *Self-Heating: evaluating and controlling the hazards*. 1984.
5. Babrauskas, Vytenis, *Ignition Handbook*. 2003.
6. Beever, P. F. (1988). Self-Heating and Spontaneous Combustion. In P. J. DiNenno, *SFPE Handbook* (1st Edition ed., pp. 1:341-1:351). NFPA.
7. Gray, B. (2002). Spontaneous Combustion and Self-Heating. In P. J. DiNenno, *SFPE Handbook of Fire Protection Engineering* (3rd Edition ed., pp. 2-211:2-228). Quincy, Massachusetts: Courier/Westford.
8. Kyoko Kamiya, Osami Sugawa, Tomohiko Imamura, and Yasushi Oka, Detection of Spontaneous Combustion of Plastic Waste by “Odor” – Evaluation on Odor

Intensity and Quality from Plastics Waste in Pre-combustion Condition -, *Fire Science and Technology*, 29, No. 1, pp. 1-14, 2010.

9. Jones, J. C., Chiz, P. S. and Matthew, J., Kinetic Parameters of Oxidation of Bituminous Coals from Heat-Release Measurements, , *Fuel*, Vol. 75, pp. 1755-1757,1996.

10. Chen, X. D., Chong, L. V. and Shaw, I. R., Thermal Ignition Kinetics of Wood Sawdust Measured by a Newly Devised Experimental Technique, *Process Safety Progress*, Vol. 14, pp. 266-270, 1995.

VI. Dissemination of Research Findings

At this time no journal or conference presentations have been made on this work. Two MS theses have been published and they are available through the University of Maryland James A Clark School of Engineering. A 60-minute presentation was offered for the 2012 NFPA Conference & Expo, but it was not accepted. Other presentations will be investigated including IAAI, NAFI and the upcoming Fire and Materials meeting in 2013 that attracts investigators. A publication on the new data for linseed oil with cotton will also be put forth.

VII. Nomenclature

$a = \lambda/\rho c$, thermal diffusivity [m^2/s]

A = pre-exponential factor [s^{-1}]

A = area [m^2]

c = specific heat [$J/kg-K$]

E = activation energy [kJ/mol]

F_{12} = view factor = 1 for parallel plates

g = gravity [$9.81 m/s^2$]

h = basket heat transfer coefficient

H = basket height [m]

r = half-width of object

R = universal gas constant [$8.314 \times 10^{-3} kJ/mol-K$]

m = mass of the basket [kg]

$$M \exp(M) = \frac{E}{R} \frac{\rho A Q}{\lambda}$$

$P = E/R$ [kJ/mol]

Q = heat of reaction [kJ/kg]

S = surface area of basket = $5 * H^2$ [m^2]

T_A = ambient temperature [K]

T_i = initial material temperature [K]

T_P = hot plate temperature [K]

T_R = reference temperature [K]

T_S = basket surface temperature [K]

W = width

Y_i = mas fraction [-]

Greek

$$\alpha = \text{Biot number} = \frac{hr}{\lambda}$$

λ = thermal conductivity [$W/m-K$]

u_∞ = measured air velocity in convection oven [m/s]

ρ = material density [kg/m^3]

σ = Stefan-Boltzmann constant [$5.67 \times 10^{-8} W/m^2-K$]