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NATIONAL BUREAU OF STANDARDS REPORT

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THE PROCESS OF IGNITION

A. F. Robertson



U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

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U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

THE PROCESS OF IGNITION

ABSTRACT

A brief elementary description is presented of factors likely to influence the process of ignition of combustible materials. Nine mechanisms for promotion of ignition are mentioned and described. A brief bibliography is included.

INTRODUCTION

The initiation of combustion or explosion of a fuel may be described as the ignition process. Because of the large variations in the combustible characteristics of fuels and variations in ambient conditions, this ignition process may assume a wide variety of forms. This paper has been written with the objective of providing a brief review of some of the conditions and manner in which ignition can take place.

MECHANISM OF IGNITION

The detailed chemical processes involved in an ignition reaction are for most materials so complex that no detailed explanation of the process can be given. There is, however, rather general agreement that many such reactions are of the chain type, reference 1. The term chain is used to describe the reaction because the process involves many different steps for completion. Each of these steps may be dependent on the prior completion of another stage of the reaction for completion of the combustion process. The fact that many fuel molecules are very complex, (cellulose molecules $(C_{6H_{10}O_{5})_x$, exist in multiples of 21 atom groups), further complicates the process by requiring that a multiplicity of reactions take place together.

In the case of low temperature heat generation, reactions of the type associated with self ignition of materials, there is evidence that the heating is largely a result of depolymerization or breaking up of the complex molecular structure of the fuel and the resulting formation of new compounds. This process of breaking large complex molecules down into smaller ones with associated oxidation and other chemical reactions seems to be taking place continually even at very low temperatures. The

rate with which these reactions take place depends on the number of molecules which are likely to have, or take on, energy sufficient to cause a reaction to occur. The kinetic theory of gases suggests that the probability that an individual molecule will have energy in excess of an amount E, at temperature T, is proportional to $e^{-E/kT}$, where k is the gas constant per molecule. Although most combustion processes are exceedingly complex, it is interesting to find that experimental data on slow combustion reactions can often be correlated on the basis of this type of relationship.

THERMAL CONSIDERATIONS

In order for an ignition reaction to be successful in initiating a combustion or explosion reaction, it is necessary that it cause the heated portion of the fuel to liberate heat at a rate faster than thermal losses take place to the surroundings. This may be illustrated by Figure 1 (see also reference 2). Here heat loss and heat generation curves are shown for a given fuel as a function of absolute temperature. The heat generation curve is of an exponential form, the rate of heating increasing as a power function of the temperature. The heat loss is assumed to be Newtonian in character. This implies that the rate of heat loss is a linear function of the temperature difference between the heated surface and ambient. This may be a considerable over-simplification but is satisfactory for illustrative purposes. The heat loss curve has been indicated for three different ambient temperatures TA, TB, and TC. For ambient temperature T_A heat generation exceeds the loss rate until T_D is reached, at which time a stable surface temperature rise $(T_{D} - T_{A})$ is reached and no further heating occurs. For ambient temperature TB there is only one point of contact, that of tangency, for the two curves. This results in an unstable temperature rise (T_E - T_B) from which it is highly likely that the fuel will continue to increase in temperature and be consumed. For any ambient temperature higher than T_B there is no point of contact of the two curves and the heating of fuel will continue until it is consumed.

Temperature T_B is for the conditions assumed in Figure 1, the lowest temperature from which self-ignition may be assumed to occur. It should be noted, however, that this temperature is not a unique property of the fuel studied but more so of the combination of fuel and experimental conditions used for its determination. Thus, if the fuel sample is changed in size or

extent of thermal contact with conducting portions of the apparatus the slope or form of the heat loss curve will be changed. This will result in a new critical ambient temperature which will be higher if heat loss rate has been increased or lower if losses are reduced. Thus a different self ignition temperature results for the same fuel.

The preceding has assumed that all heating has been a result of generation within or by the fuel. Many common combustible materials are stable under ambient conditions and the temperature rise $(T_D - T_A)$ which they develop is very small and seldom if ever noticed. These materials may however ignite and burn if an additional heat input rate is provided. Figure 2 illustrates such conditions. Here the total heating rate is the sum of the generation rate and the constant heat input rate which has been added. This results in the total heating curve being greater than the heat loss curve for all temperatures above T_D and ignition will have been completed.

Successful ignition is thus seen to have required a total heat gain rate greater than that of the losses to the surroundings.

IGNITION LAG

In the preceding discussion it was assumed that the time available for the various stages of the ignition process was not a determining factor. This assumption is often correct for self-ignition processes, but in the case of an externally applied ignition source this situation may not exist. Figure 3 shows a diagram for an unsuccessful ignition attempt. Here conditions were much the same as those shown in Figure 2. However, in this case the duration of the heat pulse was too short to prevent the heat generation curve from dropping below the loss curve. A maximum temperature $T_{\rm F}$ would be reached. When the heat input ceased, the loss rate would exceed the generation rate and the temperature would return to $T_{\rm D}$ and stabilize there.

This discussion of the ignition lag problem has been greatly simplified and is largely illustrative. It has not described one of the important causes of the delay which involves the time required to form the necessary intermediate chemicals required for completion of the chain combustion reaction.



SOURCES OF IGNITION

The variety in form and detail of successful ignition reactions may be very great. It is thus almost impossible to set forth all of them. Instead a few brief comments will be made on the manner in which several types of ignition sources may cause ignition. These include:

- Bacteriological processes 1.
- 2. Chemical heating
- 3.4. Frictional effects
- High temperature exposure
- 5. Rapid compression
- 6. Shock wave
- 7. Open flame
- Electric spark 8.
- Mechanical impact 9.

Each of these processes will be discussed separately. First, however, a brief discussion of the fuel types seems desirable. The flammability or the ease and rapidity with which ignition and combustion or explosion can take place, in a given fuel, depends largely on the chemical properties of the fuel and the shape and distribution or "geometry".

The chemical properties of interest here would include chemical composition of the fuel and kinetic reaction data for the combustion process involved. Many of the common fuels require air as an oxidizer whereas most high explosives and propellants are prepared as mixtures of fuel and oxidizer.

The geometry of the fuel is important for several reasons. In the case of common fuels, particle size is very important in determining the degree with which fuel and oxidizer are mixed. An example of high flammability resulting from this effect is evident in the occurrence of dust explosions. The use of pulverized coal, and atomized liquid fuels for power and heat production are evidences of the importance of proper fuel and oxidizer mixtures for high heat release rates. Geometry is important too in determining the heat transfer characteristics of the fuel. Thus the ease with which the flame produced by the fuel feeds back heat to unignited portions is largely influenced by its geometry or surface to volume ratio. This is true even for explosives and propellents when burned. Although with these latter materials there is evidence of a flame in close proximity with the fuel surface, it appears that the reaction rate is largely controlled by the rate of heat transfer to the fuel and thus the rate with which a combustible vapor is produced.

Most fuels will burn with flaming combustion only in the gas phase. The process seems to be one of heat transfer from the flame to the fuel which volatilizes and furnishes vapors which when mixed with air or other oxidizers help sustain the flaming. If any mechanism is devised to reduce or increase the rate with which heat transfer takes place to the fuel, the speed of the combustion process is either reduced or increased respectively.

Common liquid fuels evidence the same effects mentioned previously. Those with low vapor pressure are more difficult to ignite than highly volatile fuels. It is, however, the vapors above the liquid surface which burn and a stable flame can be produced above such a surface only after the liquid has been heated sufficiently to provide a continuing supply of vapor to the fire.

The question of explosive limits is one of importance in connection with many fuels. Thus in a poorly ventilated compartment the open storage of gasoline while not advisable may not present a serious explosion hazard while similar storage of kerosene would. The apparent anomaly here results from the difference in vapor pressures of the two fuels. The vapor pressure of gasoline is so high that the fuel vapor concentration at normal temperatures may be above the explosive limit. The vapors from kerosene on the other hand develop only a low partial pressure and thus permit maintenance of an explosive mixture with attendant hazard.

A discussion of the various ignition processes may now be presented.

<u>Bacteriological processes</u>: The production of microorganisms under the rather ideal conditions provided by stacks of agricultural products which have not been properly dried is considered as a likely source of initial heating to about 75°C, references 3 and 4. Such bacteriological activity is reported as stopping at temperatures much above this and it seems likely that further heating, when it takes place, must result from the previously mentioned depolymerization and oxidation reactions. Such reactions are only likely to occur when stacks of sufficient size are exposed in a position to reduce heat losses from the remote central regions. Bacteriological heating is reported to require both moisture and oxygen and apparently does not take place in their absence, reference 4.

<u>Chemical Heating</u>: The production of heat as the result of a chemical reaction is a common occurrence. The rate of release of heat will depend on the process involved and will thus determine the possible form the ignition process will assume. Thus absorption of water from the air may take place with liberation of heat but for most materials this is, under normal conditions, such a gradual process that it seems likely to present a serious ignition hazard only when large bulks of combustible materials are involved and other self heating phenomena can take over after this process has neared completion.

Other chemical reactions involving the production of new compounds can often result in very high heat release rates. References 5 and 6 present useful information on this type of ignition hazard.

Frictional Heating: The energy expended in rubbing two materials together is a well known source of fire. It has long been used by man as a primary source of ignition. The fire drill used by the American Indians is but one of a wide variety of friction ignition systems which have been used, see reference 7.

It seems likely that all frictional ignition phenomena will involve relative motion between solids. As in the case of the fire drill, although the rubbing members may ignite, some tinder is often involved which provides a more flammable mixture of fuel and air. Thus fires in cotton bales have been attributed to frictional heating between adjacent metal ties.

<u>High Temperature Exposure</u>: Many materials will ignite spontaneously after prolonged exposure to elevated temperatures, references 8 and 9. Most cases of such ignition actually appear to take place in the gaseous or vapor phase. Thus the distillation products resulting from heating wood provide vapors which are subject to self ignition, producing a flame which may become stabilized on the fuel itself. The ignition of fuels by radiant energy sources should be considered as a special case of ignition by high temperatures.

Rapid Compression: The Diesel engine presents one of the common examples of the use of rapidly compressed air for ignition of fuel. Although a dispersed oil is usually used, engines have been operated on pulverized solids such as coal. Earlier use of compression of air as an ignition source is

exemplified by the fire syringe or fire piston as used by natives of Burma and Siam, reference 7. Here the rapid compression of air was used for ignition of tinder. The compression of air within which a suitably prepared fuel charge is placed seems to present a reliable and often useful source of ignition.

Shock Wave: Under certain conditions shock waves can be developed in gases. Such waves result from a portion of the gas achieving a high velocity of such a character that the front of the wave assumes a discontinous aspect. Such waves may be formed when a compressed gas is suddenly allowed to expand into a region of gas at a lower pressure. When this happens, a shock is formed which travels through the low pressure gas and raises the pressure and temperature in the region through which it has traveled. When such a shock is reflected from a material boundry the pressure and temperature are again raised and material behind the shock still further heated. Combustible materials exposed to these conditions may thus become ignited; however, because of the transient nature of this process, ignition delays must be very short. This is however often possible because of the very high temperatures which may be experienced behind such shocks. Under certain conditions an oscillating gas discharge can be established in such a manner that high temperatures resulting from the shock can be maintained for an extended period. In this case the short ignition delay period is not required and ignition of massive combustibles can be directly achieved. An example of this is the wooden block and compressed air jet experiment in which a hole drilled in the block is used with the air jet to form a Hartman generator. During operation of device a cavity is burned within the block and a fire may this he started.

<u>Open Flame</u>: The open flame provides another means for application of intense local heating to a combustible and serves as an ignition source for distillation products. The question of whether or not a liquid or solid fuel will sustain combustion on removal of the flame depends largely on the composition of the fuel and the manner in which it is dispersed (geometry). The term flammability has frequently been used as indicative of the ease which which a material may become inflamed. This property is usually largely dependent on both the chemical nature of the reacting materials and the rate with which the materials become heated by the flames which are developed. The rate with which this feedback of energy in the



form of heat takes place will depend not only on the reaction under way but also on ambient conditions such as temperature and pressure. Thus fires involving materials such as propellants can often be extinguished by simply lowering the atmospheric pressure.

<u>Electric Sparks</u>: Sparks are frequently used as ignition sources for gaseous or liquid fuels, reference 2. The automobile serves as an excellent indication of the reliability of such ignition sources. Dispersed solids can also be ignited as evidenced by ignition of forest fuels by lightning. Static electricity can serve as a source of such sparks. The manner in which such electrostatic charges can be collected in a form suitable for production of a spark is almost infinitely varied and has been the subject of extensive study; references 10 and ll present good introductions to some of the problems involved.

<u>Mechanical Impact</u>: Mechanical impact may provide a source of ignition for many types of fuels. It appears however that in most instances such impact acts through other previously described ignition sources as intermediate mechanisms. Thus impact initiation of detonation in liquid explosives is currently considered to result from rapid compression of small gas inclusions in the explosive, reference 12. Similarly the percussion ignition of tinder and gases is usually found to result from the formation of small highly heated particles which when intro-duced into the fuel serve as ignition sources, reference 13. Impact can also cause frictional heating by rubbing grains of an explosive together providing another source of ignition. The fact that direct impact does not serve as a common ignition source for other than explosive materials probably results from the low compressibility of most combustible solids and the resulting small amount of compression energy that can appear in the form of heat. This together with the fact that direct mechanical impact so often causes dispersion of the material struck and thus rapid dissipation of the heated spots causes this source of ignition to be rather ineffective for most common materials. However, for sensitive materials such as explosives, propellents, etc., this source can often provide a good mechanism for the initiation of an ignition reaction.

SUMMARY

The process of ignition of combustible material may take place in an almost endless variety of ways. To be successful an ignition process must result in the establishment of a

heat generation rate greater than the loss rate to the surroundings. Once this has been achieved the process may become self-sustaining until either the readily combustible portions of the fuel or, the oxidizing agent has been consumed.

Because of the dependence of the ignition reaction on the rate of heat loss to the surroundings it is difficult if not impossible to define an ignition temperature which may be considered a unique property of the material being studied.

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