CONTROLLING MECHANISMS IN THE TRANSITION FROM SMOLDERING TO FLAMING OF FLEXIBLE POLYURETHANE FOAM

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Experiments have been conducted to study the controlling mechanisms involved in the transition from smoldering to flaming of a porous combustible material, flexible polyurethane foam, with an air flow forced across one of the porous-fuel surfaces. The experiments are performed in a small-scale, vertical, combustion wind tunnel, with the air flow forced upward and parallel to an exposed foam surface that forms one of the walls of the tunnel test section. Smolder is initiated at the bottom of the sample and propagates upward in the same direction as the forced and buoyancy-induced flows. The resulting smolder is therefore two-dimensional and forward. Thermocouple measurements of the foam interior, along with visual observations, when compared with schlieren interferometry images of the gas phase at the porous-fuel/air-flow interface, indicate that transition to flaming occurs inside the hot char region below the smolder front and not at the interface. An innovative ultrasonic imaging technique is employed to track the evolution of the char permeability in real time, evincing that the char continues to react and increase substantially in permeability long after the primary smolder front has passed. The ongoing heterogeneous reactions in the char region result in the formation of large voids that provide locations for the onset of homogeneous gas-phase reactions. Furthermore, the higher permeability of the char favors the flow of oxidizer, as well as pyrolysis vapors produced by the primary smolder reaction, into the char interior, which, in conjunction with the reduced heat losses, lead to the onset of a homogeneous gas-phase ignition. This process results in the transition from slow smoldering to fast, exothermic, gas-phase reactions, which rapidly engulfs the entire fuel sample in flames.

Introduction

Smoldering is defined as a nonflaming, self-sustaining, propagating, exothermic, surface reaction, deriving its principal heat from heterogeneous oxidation of the fuel [1]. Smoldering constitutes a serious fire risk because it typically yields a substantially higher conversion of fuel to toxic compounds than does flaming, is difficult to detect (and extinguish) in the interior of a porous material, and provides a pathway to flaming (fast, exothermic, gas-phase reactions) that can be initiated by heat sources much too weak to cause a flame directly [2]. The transition from smoldering to flaming is a gas-phase ignition process whereby heterogeneous reactions act as a source of both fuel and elevated temperature. The process is also of particular interest as a fundamental combustion problem, with, surprisingly, very little information currently available.

Ortiz-Molina et al. [3] studied the relative smoldering tendency of different flexible polyurethane foams in a horizontal natural convection configuration, by varying the ambient oxygen concentration. Although the work primarily concerned itself with the threshold conditions at which transition to extinguishment occurs, a few experiments with very high oxygen concentrations displayed transition to flaming. Chen et al. [4] examined the behavior of horizontal layers of cellulosic materials (grain and wood byproducts and paper) in a forced air flow parallel to the material surface, and observed glowing combustion with subsequent transition to flaming for airflow velocities less than 3 m/s. Ohlemiller's work [5] with cellulose remains the most detailed study on the matter to date. He examined smoldering of thick, horizontal layers of cellulosic insulation in the presence of flowing air and found that while opposed smolder responded only weakly to an increased air
flow with no transition to flaming at flow velocities up to 5 m/s, forward smolder responded strongly to increased air flow and yielded transition to flaming at about 2 m/s. Transition to flaming has also been observed in related works of one-dimensional, forward smoldering of polyurethane foam for increased oxygen supply (naturally induced and forced) [6,7].

The smolder studied in the present work is of the forced flow, forward, two-dimensional type. The foam is ignited at the bottom, and the smolder reaction propagates in the same direction as the forced air flow at the porous-fuel/air-flow interface, as well as the upward, buoyancy-induced flow within the sample. In a previous paper [8], preliminary results of the transition from smoldering to flaming of flexible polyurethane foam in the same configuration were presented. The study included the effect of airflow velocity on the transition to flaming, along with some treatment of sample size and ignition power and duration. Consistent transition from smoldering to flaming occurs for air-flow velocities ranging from 0.25 m/s to 2.0 m/s. This paper presents a more detailed investigation of the mechanisms involved in the transition to flaming within this air-flow regime, with emphasis in determining the processes leading to flaming.

**Experiment**

A schematic of the experimental facility is shown in Fig. 1. The experiments were conducted in a test facility that involves a small-scale, vertically oriented, combustion wind tunnel along with the supporting instrumentation. All tests were conducted using open-cell, unretarded, flexible polyurethane foam (26.5 kg/m³ and 0.975 void fraction) with air as oxidizer. In addition to its common usage, polyurethane foam permits upward smolder experiments without fuel collapse and material erosion problems.

**Smolder apparatus**

Smolder tests were conducted in the wind-tunnel test section (0.6 m long with a rectangular cross section 0.127 m wide by 0.07 m deep). Three of the test-section walls are made of quartz for optical access; and the fourth wall is established by the exposed surface of the foam sample, mounted flush with the wind-tunnel wall. The foam sample was a rectangular parallelepiped (0.406 m long with a cross section 0.127 m by 0.14 m). Three side surfaces and the top of the sample were insulated with Fiberfrax sheets. House-compressed air flowed through the tunnel settling chamber and a converging nozzle before entering the test section. The flow velocity was controlled with critical flow nozzles and measured with a TSI VelociCheck 8330 air velocity meter.

Smolder ignition was accomplished with an electrically heated igniter placed in contact with the foam at the sample bottom. The heater consists of a Nichrome wire placed in between two, 5-mm-thick, 0.1-m-diameter, honeycomb ceramic plates that provide rigidity to the igniter. During the ignition period, uniform air was forced upward through the igniter and subsequently through the foam at a very low velocity (0.124 mm/s). The air flow was supplied with bottled, dry air and metered by a Brooks 5858A mass flow controller. This flow aids ignition by adding oxidizer to the reaction and also provides consistency to the ignition process. The foam ignition required a supply of 70 W for 3000 s, heating the igniter to ~500°C. At that time, the heater and igniter flow were turned off, and the external air flow was turned on and forced upward and parallel to the exposed foam surface.

**Instrumentation**

**Thermocouple probing**

Temperature, smolder propagation velocity, and transition to flaming location were obtained from the
temperature histories of a 2-D matrix of 42 thermocouples (chromel/alumel in a 0.8-mm-diameter stainless steel sheath), which were embedded at predetermined positions in the foam with their junctions placed along the fuel centerline in the plane orthogonal to the exposed foam surface. Thermocouple voltages were multiplexed, subject to A/D conversion, and recorded onto a computer.

Pulsed ultrasonic imaging

During this work, a novel ultrasonic imaging technique for determining the permeability of the char and the progress of the smolder wave was developed. The technique represents an important step forward in the study of smoldering combustion, with potential application in studies of other heterogeneous combustion processes. The technique is based on the observation that transmission of an ultrasonic signal through a porous material increases with increasing permeability. Thus, since a propagating smolder reaction leaves behind a higher-permeability char, ultrasonic transmission can be employed to differentiate virgin material from char and to monitor any permeability variations of a smoldering material. In this work, the technique is used to determine the permeability evolution of the char in real time with a line-of-sight transmission. Two-dimensional transmission images, giving information about char permeability, were produced by scanning the samples with a single set of speaker and microphone, mounted to a dual-axis UniSlide linear translation assembly. Pulsed signals of 40 kHz with 6 periods per wave-train, amplified to 40 V peak-to-peak, were sent from the speaker. Signals received by the microphone were amplified, superimposed with the original pulse train from the speaker, converted to a DC RMS signal, sampled by a high-speed A/D board at 250 kHz, and recorded onto a computer. The first peak in the received wave-form identifies the desired transmitted signal through the foam/char, distinguishing it from reflection and other interference signals. The spatial resolution is of the order of 1 cm, corresponding to the sonic wavelength and the size of the diaphragm of the microphone. The permeability calibration for the ultrasonic imaging technique was made by varying the thickness of a virgin foam sample, while keeping the distance, L, between speaker and microphone fixed. Assuming that attenuation of a transmitted ultrasonic signal is only a function of permeability, such a calibration is possible through the use of Darcy’s law: $u = -\frac{K}{\mu} \frac{dP}{d\ell}$, where $u$ is average velocity, $K$ is permeability, $\mu$ is dynamic viscosity, $dP$ is pressure drop, and $d\ell$ is sample thickness. Fixing $u$, $\mu$, and $dP$, $K$ becomes proportional to $d\ell$. Thus, $K_{\text{effective}} = K_{\text{foam}} L/d\ell$, and permeability as a function of ultrasonic attenuation can be obtained accordingly.

Local gas probing

Syringe needles, embedded at predetermined positions in the foam with their ends placed along the fuel centerline, collected 2.5-ml local gas samples at discrete times just prior to transition to flaming. These samples were later analyzed for O$_2$, CO, CO$_2$, and hydrocarbons by a Hewlett Packard 5890 Series II gas chromatograph with thermal conductivity and flame ionization detectors.

Exhaust gas analysis

Unburned hydrocarbons, CO, and CO$_2$ species histories of mixed-aggregate exhaust gases were measured with Horiba (flame ionization and infrared) gas analyzers in real time, and recorded onto a computer. The gas sampling provides comparison with temperature data, adding to qualitative diagnosis of the smolder behavior and enhancing the perceptibility of some preflaming phenomena.

Results and Discussion

In the upward, forward smoldering configuration treated here, the elevated temperature product gases from the smolder front are convected downstream, preheating the virgin foam and, thereby, reducing the additional thermal energy required to pyrolyze the foam and initiate its oxidation. Consequently, local temperatures and smolder propagation velocities can increase, accelerating perhaps to a transition to flaming. Although this is a possible mechanism for the phenomenon [2,6,7], experiments indicate that transition from smoldering to flaming in the present arrangement proceeds by a different path [8].

In the smolder mechanism of flexible polyurethane foam, a complex polymer, C$_{1.0}$H$_{1.7}$N$_{0.07}$O$_{0.3}$, is converted to a char-like material of approximately C$_{7.2}$H$_{5}$NO [9]. Noteworthy, the char is also oxidizable, exhibiting experimentally that it is somewhat more resistant to oxidation than the original foam, but once reacted, is more exothermic. This process is documented in the literature [1,2,6,7,9–13] and is commonly referred to as secondary char oxidation. Ohlemiller [2] recognizes that the course of secondary char oxidation can be energetic enough to ignite flammable gases, initiating a transition to flaming. As will be discussed later, it is this process that provides the pathway to flaming in the present experimental setup.

Visual observations and thermocouple histories, when compared to analyses of schlieren interferometry [14,15] images of the gas phase at the foam/air-flow interface, reveal that transition to flaming occurs inside the hot char region below the smoldering zone and not at the interface. Although one might expect flaming ignition to occur at the interface where exhausted pyrolysis vapors meet fresh ox-
idizer, thermocouple measurements indicate that the interface is too cold (<400°C) for gas-phase ignition to occur. Transition to flaming requires both a mixture of combustible gases and air that are within the flammability limits and also a sufficient heat source, or heat insulation, for the mixture to ignite [2]. Apparently, for these air-flow velocities, oxidizer can be sufficiently transported to the char, such that its oxidation generates enough heat flux to compensate for any heat losses due to the entrainment.

A characteristic example of the temperature history is given in Fig. 2. The first thermocouple is in contact with the igniter; the others are spaced 25.4 mm apart, spanning the length of the sample. The rapid drop in temperature of the igniter thermocouple at 3000 s marks the switching off of the igniter power. As evinced by Fig. 2, thermocouple traces higher than 51 mm above the igniter divulge a trend of continual temperature increase for the remainder of the experiment. The unsteady oscillations in the temperature curves (>)400°C) reflect secondary char oxidation reactions that propagate intermittently in seemingly random directions throughout the char region left by the main smolder front. These secondary reactions are generally characterized by faster propagation rates and higher temperatures than the primary smolder reaction [6]. Because of the immediate initiation of secondary char oxidation by the original smolder front, the smolder temperature and smolder wave thickness are difficult to define from the thermocouple histories. With no clearly defined maximum in the temperature profile, the arrival of the smolder front is determined by drawing tangents to the temperature curves and cutting them by a line at a predetermined temperature (350°C). Characteristic smoldering temperatures for flexible polyurethane foam have been observed by several authors [9–12] to be approximately 350–400°C. The smolder velocity is calculated from the time lapse between two consecutive intersections. The smolder velocities of experiments with the same air-flow velocity do not follow a typical trend toward transition to flaming. As transition to flaming is approached, smolder velocity increases in some cases and decreases in others, suggesting that increasing smolder velocity is not the direct cause for transition to flaming.

Figure 3 shows the temperature distribution along the length of the sample for increasing time for a single experiment, elucidating the absence of a well-defined smolder temperature and the blurring of the smolder zone, but clearly manifesting the propagating smolder front. Note that Fig. 3a and 3b are presented separately to better explain the results of the experiment. Data for 0.75-m/s air-flow velocity are displayed, simply, because from all of the experimental data, these plots most nicely and clearly present the discussion. Nonetheless, these plots are representative and consistent with all air-flow velocities (including 0.25 m/s) examined exhibiting transition from smoldering to flaming. Fig. 3a elucidates a domain of smolder propagation along with an initial secondary char oxidation wave, and Fig. 3b reveals a domain of intense secondary char oxidation. In the first domain (Fig. 3a), the temperature of the sample increases regularly with time as the smolder reaction propagates upward and as the secondary char oxidation zone expands gradually and propagates down to the igniter from the smoldering zone. Once the
char temperature at the igniter starts to increase, the second domain (Fig. 3b) prevails. Here, the temperature profiles often fluctuate with time, but with a general disposition of significant temperature increase. The reactions seem to be more exothermic than those in the preceding domain.

In this second domain, the char region below the smolder front increases in temperature fairly uniformly along its length, with the hottest region at \( \sim 600^\circ \text{C} \). At this point, another interesting phenomenon is encountered. Extremely localized, high temperature rises (up to \( 1200^\circ \text{C} \)), virtually unnoticed by thermocouples just 25.4 mm away, in the char region precede observation of flaming at the interface (by \( \sim 100 \) s). The time scale for this ignition delay seems to be too large to be the induction time normally associated with the ignition of a combustible mixture. A possible explanation is that a well-insulated, exothermic surface reaction proceeds within the oxygen-limited char until a sudden influx of oxidizer, brought to this location by void formation within the char region, triggers the transition to flaming.

The increase in char permeability and the formation of voids as smolder progresses are confirmed by
Fig. 4. (a), Ultrasound image of a sample just prior to flaming. The forced airflow velocity is 0.25 m/s. (b), Ultrasound image of a sample just after flaming. Note: Combustion is extinguished with a nitrogen purge upon flaming. The forced airflow velocity is 0.25 m/s.

Fig. 5. Time evolution of char permeability at a single location. The forced airflow velocity is 0.25 m/s.

Applying the ultrasonic imaging technique to the smoldering sample, ultrasonic images of the sample at two periods during its smolder are presented in Fig. 4. Producing a single image requires approximately 10 min due to scanning and data storage limitation rates. Figure 4a corresponds to a period prior to flaming when the smolder front is propagating at 29 cm from the igniter. Fig. 4b corresponds to the sample immediately after flaming; note that combustion is immediately extinguished with a nitrogen purge upon flaming. The shades of gray-scale describe the line-of-sight value of permeability, with white corresponding to virgin foam and black to air (void). The technique provides information about the location of the smolder front and the changes in permeability throughout the char region. The presence of voids is clearly observed in Fig. 4, and further corroborated with visual observation of the char after completion of an experiment.

By scanning in a reduced region, the ultrasonic imaging technique can also be used to obtain the evolution of the char permeability at a particular location in the sample (Fig. 5). The results show that the char continues to react and increase substantially in permeability long after the primary smolder front has passed, confirming that secondary char oxidation is responsible for the formation of the voids.

The high temperatures and varying smolder velocities leading up to flaming (Fig. 3), together with the increase in char permeability (Fig. 5), imply that secondary char reactions are intimately coupled with the primary smolder reaction to provide the driving force for the event. As indicated by the thermocouple histories, the primary smolder front initiates the downward-propagating secondary char oxidation fronts. Local gas sampling, analyzed by gas chromatography, indicates that although the low-permeability char near the smolder front is also an oxygen-limited region, oxidizer can still be transported...
TRANSITION FROM SMOLDERING TO FLAMING

Fig. 6. Gas analyzer data of mixed-aggregate exhaust as a function of time. Note: 3000 s is the time that the igniter is turned off and the air flow is turned on. The forced airflow velocity is 0.75 m/s.

Concluding Remarks

The present work provides additional information about the controlling mechanisms of the exothermicity in the region, although flaming ignition may not yet have occurred. The larger pore size in the char favors gas-phase radical chain reactions; in contrast, the smaller pore size (~200 μm [17]) near the smolder front tends to suppress gas-phase reactions by surface quenching of the free radicals, encouraging solid surface attack of oxygen [1]. These gas-phase reactions in the char can then act to “insulate” the intense heterogeneous reactions occurring at the char surface. Although a localized char surface may be at a high temperature and surrounded by a combustible mixture where gas-phase reactions are occurring, flaming ignition is not requisite. Temperature gradients in a reacting mixture are always accompanied by composition gradients [18]. In the immediate vicinity of the local char surface, the concentration of oxygen will be the lowest (compounded by the fact that surface reactions are competing with gas-phase reactions for oxidizer) and that of the fuel and products will be the highest. Thus, within this localized oxygen-limited region, as long as there exists solid-phase fuel to be reacted, we can expect high temperatures to be reached without transition to flaming. The proposed sudden influx of oxidizer, allowed in by increased permeability of the char, provides the impetus needed for the transition.

Once transition to flaming occurs in the char, flame propagates outward to the interface where it anchors itself and engulfs the entire sample. This phenomenon can be viewed as a true transition from smoldering to flaming because the flames move into virgin fuel, consuming self-generated pyrolysis vapors [5]. As seen from Fig. 6, gas analyzer data of mixed-aggregate exhaust gases show notable increases in CO and CO₂ production as the smolder nears transition to flaming. The aforementioned gas-phase reactions that precede transition to flaming are probably CO burning, Ohlemiller [5] recognizes the importance of the inclusion of this process in any attempt at describing transition from smoldering into flaming. Because of the relatively low temperatures encountered before flaming, the increase in CO₂ production is more likely a result of pyrolytic reactions or low-temperature CO heterogeneous oxidation. Similarly, in experiments on fluidized beds of carbon particles, Purcer et al. [19] observes CO and CO₂ at low temperatures where gas-phase CO oxidation cannot occur; with CO production peaking at 650 K with 50% of the CO₂ being formed at the surface. Hydrocarbon pyrolysis vapor and CO reactions are most likely responsible for the initiation of flaming. Because the spread of the flames over the entire sample is so fast (within seconds), we are confident that a true transition from smoldering to flaming combustion of pyrolysis vapors is occurring.

The present work provides additional information about the controlling mechanisms of
two-dimensional smoldering and its transition to flaming. The experimental results seem to indicate that smoldering with transition to flaming is influenced by the transport of oxidizer and volatiles to the char interior. In the present experiment, transition to flaming is not the result of an accelerating smolder, but of the onset of gas-phase reactions in the char left behind by the propagating smolder reaction. The increasing permeability of the char, which favors the flow of oxidizer to the sample interior, in conjunction with the reduced heat losses, results in the transition to flaming.

The complex chemistry and unclear understanding of heat and mass transfer in porous media make the task of modeling transition from smoldering to flaming a complicated one. Moreover, to describe the transition to flaming, it will be necessary to abandon a spatial-averaging technique and adopt a "single particle" treatment, due to the large voids in the char region. However, the innovative ultrasonic imaging technique employed here to observe the evolution of the char permeability is especially informative concerning char development and void formation. Development of this technique into an ultrasonic tomography of material permeability and temperature field for a smoldering fuel in real time is a goal worth pursuing.

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REFERENCES


COMMENTS

Takashi Kashiwagi, NIST, USA If I understand correctly, you have measured the gaseous composition in the pores of the sample. Do you have any suggestion how flaring is initiated from either CO or hydrocarbons?

What is the control factor which initiates the transition from smoldering to flaming; is it temperature, oxygen, fuel or something else such as residence time in the pores?

Author’s Reply. Oxidizer transport into the hot char region below the smolder front seems to be the controlling factor in the transition to flaming, given that the geometry and size of the sample can allow for reduced heat losses such that void-forming secondary char reactions occur. Extremely localized, high temperature rises (up to 1200°C) within the char region precede flaming by ~100 s. The time scale for this ignition delay is too large to be the induction time normally associated with the ignition of a combustible mixture. However, flaming ignition is not guaranteed, even if a localized char surface may be at a high temperature and surrounded by a combustible mixture; temperature gradients in a reacting mixture are always accompanied by composition gradients. In the immediate vicinity of the local char surface, the concentration of oxygen will be the lowest (compounded by the fact that
surface reactions are competing with gas-phase reactions for oxidizer) and that of the fuel and products will be the highest. Thus, within this localized oxygen-limited region, as long as there exists solid-phase fuel to be reacted, we can expect high temperatures (perhaps even superadiabatic) to be reached without transition to flaming. The sudden influx of oxidizer, allowed by void formation in the char, provides the impetus needed for flaming ignition of CO and hydrocarbon pyrolysis-vapors that are circulating in convection currents within the char.

Dr. Jon Gibbins, Imperial College, UK. Since char void formation appears to be critical for the transition would the authors like to comment on the relative roles of char shrinkage and char combustion (ie removal by heterogeneous combustion) in void production.

Author’s Reply. Both char shrinkage (due most likely to pyrolysis) and char combustion can result in void formation. However, our experiments seem to indicate that char combustion greatly dominates. Thermocouple histories show a primary smolder front that initiates downward-propagating secondary char oxidation fronts. These secondary char oxidation reactions are characterized by higher temperatures than the primary smolder front. In addition, due to the geometry of an exposed foam surface, plenty of oxidizer can be transported to the char interior, favoring combustion versus pyrolysis (of the char).

Richard G. Genn, NIST, USA. This is an excellent piece of work. We are now starting to learn how the evolution of a serious fire hazard can arise. If you were to provide guidance to foam manufacturers as to what to do (or not to do) to their foam to prevent the transition to flaming; what would you tell them?

Author’s Reply. The experiments indicate that transition from smoldering to flaming of flexible polyurethane foam occurs inside the hot char region below the smolder front due to the formation of large voids which provide locations for the onset of homogeneous gas-phase ignition. If foam manufacturers can produce a material, which when smoldered, produces a char that does not continue to react or increase substantially in permeability (via void formation) after the passage of the primary smolder front, then the potential fire hazard would probably be greatly reduced. Furthermore, foam manufacturers should perhaps investigate developing a new material that possesses many of the physical cushioning characteristics of open-celled foams, but with a structure more similar to that of closed-celled foams. Closed-celled materials, although still prone to smoldering due to oxidizer already present within the pores, restrict the flow of ambient/external oxidizer through the material, until the smolder process breaks the cell structure. Consequently, such an extremely low-permeability material would not only impede the flow of oxidizer, but also of pyrolysis-vapors produced by the primary smolder reaction, into the char interior. Finally, a very important aspect of the onset of smolder and subsequent transition to flaming is heat losses to the surrounding environment. Experimental observations suggest that larger sample sizes provide not only more fuel but also better self-insulation, resulting in stronger reaction fronts with less heat losses per unit volume of smolder material to the surrounding ambient. Smaller sample sizes would expose the void-filled char to higher convective heat losses and perhaps quench any heterogeneous or homogeneous reactions. Therefore, the size of the foams should also be considered as an important parameter in terms of transition to flaming potential.