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Natural Convection Smolder of Polyurethane Foam, Upward Propagation

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ABSTRACT

An experimental study is conducted of upward smolder of polyurethane foam in natural convection. The objective of the study is to provide further understanding of the mechanisms controlling upward smolder, and verification of theoretical models of the problem. Measurements of the temperature histories at several locations through the foam sample are used to infer the characteristics of the smolder process, and to calculate the smolder propagation velocity as a function of the location along the sample length and the sample size. Particularly interesting is the observation that in upward smolder there is a transition from an initial smolder process that is characterized by the propagation of a single oxidation reaction (smolder) to one that consists of an endothermic pyrolysis reaction that precedes the smolder reaction. Also interesting is the observation that this change in smolder pattern appears to be generated by the onset of oxidation reactions in the char left behind by the smolder reaction, which deplete the oxygen from the oxidizer gas flow. Since in upward smolder the oxidizer is induced upward in the same direction of smolder propagation, the experimental data are compared with the predictions of previously developed models of forward smolder. The good agreement between theory and experiments verifies that the smolder controlling mechanisms and simplifying assumptions implicit in the models are appropriate at least for the present experimental conditions. This type of smolder is only characteristic of forward smolder, since for the above mechanisms to happen the fresh oxidizer must flow through the char prior to reaching the

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smolder reaction. Also particular to this type of smolder is the transition to flaming since it appears to be generated through the onset of strong oxidation reactions in the char.

NOTATION

C_{p}	Specific heat capacity
\dot{K}	Permeability
g	Gravitational Acceleration
L	Length
n	Number of moles
P	Pressure
Q	Energy released per mass of O ₂ consumed
Q_{p}	Energy of pyrolysis
$Q_{ m p} \ \dot{q}_{ m ig}''$	Heat flux from the igniter
T	Temperature
u_{D}	Velocity induced by natural draft
$u_{\rm g}$	Total average air flow velocity
$ec{U_{ m S}}$	Smoldering velocity
U^{x}	Ratio of experimental to theoretical smolder velocities
X	x co-ordinate
Y	Mass fraction

Greek

δ	Boundary layer thickness
μ	Dynamic viscosity
ϕ	Void fraction
μ	Density
ν	Stoichiometric coefficient

Subscripts

A	Air
C	Cold
CH	Char
F	Foam

- H Hoti InitialO OxygenP PyrolysisS Smoldering
- W Wall

Superscripts

- " Per unit area
- " Per unit volume
- · Per unit time

INTRODUCTION

Smolder is a heterogeneous, surface combustion reaction that takes place in the interior of porous combustible materials. Smoldering is a weakly reacting phenomenon, and the heat released at the reaction is generally low. In spite of this, smoldering has significant importance in fire safety because its combustion products are toxic, it is difficult to detect and can lead to the initiation of flaming fires through the transition from smoldering to flaming.

Smoldering is frequently oxygen limited, and thus the supply of oxidizer to the reaction zone is a controlling factor in smoldering. It limits the overall reaction rate, the amount of fuel reacted, and consequently the rate of heat release. The balance between the rate of heat release at the reaction and the rate of heat transfer from the reaction determines the rate of smolder propagation.²⁻⁵ In smolder the reaction can follow the alternative, and sometimes competing, pathways of endothermic pyrolysis and exothermic oxidation. Oxygen depletion tends to reduce oxidation and favour pyrolysis.⁶ Oxidation is favoured by slow heating, and pyrolysis by high heating rates.³ Thus heating rates and oxygen supply are the two primary mechanisms that determine the characteristics of a smolder reaction.

The transport of energy and species inside the porous medium, is accomplished by diffusion, convection and radiation. In most fire situations convective heat and mass transport through the material interior is by natural convection only. If the fuel is ignited at the

bottom the reaction will propagate upward, in the direction of the buoyantly induced oxidizer flow, thus, the smolder is of the forward type.^{1,7} A practical example of an upward smolder fire is that caused by the heating of attic insulation by a recessed light fixture. In forward smolder the oxidizer reaches the reaction zone after passing through the hot char, and the hot post-combustion gases flow through the virgin fuel ahead of the reaction, pre-heating it. Thus, increasing the oxidizer flow rate increases the oxygen supply to the reaction zone, which enhances it, and increases the fuel pre-heating, which also favours the reaction. However, the post-combustion gases will also tend to dilute the oxidizer inside the pores and thus lower the oxygen concentration ahead of the reaction. 6.8 Furthermore, oxidation of the char may deplete the oxygen in the gas flow. Since the virgin foam will then be heated in a non-oxidising environment, endothermic foam pyrolysis may occur ahead of the smolder front. Another important process that may occur in forward smolder is the transition from the surface oxidation reaction to a gas phase combustion reaction (flaming), which may be caused by the acceleration of the smolder reaction (due to fuel pre-heating) or by the vigorous oxidation of the char. Thus, upward smolder is a complex combustion process that has not only a practical interest in fire research, but also encompasses a number of fundamental combustion problems of interest in other fields.

Considerable work has been conducted to date on smoldering: reviews of the subject can be found in the works of Ohlemiller¹ and Drysdale. Most studies deal with smolder in the opposed configuration and only limited attention has been given to smoldering combustion in the forward configuration. 1,6-11 Forward smoldering of cigarettes (air in-draw) was studied by Summerfield et al, 11 A numerical model using a two-step chemical reaction was developed and compared with reasonable agreement to experimental results. Ohlemiller & Lucca⁶ identified quantitative and qualitative differences between opposed and forward forced flow smolder of different materials. Forward smolder was modelled by Dosanjh & Pagni¹⁰ by using a non-oxidative pyrolysis reaction front followed by a char oxidation front. Torero et al.8 conducting experiments in an aircraft following a parabolic trajectory, made some preliminary observations on the effect of gravity changes on forward smolder of polyurethane foam. The results showed the presence of a pyrolysis reaction preceding the smolder reaction, which under those particular conditions lead to extinction.

In the present work a study is conducted of free convection, upward propagation of a smolder reaction through flexible polyurethane foam, with the objective of determining the controlling mechanisms of

smolder in natural convection. The smolder parameters studied are the smolder velocity and reaction temperature as a function of the fuel height and distance from ignition. The results are compared with the predictions of a previously developed theoretical model of forward smolder propagation to determine the controlling smolder mechanisms.

EXPERIMENT

Experimental apparatus

A schematic diagram of the experimental apparatus is shown in Fig. 1. It consists of a 450 mm long vertical duct with a 150 mm side square cross section, made of insulating 10 mm thick Fiberfax walls mounted on an aluminium frame. The duct is divided into two sections, a top one, 300 mm long, containing the fuel, and a bottom one, 150 mm long, containing the igniter and insulating char. The fuel used in the experiments is a non-fire retarded, open celled, white polyurethane foam, with a $26.5 \, \text{kg/m}^3$ density and 0.975 void fraction. Its thermophysical properties are given in Table 1. The char is from the initial zone of an already smoldered sample, and it is used to insulate the

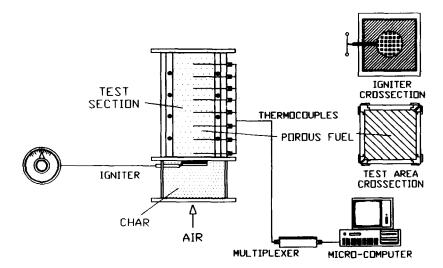


Fig. 1. Schematic of experimental apparatus.

TABLE 1
Properties

$C_{p_A} = 1.088 \text{kJ/kg}$	$n_{\rm C} = 0.755 0 \rm moles$
$C_{p_F} = 1.700 \text{ kJ/kg}$	$n_{\rm H} = 2.872$ moles
$K_{\rm CH} = 8.40 \times 10^{-7}$	$T_{\rm i} = 293 \; {\rm K}$
$K_{\rm F} = 2.76 \times 10^{-9}$	$Y_{O,i} = 0.235$
$L_{\rm C} = 150 {\rm mm}$	$\mu = 1.50 \times 10^{-5} \text{kg/ms}$
W = 150 mm	$\phi_{\rm CH} = 0.977.5$
$Q_1 = 3200 \text{kJ/kg}$	$\phi_{\rm F} = 0.9750$
$Q_2 = 3900\text{kJ/kg}$	$\rho_{\rm CH} = 1.225 \text{ kg/m}^3$
$Q_P = 300 \text{ kJ/kg}$	$\rho_{\rm F} = 1.034 \cdot 0 \mathrm{kg/m^3}$

ignition zone and simulate an ongoing smolder process. Heat losses to the environment play an important role in smolder and the char, if it is not too porous, provides insulation. A gap is set between the char and igniter to avoid the latter initiating an opposed type smolder of the char. Although the char is cold, it partially helps simulate a smolder that has been going on for some time. The igniter consists of a Nichrome wire sandwiched between two, 5 mm thick, porous ceramic honeycomb plates. The onset of foam smoldering occurs only under very restrictive conditions of igniter type, temperature and time.^{2,3} With the present igniter, the foam ignition requires a supply of 1.70 kW/m² for approximately 1800 seconds.

The rate of smolder propagation is obtained from the temperature histories of six to eight, 0.8 mm diameter, sheathed Chromel-Alumel thermocouples embedded at predetermined positions in the porous fuel with their junction placed at the fuel centreline. The smolder velocity is calculated from the time lapse of reaction zone arrival to two consecutive thermocouples, and the known distance between the thermocouples. A more detailed description of the experimental apparatus and procedure can be found in Refs 2 and 7.

Experimental results

The experiments are performed with foam samples of 150 mm side square cross sections and with heights of 150 mm, 175 mm, 200 mm, and 300 mm. The different sample lengths are used to determine the effect of scale on the foam smolder. Examples of the temperature histories

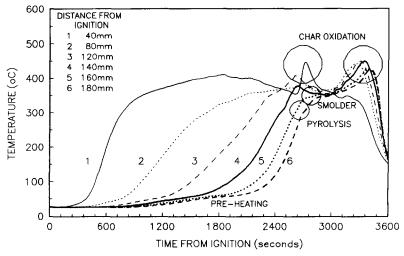


Fig. 2. Temperature histories for six thermocouples, 200 mm sample.

measured during the smolder of a 200 mm and a 300 mm long sample are given in Figs 2 and 3, respectively. The data is characteristic of upward smolder without and with transition to flaming, respectively. A general interpretation of the temperature profiles is as follows: as the smolder reaction approaches the thermocouple location, heat transfer from the reaction to the foam ahead, causes the foam temperature to increase until it reaches a high enough value for the smolder reaction

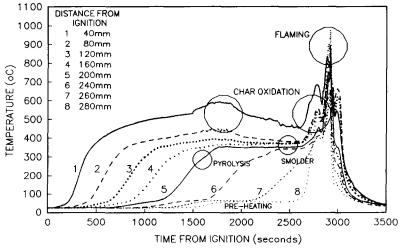


Fig. 3. Temperature histories for eight thermocouples, 300 mm sample.

to start, at which point the temperature starts to level off as the reaction is completed. Under self-propagation conditions, the upward smolder temperature for polyurethane foam is of the order of 360°C. In the region where smolder is assisted by the igniter the smolder temperatures are higher (first thermocouple). Also, since in upward smolder the hot post-combustion gases move ahead of the smolder front, they pre-heat by convection the virgin fuel. This pre-heating effect, which is observable in the temperature profiles of Figs 2 and 3, is however small because of the low density of the gas.

The above description corresponds to a smolder process characterised by the propagation of a single exothermic oxidation reaction (smoldering). In upward smolder it takes place in the lower region of the foam, as is observed in the temperature profiles of Figs 2 and 3 (first three thermocouples). As the smolder reaction propagates upward, both oxidative reactions in the char and pyrolysis reactions in the virgin fuel appear together with the smolder reaction (thermocouple 4 and up).

Smoldering is generally an oxygen limited process, and consequently not all the fuel is consumed by the reaction and a hot char with a large fuel content, susceptible to further oxidation, is left behind. If the char oxidation reaction is vigorous, its presence in the temperature profiles is characterised by a sharp temperature increase followed immediately by a temperature decrease. The temperature decrease indicates the termination of the char oxidation reaction, and is caused by either depletion of oxidizer (the temperature levels off at smolder levels) or depletion of fuel (the temperature drops to ambient levels). Under certain conditions the char oxidation reaction can trigger the transition to flaming, as it is seen in Fig. 3. Transition to flaming appears to occur when the char oxidation reaction is vigorous and shortly after it starts to extinguish due to oxygen depletion. During this extinction period the fuel continues to be pyrolyzed, and when the oxygen is again replenished to levels where a flammable mixture is present in the gas phase, ignition occurs. Once flaming occurs, the whole sample burns quickly to completion and the temperature drops sharply (Fig. 3).

Another specific aspect of upward smolder is the formation of an endothermic pyrolysis reaction preceding the smolder front. Oxidizer depletion by post-combustion gases and char oxidation reactions result in the virgin foam being heated in a non-oxidising environment, which leads to the endothermic pyrolysis of the foam ahead of the smolder front. This mechanism is characterised by the presence of a small plateau at 300°C, product of the endothermic character of the pyrolysis reaction (Fig. 3, thermocouples 4 and up). The pyrolysis reaction and

vigorous char oxidation appear simultaneously (Figs 2 and 3), indicating that the primary mechanism for the generation of a pyrolysis reaction is oxidizer depletion in the char. From the present experiments it appears that the propagation velocity of the pyrolysis and smolder fronts is the same. This is in contrast with the predictions of Dosanjh & Pagni¹⁰ of a pyrolysis front that propagates faster than the oxidation front.

Temperature histories as those in Figs 2 and 3, are used to calculate the smolder propagation velocity. The calculated propagation velocities of the smolder reaction at different locations along the foam sample are presented in Fig. 4 for the different sample sizes tested. Each data point is an average from six tests, and the bars indicate the maximum deviation from the mean. The data of Fig. 4 show that close to the igniter smolder velocities are somewhat elevated and decrease as the reaction propagates away from the igniter. Smolder velocities remain almost constant after the first 50 mm of the sample and increase only slightly as the reaction propagates further in the fuel. Finally, at the upper end of the sample, a strong increase in the smolder velocity is observed. The maximum smolder velocity increases with the sample length, and for experiments conducted with 300 mm samples transition to flaming was consistently observed. No apparent effect of the onset of the pyrolysis reaction on the smolder velocity is observed. The

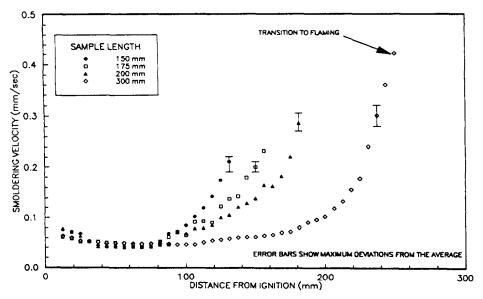


Fig. 4. Variation of the smolder propagation velocity as a function of the distance from ignition, for several sample lengths.

magnitudes of smolder velocities agree with others previously reported.^{6,8}

The rate of fuel consumption increases as the smolder reaction propagates through the foam sample due to the increase in the buoyantly induced flow (see below). As a consequence, the characteristics of the char left behind by the reaction also change along the sample length, from a char with a compact structure in the initial sample region to one with an increasingly open structure toward the end of the sample. In the present experiments, we have not measured the variation of the char void fraction along the sample length. Instead we have limited the measurements to an average value, which is sufficient for the implementation of the model presented below.

THEORY

Modelling of forward smolder has been proved very difficult¹ due to the combined effects of a complex flow structure and chemistry, and the simultaneous onset of pyrolysis and oxidation reactions. Although, it has been thought unrealistic, due to the complexity of buoyantly induced flows in a porous medium, a common simplification is to assume one-dimensional smolder propagation to theoretically predict smolder velocities.¹¹ Since smolder velocities are in general much smaller than buoyantly induced air flow velocities,² for the following analysis, the smolder front is considered quasi-stationary when calculating the air flow velocity. With this assumption an average velocity can be used to determine the oxidizer mass flux for each location along the fuel sample, and consequently a one-dimensional model to correlate the experimental data.

Energy analysis

Previously developed models for forward smolder can be used as the basis for the development of a simplified expression for the upward smolder velocity. Since the experiments show that the pyrolysis reaction does not appear until the smolder has propagated into the middle to upper regions of the foam (Figs 2 and 3), two different analyses are developed to correlate the experimental data. One that considers only char and foam oxidation and that applies in the lower region of the

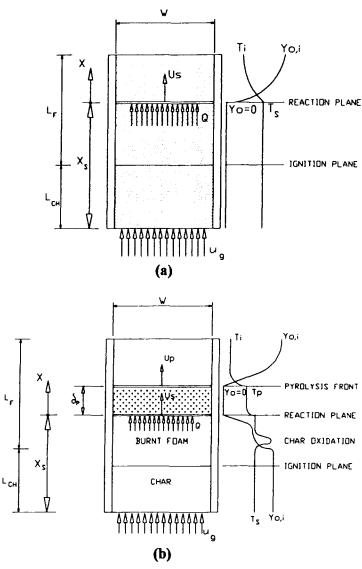


Fig. 5. Schematic of a one-dimensional smolder reaction with the origin anchored to the reaction front for (a) one step reaction and (b) two step reaction.

sample [Fig. 5(a)], and another that considers both pyrolysis of the virgin foam and oxidation of the char/foam and that applies in the middle to upper region of the sample [Fig. 5(b)].

For the initial stages of smolder propagation, before the appearance of fuel pyrolysis, the theoretical model developed by Johnson *et al.*¹² for the forward propagation of a regeneration reaction through a porous

bed of catalyst is applied here. The model is a solution for forward propagation of an exothermic reaction in the absence of pyrolysis as a heat sink. Assuming that the oxidation reaction is described by a one step chemical reaction of the form

$$v_{\rm F}[{\rm FOAM}] + v_{\rm O}{\rm O}_2 \rightarrow v_{\rm CH}[{\rm CHAR}] + v_{\rm gp}[{\rm GAS\ PRODUCTS}] + {\rm Q}v_{\rm O}{\rm M}_{\rm O}$$

where the char is considered as a solid fuel product (not necessarily with the same composition as the reactant fuel) and that the oxidizer entering the upstream edge of the sample is totally consumed at the smolder reaction front, solution of the appropriate energy conservation equation provides the following expression for the smolder velocity.

$$U_{\rm S} = \frac{\rho_{\rm A} {\rm QY_{\rm O,i}} {\rm u_g} + \dot{\rm q}_{\rm ig}''(x)}{[\rho_{\rm A} C_{\rm p_A} \phi_{\rm F} + \rho_{\rm F} C_{\rm p_F} (1 - \phi_{\rm F})] (T_{\rm S} - T_{\rm i}) - (1 - \phi_{\rm F}) Q_{\rho_{\rm A}} Y_{\rm O,i}}.$$
 (1)

For the latter stages of smolder, a pyrolysis front is considered to propagate ahead of the char oxidation front, and a modified version of the model of Dosanjh & Pagni¹⁰ is used here. Assuming a two step chemical reaction consisting of a non-oxidative, endothermic first step (pyrolysis) followed by an exothermic oxidation of the char, as described by

$$v_{\rm F}[{\rm FOAM}] + {\rm Q}_{\rm P}v_{\rm F}{\rm M}_{\rm F} \rightarrow v_{\rm CH}[{\rm CHAR}] + v_{\rm gp}[{\rm GAS\ PRODUCTS}]$$

 $v_{\rm CH}[{\rm CHAR}] + v_{\rm O}{\rm O}_2 \rightarrow v_{\rm gp}[{\rm GAS\ PRODUCTS}] + {\rm Q}v_{\rm O}{\rm M}_{\rm O}$

and solving the one-dimensional energy equation assuming that pyrolysis and smoldering propagation velocities are equal, and that the pyrolysis reaction occurs at a constant temperature, 4.7.9 the following expression for the smolder velocity is obtained

$$U_{\rm S} = \frac{\rho_{\rm A} Q Y_{\rm O,i} u_{\rm g}}{[\rho_{\rm A} C_{\rm p_A} \phi_{\rm F} + \rho_{\rm F} C_{\rm p_F} (1 - \phi_{\rm F})][(T_{\rm S} - T_{\rm i}) - [Q_{\rm p} \rho_{\rm F} + Q_{\rho_{\rm A}} Y_{\rm O,i}](1 - \phi_{\rm F})}.$$
(2)

Unknowns in eqns (1) and (2) are the smolder temperature T_s , the initial temperature T_i , the oxidizer velocity u_g , the heat of combustion for smoldering Q and the heat of pyrolysis Q_p . The smolder reaction temperature is obtained from the experimental data. An integral solution for a semi-infinite slab with constant heat boundary condition^{7,13} is used to calculate the heat conducted by the igniter $|\dot{q}_{ig}^{\prime\prime}(x)|$ and the initial foam temperature $T_i(x)$ as a function of the

distance from the igniter. Away from the igniter influence the initial temperature of the foam is obtained from the measured temperature histories. The heats of oxidation, Q, and pyrolysis, Q_p are not well determined for smoldering combustion. In this work they are selected so that the correlation of the experimental data with the above equation is optimized. The resulting values of Q and Q_p are presented in Table 1. The value of Q that fits the data best is smaller when only oxidation is present (Q_1) than when both pyrolysis and oxidation are present (Q_2) . This difference may be due to the presence of strong char oxidation reactions in the latter case. Both values, however, agree fairly well with those previously reported for smolder combustion. Finally, the velocity u_g must be determined by calculating the potential buoyant flows that can be generated in the duct, foam or char. This is done in the next section.

Oxidizer flux analysis

The mass flux of oxidizer at the smolder reaction zone is a combination of the flow induced upward by natural draft, the boundary layer flow generated at the duct walls by the temperature gradient between the cold walls and the hot char, the oxidizer flux resulting from the propagation of the reaction into the porous fuel, and the diffusion of oxidizer to the reaction zone. Initial estimation of these different fluxes shows that the most important flux is that induced by natural draft through the duct, and that the others have a secondary importance.⁷ Thus, only the former will be considered here.

Natural draft through the duct

The natural draft induced through the porous foam by the density difference between the hot gases in the duct and the cold air outside can be treated as a one dimensional problem where the equation for conservation of momentum is substituted by Darcy's formulation.¹⁴ Making the usual assumptions for Darcy flow,¹⁵ the flow field is described by the following equation

$$u = -\frac{K}{\mu} \left(\frac{\mathrm{d}P}{\mathrm{d}x} - \rho \mathbf{g} \right). \tag{3}$$

Since the virgin foam and the char have very different permeabilities,² this equation is then integrated in two separate regions, the unburned foam region and the char region. By use of the stoichiometric coefficients proposed by Summerfield & Mesina¹⁶ and

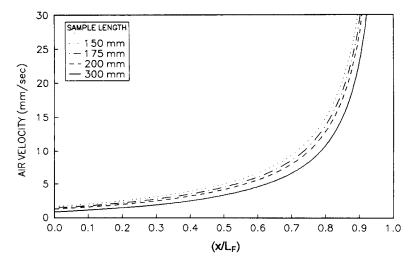


Fig. 6. Variation of the air flow velocity as a function of the distance from ignition, for several sample lengths.

the ideal gas law, the following expression is obtained for the average velocity induced by natural draft through the duct:⁷

$$u_{\rm D} = \frac{g(\rho_{\rm H} - \rho_{\rm C}) \left(\frac{x}{L_{\rm F}}\right)}{\frac{\mu}{K_{\rm F}} \left\{ \left[\left(\frac{1 + L_{\rm CH}}{L_{\rm F}}\right) - \left(\frac{x}{L_{\rm F}}\right) \right] + \left(\frac{K_{\rm F}}{K_{\rm CH}}\right) \left(\frac{\phi_{\rm F}}{\phi_{\rm CH}}\right)^{2/3} \left(\frac{n_{\rm C}}{n_{\rm H}}\right) \left(\frac{T_{\rm S}}{T_{\rm i}}\right) \left(\frac{x}{L_{\rm F}}\right) \right\}} . \tag{4}$$

In the above expression, the char density, porosity and void fraction are taken as their average value. This does not introduce significant errors because the determining factor in the generation of the buoyant flow is the pressure loss through the virgin foam and not through the char, due to the large differences in permeabilities. The resulting variation of the oxidizer flow velocity as the smolder propagates along the sample height is given in Fig. 6. It is seen that the predicted oxidizer flow velocity increases strongly as the smolder reaction reaches the end of the sample.

DATA CORRELATION AND DISCUSSION

The ratio of the experimentally measured and theoretically calculated smolder velocities (U^x) , as a function of the non-dimensional distance from the igniter is presented in Fig. 7. The theoretical smolder velocity is calculated with either eqn (1) or (2), depending on the sample

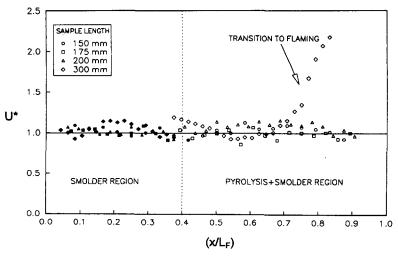


Fig. 7. Correlation of experimental and theoretical smoldering propagation velocities as a function of a non-dimensional distance from ignition.

location, with the oxidizer velocity obtained with eqn (4) and the values of the fuel and oxidizer properties given in Table 1. The experimental data are presented in Fig. 4.

The initial data correlation showed that eqn (1) predicts the smolder velocity very well for $(x/L_E) < 0.4$, but over-predicts the smolder velocity for $(x/L_F) > 0.4$. Similarly, eqn (2) predicts the smolder velocity very well for $x/L_E > 0.4$ (except the transition to flaming), but under-predicts it for smaller distances. These results verify the presence of the two modes of upward smolder propagation described above. In the early stages, smolder is characterised by the presence of only an oxidation reaction. On the other hand, in the later stages the process is characterised by the presence of both a pyrolysis and an oxidation reaction. It is interesting to note that independently of the sample length, the change in the applicability of eqns (1) and (2), always occurs at a fixed value of $x/L_{\rm F}$ (approximately 0.4). The flow rate of oxidizer for $x/L_F \approx 0.4$ is approximately constant for all values of L_F suggesting that this result is related to the oxidizer flow rate. A possible explanation is that a pre-determined flow rate of oxidizer is necessary for the onset of the char oxidation reactions that seem to precede the appearance of the pyrolysis reactions, and consequently the change in applicability of eqns (1) or (2).

Equations (1) and (2), can also be used to explain some of the above indicated experimental observations. For example, in the zone near the igniter, the corresponding increase in the heat flux and in the foam

temperature appears in eqn (1) through $\dot{q}''_{ig}(x)$ and $T_i(x)$. Since in this zone they decrease with the distance from the igniter, and u_g is approximately constant, eqn (1) predicts a smolder velocity that decreases as the smolder propagates away from the igniter, as observed experimentally (Fig. 4). After the first 50 mm, the igniter effect is no longer important, and as is seen from Fig. 6, the oxidizer flow rate increases only slightly with the distance from the igniter. Thus, according to eqns (1) and (2) the smolder velocity should increase only weakly. Toward the end of the sample the oxidizer supply increases sharply (Fig. 6), and as predicted by eqn (2) the smolder velocity increases sharply (Fig. 4).

For the experiments where transition to flaming was observed, the model predicts the smolder propagation velocities well until $(x/L_{\rm F})=0.7$, but then under-predicts the smolder velocities. Modelling the events leading to the transition to flaming requires the study of both the solid and gas phases, including the onset of the gas phase ignition, which escapes the scope of the present work.

CONCLUDING REMARKS

The present experimental observations have provided further understanding of the mechanisms controlling upward smoldering, and have helped to verify currently available models of the process. They have also provided information of practical interest in fire safety.

In upward smolder there is a transition from an initial smolder process that is characterised by the propagation of a single oxidation reaction (smolder) to one that consists of an endothermic pyrolysis reaction that precedes the smolder reaction. This change in smolder pattern appears to be generated by the onset of oxidation reactions in the char which deplete the oxygen from the oxidizer gas flow. This type of smolder is only characteristic of forward smolder, since for the above mechanisms to happen the oxidizer must flow through the char prior to reaching the smolder reaction. Also particular to this type of smolder is the transition to flaming since it appears to be generated through the onset of strong oxidation reactions in the char.

The fact that simple, heat transfer based, theoretical models of the problem are able to predict well the smolder propagation velocity, does not imply that chemical kinetics are not important, but only that the problem is controlled by the rate of heat realeased (and absorbed) by the reactions. The heat released is the result of complex thermochemical reactions, and in this work, it is not calculated but selected to

maximise the fitting of the data with the theory. Furthermore, the models have the implicit assumption that all the oxidizer is consumed by the fuel and char oxidation reactions. Thus they will not be able to predict smolder under conditions where there is leakage of oxidizer through the reaction, i.e. weak or near extinction smolder.

Particular aspects of the present experimental observations that have a direct fire safety application are those observations regarding minimum conditions for smolder initiation, production of toxic species and the transition to flaming. Heat losses to the environment are a major deterrent for smolder self propagation. Our experiments indicate that for the polyurethane foam used, samples with widths larger than 150 mm are necessary in order for the smolder to self propagate (the ratio of heat losses through the perimeter to heat generated at the reaction decreases as the perimeter is increased). Natural induced air flows through the sample seem to provide enough oxidizer to sustain smolder, although as the sample length is increased, and less air flows initially through the sample, larger heating times are necessary to initiate smolder. The gaseous smolder products condense inside the virgin foam as they flow ahead of the reaction front, and significant quantities of products are not observed to flow outside the sample until the reaction reaches the last 50 mm of the sample. Transition from smolder to gaseous flaming does not occur for samples with lengths smaller than 250 mm.

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