

A Combustibility Study of the Gaseous Pyrolysates Produced from Some High-Performance Fabrics*

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Synopsis

The flammability limits of the gaseous pyrolysates obtained from a series of conventional, flame-retarded, and high-performance textile fabrics have been measured, and the results compared. These data have been utilized to develop a fire hazard index associated with the ignitability and combustibility of the gaseous products of thermal degradation as a result of exposure to a high radiative thermal fire load. Generally, it was found that the high-performance fabrics behaved better than the flame-retarded fabrics, which themselves were superior to untreated materials.

INTRODUCTION

High-performance fibers, because of their exceptional physical properties, have found extensive usage in a wide number of applications both alone and in combination with other materials as reinforcement. Examples of areas of application include automotive, aerospace, electrical, electronic, aviation, and consumer product markets. Because high performance fibers are normally associated with the characteristics of thermal stability and flame resistance, they usually have little difficulty meeting the flammability requirements issued by the various regulatory agencies. However, owing to the increased utilization of these polymeric materials in commercial aircraft and the possible increased hazard they may pose in a post-crash fire, there is a need to examine the potential fire hazard associated with these materials using a laboratory scale apparatus under severe fire exposure conditions.

Although the thermal and flammability properties of these materials have been evaluated using a variety of techniques, most relate to parameters measured under low radiative heat flux conditions. The oxygen index is one such test which has been widely used to rate these materials in terms of ease of ignition or extinguishment^{1,2} along with measurements of char yield.^{2,3} However, like the majority of fire tests, the results are not an intrinsic property of the material, since they are dependant upon sample size, geometry, and density.⁴⁻⁶ Despite these limitations, the test can provide valuable information regarding certain aspects of the flammability of a material. For materials which are designed to withstand high temperatures, the effect of temperature on the oxygen index should be considered.^{6,7} In fact, it has been suggested⁸ that a temperature index (defined as the temperature at which the oxygen index of a material is coincident with the percentage of oxygen in air) provides a more meaningful measure of the performance of a material in a real fire situation.

The ignition process is known to be a very complex phenomenon dependent

* Issued as NRCC #21348.

upon many physical and chemical processes. In order to obtain ignition of a solid polymer, it must first be heated to a sufficiently high temperature that the material decomposes to give combustible gaseous products since flaming combustion is usually a gas phase process. However, before this gaseous fuel can ignite, it must be mixed with air (or another oxidizing atmosphere) to form a combustible fuel/air mixture. If insufficient fuel is produced per unit time, such that the lower flammability limit of the gaseous fuel is not exceeded, ignition and subsequent combustion will not occur. Likewise, if the concentration of gaseous fuel in air exceeds the upper flammability limit to give a fuel rich mixture, ignition will not be obtained. These flammability limits of a gaseous fuel serve as an indication of the ignitability and combustibility of the degrading polymer under a set of defined experimental conditions. Although flammability limits of polymer pyrolysates, like the oxygen index, are not an intrinsic property of a material, it is felt that they offer another useful value in quantifying the potential fire hazard of a material. However, any experimental values obtained for the flammability limits of a polymeric material are going to be dependent upon such factors as sample size, air volume, heating rate, sample geometry, ignition source, and temperature.

The value and usefulness of determining the flammability limits of polymer pyrolysates has been demonstrated by Brown and Comeford⁹ and Fewell,¹⁰ who used a technique which measured the flash-fire propensity of the combustibles generated during the thermal degradation of materials under specific test conditions. In terms of relevance to real fire situations, the importance of evaluating flammability limits (or flash fire propensities) can be appreciated by considering a compartment containing so-called "nonflammable materials." An example could be an aircraft cabin interior. Statistics indicate that the most likely fire occurrence would be a post-crash situation typically involving breakage of the fuselage and ignition of ruptured fuel tanks outside of the cabin. In this scenario, the cabin interior materials are subjected to an impressed heat load, which, depending on the severity of the fire, is capable of causing degradation of the materials to give rise to the buildup of gaseous pyrolysates within the cabin. Ignition of these pyrolysates and the development of a flash fire is going to be a factor in the safe evacuation of passengers within the cabin. The usage of interior materials with greatly reduced ignitability and combustibility can therefore increase fire safety in a post-crash situation.

In this study, we have attempted to assess several materials in terms of the potential fire hazard they could pose in a developing fire situation, such as the one described above. Although our main objective was to compare the performance of the high-performance fabrics, several conventional fabrics have been included in our investigation and comparisons made with results obtained in an earlier study.¹¹

EXPERIMENTAL

Materials. The fabrics used in this investigation are listed in Table I. All the fabrics, which were obtained from a variety of sources, were used as received without further treatment.

Apparatus and Procedure. The flammability limit determinations were carried out using the equipment and method described in detail in an earlier

TABLE I
Fabrics Tested

Fiber	Type	Source	Weight (g/m ²)
Polyester	Spun woven fabric	Test Fabrics Inc. Style 767	127
Cotton	100% bleached sheeting	Test Fabrics Inc. Style 405	176
FR Cotton	Proban-treated curtain fabric	Dominion Textiles, Ltd.	187
Wool	Worsted flannel	Test Fabric Inc. Style 523	193
Zirpro wool	Worsted flannel	International Wool Secretariat	247
Nomex	Twill	Lincoln Fabrics	200
Kevlar	Woven fabric	E. I. DuPont de Nemours	290
Kynol	Needled nonwoven	American Kynol Inc.	146
Enkatherm	Worsted fabric	Enka Glanzstoff	247

paper.¹² All previous studies with this equipment¹¹⁻¹⁴ have employed a lamp voltage of 80 V, which gave an incident radiative heat flux intensity at the sample of about 13.25 W/cm². Employing these conditions, it was not possible to obtain results for Nomex fabrics.¹¹ In this present study, it was therefore decided to employ a higher lamp voltage of 100 V, which gave an incident flux at the sample of 18.5 W/cm². Attempts to employ even higher fluxes were unsuccessful due to problems with the thermal stability of the mica windows. The platinum/platinum 10% rhodium thermocouple was also replaced with a 41-gauge tungsten 5% rhenium/tungsten, 26% rhenium thermocouple.

RESULTS AND DISCUSSION

Operation of the test equipment with a higher lamp voltage resulted in the samples being exposed to higher degradation temperatures than those employed in our previous study.¹¹ In Figure 1, the actual sample temperatures in this study are compared to those obtained previously. It will be noted that while sample temperatures of the order of 230–330°C were obtained previously, the higher

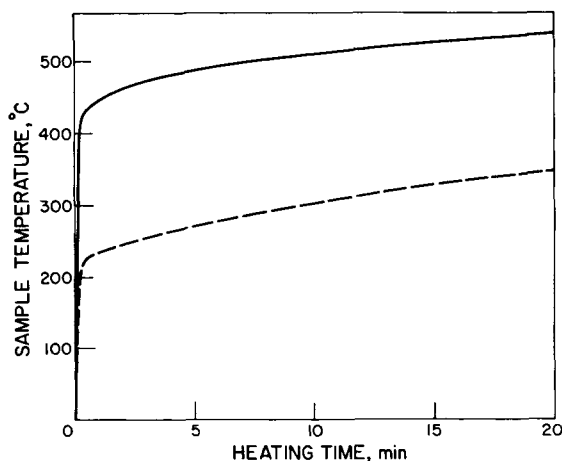


Fig. 1. Sample temperature as a function of heating time when employing lamp voltages of 100 V (—) and 80 V (---).

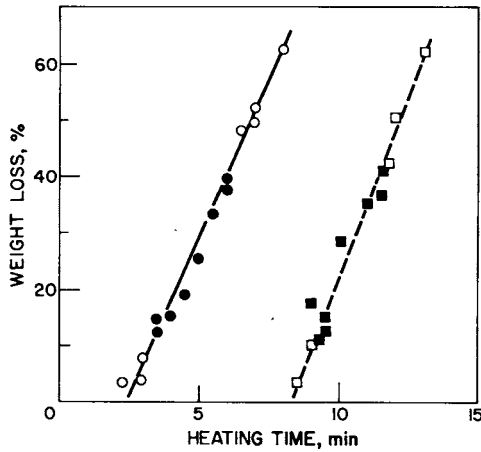


Fig. 2. Percentage weight loss values for polyester fabric on heating with lamp voltages of 100 V (O) and 80 V (□) with combustible mixtures denoted ● and ■, respectively.

lamp voltage of 100 V produced temperatures in the 430–520°C range, sufficient to decompose most high-performance fibers.

In view of the fact that a large amount of data has already been obtained in our laboratories with the polymer poly(ethylene terephthalate) (PET), it was decided first to compare data employing the new conditions with those obtained in a previous study¹¹ using the less severe heating conditions.

These results are presented in Figures 2 and 3, which indicate the weight losses

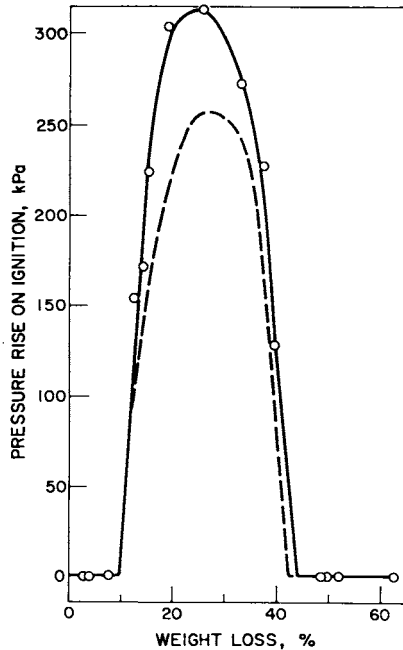


Fig. 3. Pressure rise on ignition noted for polyester fabric as a function of percentage weight loss. Results obtained with 80 V lamp setting shown (---).

as a function of heating time and pressure rises on ignition at the various weight losses, respectively. As would be expected, shorter heating times were required with the higher lamp voltage than were required for the lower voltage setting in order to obtain corresponding weight losses. Interestingly, however, the determined flammability limits were almost identical for the two sets of heating conditions. This suggests that in terms of chemical composition, the pyrolysates produced are very similar in both sets of experiments. The similarity of the weight loss/heating curves would also suggest similar degradation mechanisms in both cases, as would be expected in the production of a consistent fuel. Although the flammability limits were the same in the two determinations, there was a difference in the pressure rise obtained on ignition, with the high voltage experiments giving consistent higher values for a given weight loss value. It has been our contention¹¹ that the values obtained for the lower flammability limit, the flammability range (difference between the upper flammability limit and the lower flammability), and the pressure rise on ignition provide fundamental information on the ignitability, combustibility, and heat output, respectively. Thus, in terms of the pyrolysate produced on degrading PET, the ignitability and combustibility are unaffected by pyrolysis temperature while there is an increase in the heat output on combustion.

The results obtained with the untreated cotton sample are presented in Figures 4 and 5, which once again include a comparison of the low voltage and high voltage experiments. Once again, as was observed with the PET samples, the flammability limits obtained in the two sets of experiments were very similar, and the pressure rise on ignition was higher in the experiments performed with the higher lamp voltage. It would therefore appear that the degradations of both the polyester and the cotton fabrics are not overly sensitive to changes in flux intensity from 13.25 W/cm^2 (with the 80 V setting) to 18.5 W/cm^2 (with 100 V setting).

Also included in Figures 4 and 5 are the results obtained with a flame-retardant

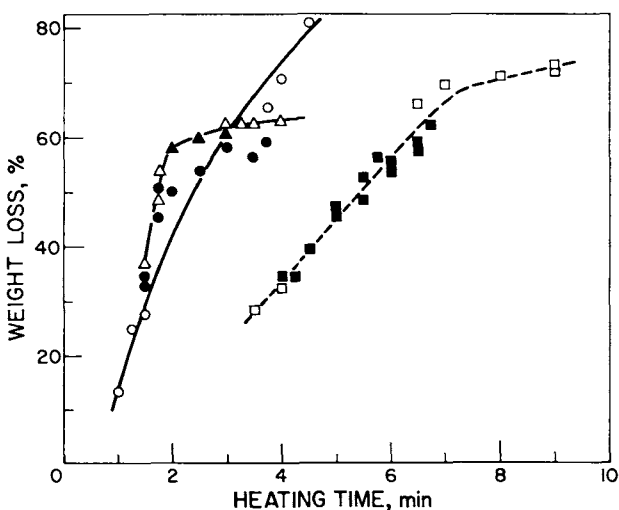


Fig. 4. Percentage weight loss values for cotton (O) and flame retarded cotton (Δ) as a function of heating time with the combustible samples denoted \bullet and \blacktriangle . Results of the cotton sample obtained with 80 V lamp setting denoted \square and \blacksquare .

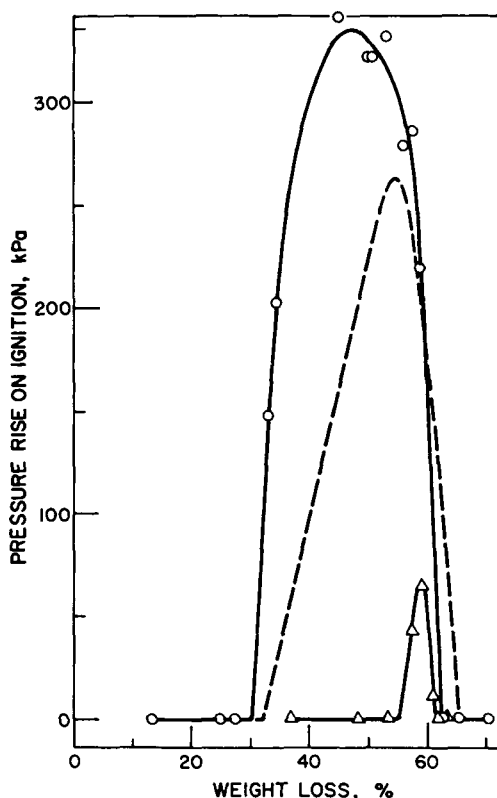


Fig. 5. Pressure rise on ignition for cotton (O) and flame retarded cotton (Δ) samples as a function of percentage weight loss. Cotton results obtained with a 80 V lamp setting shown (---).

cotton fabric employing the higher voltage setting only. Examination of Figure 4 immediately reveals that the flame-retardant cotton has an initial weight loss greater than that of the untreated cotton, but as the degradation proceeds, greater char formation occurs resulting in a pronounced leveling off of the weight loss at about 60%. This observation is consistent with generally accepted theories of flame-retarding cotton due to enhancement of carbonaceous char formation.¹⁵ In terms of combustible material liberated by the degrading flame retarded cotton, Figure 5 clearly indicates that there is a dramatic increase in the lower flammability limit and substantial reduction in the pressure rise on ignition due to the presence of the flame retardant. These observations demonstrate the ability of this flame-retarding system to reduce markedly the ignitability of the gaseous pyrolysis products produced by the cotton and at the same time to be responsible for a reduction in the energy release on combustion. These findings therefore appear to confirm the mechanistic action proposed in other studies of flame-retardant cotton systems in which the fuel-producing reactions are being reduced in favor of the char formation processes.¹⁵

Wool is generally regarded as a material which poses a low flammability hazard; however, in recent years flame-retardant treatments have been developed to extend its area of utilization, especially in the transportation field. The behavior of untreated wool and wool commercially treated by the Zirpro process^{16,17}

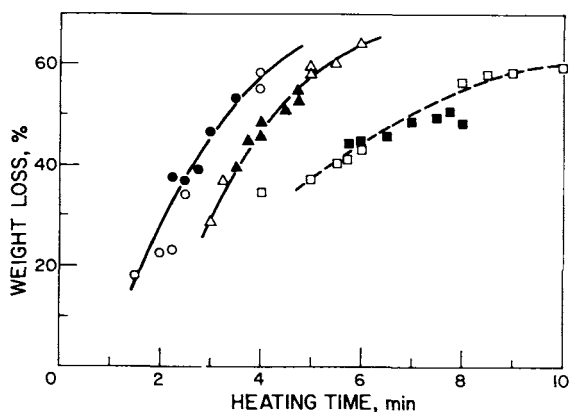


Fig. 6. Percentage weight loss values for wool (O) and Zirpro wool (Δ) as a function of heating time, with the combustible samples denoted \bullet and \blacktriangle . Wool results obtained with a 80 V lamp setting denoted \square and \blacksquare .

are given in Figures 6 and 7. The untreated wool sample was also examined at the two heat flux profiles as were the polyester and cotton samples. However, unlike these two materials, the untreated wool showed marked differences in behavior under the two sets of experimental conditions. Not only were the shapes of the degradation curves different (Fig. 6) but so were the pressure rise curves (Fig. 7). The nonsimilarities in the shape of the weight loss curves as a function of heating time would suggest that the actual mechanism of degradation under the two sets of conditions are different, leading to the production of a different gaseous fuel mixture. This latter point is supported by the observed changes in the flammability limits. Comparison of the behavior of the treated wool and the untreated sample indicates close similarities in their weight loss curves and actual limits of flammability. The Zirpro wool sample does, however,

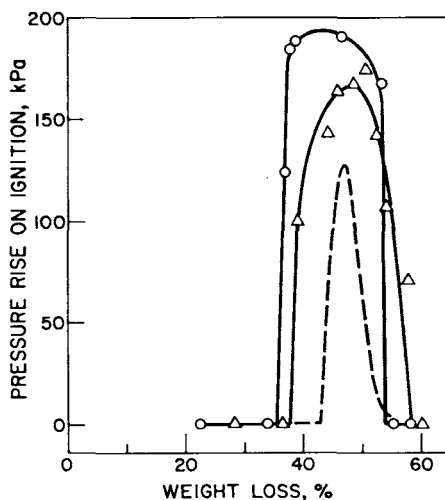


Fig. 7. Pressure rise on ignition for wool (O) and Zirpro wool (Δ) samples as a function of percentage weight loss. Wool results obtained with a 80 V lamp setting shown (---).

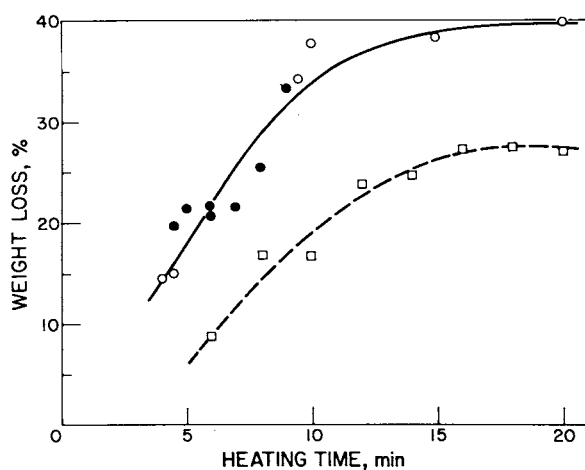


Fig. 8. Percentage weight loss values for Nomex heated with a lamp voltage of 100 V (O) and 80 V (□) with combustible samples denoted ●.

show a slightly delayed degradation, indicating its greater thermal stability while also showing a slightly higher lower limit than the untreated sample, indicating reduced ignitability. The energy release on ignition was also slightly reduced for the treated sample. It can therefore be concluded that, in all parameters, degradation time, lower limit, and energy release show beneficial effects of the flame-retardant treatment.

Nomex was examined in our previous study¹¹ employing the lower heater setting, but no combustible gas mixtures were obtained. It was therefore concluded that this material was too thermally stable to obtain a flammable gas/air mixture. It was therefore a little surprising to find in the present study (see Figs. 8 and 9) combustible gas mixtures at weight loss values as low as 20%, values exceeded in the previous investigation. This suggests that, for a particular weight loss condition, the gaseous pyrolysates obtained under the two conditions are

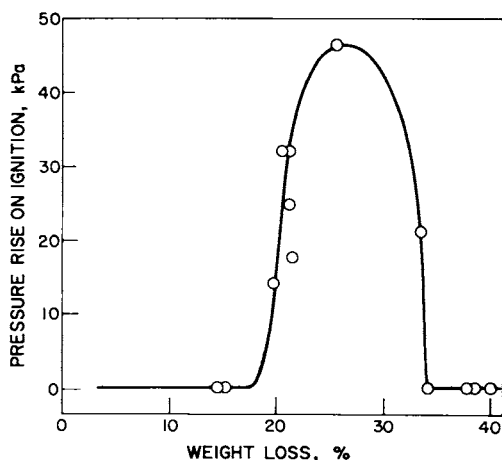


Fig. 9. Pressure rise on ignition for Nomex as a function of percentage weight loss.

different since in one case a flammable mixture is obtained and in the other case it is not. However, it is possible that, because of the higher temperature being employed in the higher lamp voltage experiments, the gas composition could be similar, and yet the reason for combustion is associated solely with the temperature effect, which is capable of causing a widening of the flammability range as the temperature increases.¹⁷ The lower flammability limit actually observed for the Nomex is, however, rather low in comparison with the data obtained with the wool and cotton samples, indicating the gases evolved have a higher ignition potential. However, in terms of the heating time to achieve a flammable mixture, the value is greater for the Nomex than wool or cotton, indicating its greater thermal stability. The energy release (i.e., pressure rise on ignition) is also small in the case of Nomex, indicating that it has a small heat feedback effect upon the continued combustion cycle.

The weight loss/heating time curves for the other three fabrics examined are presented in Figure 10. It will be noted that, at the high heat flux condition employed in this study, all the materials showed appreciable weight losses, especially the Enkatherm sample, which rapidly degraded to an approximate 50% weight loss value before leveling off. However, despite the relatively large amounts of gaseous pyrolysates produced from these systems, only the Kynol fabric was observed to give a combustible pyrolysate/air mixture with the associated pressure rises on ignition, as presented in Figure 11.

The behavior of the Kevlar fabric was very much as expected in that it showed an almost linear dependence of weight loss on heating time, which was the least of all the fabrics studied in this investigation. The greatest surprise was the rapid weight loss observed with the Enkatherm fabric whose behavior was very similar to that of the untreated cotton (see Fig. 4). However, in spite of the formation of large amounts of gaseous pyrolysates, no combustible pyrolysate/air mixtures were noted.

The formation of combustible pyrolysate/air mixtures with the Kynol samples especially at low percentage weight loss values were rather surprising. This finding suggests that, in terms of ignitability, the Kynol samples do not provide a significant safety factor under these high heat conditions. In terms of energy

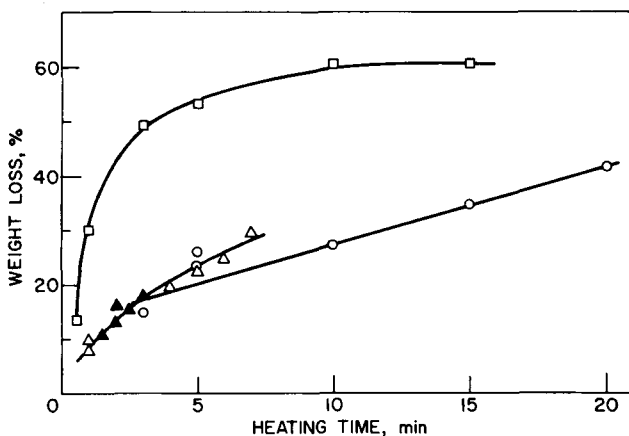


Fig. 10. Percentage weight loss values for Kevlar (O), Enkatherm (□), and Kynol (Δ), with combustible samples denoted ▲.

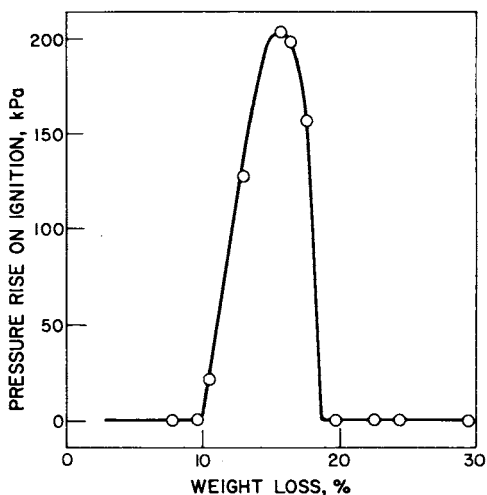


Fig. 11. Pressure rise on ignition for Kynol as a function of percentage weight loss.

release, Kynol also showed rather large pressure rises on ignition, indicative of a large heat feedback potential as a result of the combustion process.

In terms of evaluating the relative performance of the materials examined in this study, it is essential to consider all the data and not just one parameter in isolation. This study has provided data on several aspects of the ignition, combustion, and heat release potential of several materials on exposure to high radiative heat loads. In terms of ignitability, a material which produces a combustible pyrolysate/air mixture at relatively small weight loss values (corresponding to low degrees of thermal degradation) is going to be potentially more hazardous than one which has to be heated to higher degrees of degradation (i.e., high weight loss values) in order to obtain a combustible pyrolysate/air mixture. However, it should not be forgotten that the process of producing the gaseous pyrolysate is a dynamic process, and, consequently, the actual heating time to obtain a combustible pyrolysate/air mixture is also important. For example, in a burning room the time between fire initiation and flashover is a critical factor in determining safe egress time. The greater the time for the generation of a combustible/air environment in a burning room situation, the greater will be the time for safe escape. Consequently, in terms of our experimental situation, the greater the heating time for the pyrolysate to reach the lower flammability limit, the safer will be the material in a preflashover fire situation, all other factors being equal. In terms of the overall combustibility of the pyrolysate being produced from a given material, the actual flammability range is a useful parameter. For example, if the nature of the gaseous pyrolysate being produced is such that it is flammable only over a very narrow flammability range, it will pose less of a hazard than a material which has a wide flammability range. This arises since on heating and degradation a material with a narrow flammability range produces a gaseous pyrolysate which rapidly passes from being fuel-lean to one which is fuel-rich, both situations in which no ignition can be obtained. This in part explains why hydrogen with flammability limits of 4–70% is regarded as being more hazardous than methane with flammability limits of 1.8–8.4%¹⁸ despite the smaller lower flammability of the latter material. The importance of heat

feedback from the combustion process to the solid phase decomposition processes cannot be overlooked in understanding the burning process as a whole. In order for the burning process of a material to be self-supporting, the heat feedback has to be sufficient to maintain an adequate supply of gaseous fuel for the combustion process (assuming an adequate air supply). The pressure rise on ignition has been shown to be a useful measure of this heat feedback potential. In terms of ranking materials, those with low pressure rises are judged to be safer than those with large pressure rises on ignition.

Having established the importance of four parameters—lower flammability limit, heating time to lower limit, flammability range and pressure rise on ignition—as being important in any evaluation scheme, it therefore remains to combine them into some relationship to come up with a hazard index assessment. To facilitate the establishment of such an index, it was decided to follow a simplistic approach in which each parameter would be assigned a value 0–100 (0 best and 100 worst) and then all four values for a given material would be given equal weight in evaluating the composite index.

For the lower flammability limit, since it is recognized that a material with a value of 0.1% represents a greater hazard than one with a value of 99.9%, it was decided to subtract the % weight loss at the lower flammability limit from 100 to give the ignition index I , i.e.,

$$I = 100 - \% \text{ wt loss at lower flammability limit}$$

In view of the fact that all samples examined in this study which gave combustible gas/air mixtures did so at heating intervals of 5 min or less, it was decided to choose 5 min as the ideal case. The heating time index (H) was then calculated using the following expression:

$$H = 5 - \frac{[\text{minimum heating time (min) to obtain lower flammability limit}]}{5} \times 100$$

The flammability range expressed as the difference between the upper and lower flammability limits was used directly as the index value F for the flammability range, i.e.,

$$F = \% \text{ wt loss at upper limit} - \% \text{ wt loss at lower limit}$$

In order to get an energy feedback index (E), a value of 500 kPa was arbitrarily chosen to represent the worst case situation. The index E was then determined using the following expression:

$$E = \frac{\text{max pressure rise on ignition (kPa)}}{500} \times 100$$

The overall composite fire hazard index (FHI) was then calculated as follows:

$$\text{FHI} = \frac{I + H + F + E}{400} \times 100$$

The values obtained for the materials examined in this study are presented in Table II along with the basic data used in their evaluation. The general overall classification of the fibrous materials presented in this table follow the anticipated behavior one would expect based upon their performance in other flam-

TABLE II
Summary of Data and Calculated Flammability Hazard Index (FHI)

Fiber	Flammability limits (% wt loss)		Flammability range (% wt loss)	Max pressure on ignition (kPa)	Min heating time (min)	FHI
	Lower	Upper				
Cotton	30.3 ± 2.8	62.2 ± 3.5	31.9	336	1.5	59.7
Polyester	9.9 ± 2.3	44.0 ± 4.3	34.1	313	3.5	54.2
Kynol	10.1 ± 0.4	18.7 ± 1.0	8.6	203	1.5	52.3
Wool	35.4 ± 1.5	54.2 ± 0.9	18.8	194	2.4	43.6
Zirpro wool	37.9 ± 1.4	56.0 ± 0.2	18.1	168	3.5	35.9
F.R. cotton	55.5 ± 2.1	61.2 ± 0.6	5.7	65	2.0	30.8
Nomex	17.5 ± 2.2	33.9 ± 0.4	16.4	46	4.5	29.5
Enkatherm	—	—	—	—	—	—
Kevlar	—	—	—	—	—	—

mability tests with the possible exception of Kynol. However, it should not be forgotten that the flammability evaluations being made in this particular study are specific to high heat flux conditions. Thus while Kynol may not pose a strong fire threat under normal ambient conditions, its ignitability, combustibility and heat output under fully developed fire conditions, such as a post-crash fire situation, could possibly pose potential fire problems.

CONCLUSIONS

This study has attempted to identify the potential fire hazard of certain materials in a developing fire situation. The results obtained have enabled a fire hazard index to be calculated in order to compare certain aspects of the burning behavior of these materials under high radiative flux conditions. The indices calculated by this method, however, only consider specific aspects of threat to life while neglecting others such as toxic gases and smoke. It is possible, nevertheless, that the technique described may prove useful in understanding the complex processes that occur in the combustion of polymeric materials.

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Received November 1, 1982

Accepted June 18, 1983