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FIRE HAZARD EVALUATIONS OF MINE MATERIALS IN A SMALL-SCALE COMBUSTIBILITY APPARATUS

Contract J0395125
Factory Mutual Research Corporation
1151 Boston Providence Turnpike
Norwood, Massachusetts 02062

BUREAU OF MINES
UNITED STATES DEPARTMENT OF THE INTERIOR

FINAL REPORT

FIRE HAZARD EVALUATIONS OF MINE MATERIALS IN A SMALL-SCALE COMBUSTIBILITY APPARATUS

Prepared for
U. S. Bureau of Mines
Pittsburgh Research Center
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16. Abstract

Combustibility data are presented for 14 samples representing commonly used mine materials (treated and untreated wood, conveyor belt and brattice cloth). The combustibility data were obtained in the Factory Mutual Small-Scale Combustibility Apparatus (sample area ~0.008 m^2).

The hazards associated with the mine materials were evaluated in terms of: 1) ignition/surface flame spread using an ignition parameter (IP). A reasonable correlation was found between IP values and U.S. Bureau of Mines ratings for conveyor belts and brattice cloth and large-scale fire test data for treated and untreated timber sets; 2) generation of combustible vapors, using a vapor generation parameter (VP); 3) heat release using a heat generation parameter (HP). A reasonable correlation was found between HP values and the large-scale fire test data for treated and untreated timber sets; 4) generation of "smoke," toxic and corrosive products using a chemical compound generation parameter (CP); and 5) light obscuration by "smoke" using the light obscuration parameter (LP).

All the wood treatments, except Fireguard, were found to be effective in reducing the fire hazard. The effectiveness of the treatment appears to be due to enhancement of carbon formation in the solid phase and enhancement of water formation in the vapor phase.

Concepts are presented for establishing 1) the relationship between various parameters (IP, VP, HP, CP, and LP) and basic properties of materials, and 2) the usefulness of the parameters as criteria for the combustibility and fire hazard evaluations of the mine materials.

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Combustibility of mine materials, fire hazards, combustibility ratings, correlations between small- and large-scale fire tests, treated/untreated wood, conveyor belt, brattice cloth.

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FOREWORD

This report was prepared by Factory Mutual Research Corporation, Norwood, Massachusetts under U.S. Bureau of Mines Contract No. JO395125. It was administered under the technical direction of the U.S. Bureau of Mines Pittsburgh Research Center with Dr. F. J. Perzak as Technical Project Officer and Mr. Patrick J. Neary as the contract administrator. This report is a summary of all work completed under this contract during the period July 12, 1979 to July 31, 1982. The report was submitted by the author on June 25, 1982.

The author gratefully acknowledges Mr. S. D. Ogden of the Factory Mutual Research Corporation for performing the experiments. Numerous technical discussions with Dr. F. J. Perzak of the Pittsburgh Research Center, the technical project officer are deeply appreciated.

SUMMARY

The objective of this study was to evaluate fire hazards associated with representative mine materials using a small-scale combustibility apparatus.

The experimental approach taken in the study was based on the concepts which have been developed at the Factory Mutual Research Corporation (3-15). Combustibility of materials is evaluated under the following simulated large-scale fire conditions: 1) fire environment (external heat flux and flame radiative heat flux); 2) ventilation (over- and underventilated fires); and 3) generic nature, shape, size and arrangement of the combustibles. Interactions between fire environment, ventilation, and combustibles are quantified for the evaluation of the fire hazards and protection from the hazards.

In this study 14 samples were tested representing commonly used mine materials (treated and untreated wood, conveyor belt and brattice cloth). The apparatus selected for the tests was the Factory Mutual Small-Scale Combustibility Apparatus with a ~0.008 m^2 sample area. The data obtained from this apparatus and predictions of the data for large-scale fires have been successfully validated for various combustibles (polymethylmethacrylate, polystyrene, polyurethane foam in corrugated paper cartons, heptane, methanol, transformer fluids, and treated and untreated timber sets) (4-6,14).

In this study, only external heat flux was used as a variable for overventilated fire conditions. For correlations with other tests, data were used from 1) the large-scale fire tests for treated and untreated timber sets in the simulated mine gallery; 2) the U.S. Bureau of Mines fire resistance test method for conveyor belts (26); 3) the Ohio State University Apparatus (26), and 4) the stagnation burner test (25).

For the evaluation of fire hazards, the following parameters were used:

1. Ignition Parameter (Appendix B)

Critical heat flux is defined as a flux below which piloted or autoignition is not expected to occur. Ignition parameter (IP) is the inverse of ignition energy (external heat flux x time to ignition). The smaller the value of critical heat flux and the larger the value of IP, the shorter is the time to ignition and the faster the surface flame spread, and, thus the higher the fire

hazard expected. All the wood treatments were found to be effective in increasing the critical heat flux value and reducing the IP values for piloted ignition. Analysis of the literature data and data from this study suggests that the effectiveness of the wood treatment appears to be due to enhancement of carbon formation in the solid phase.

The average critical temperatures for fire propagation for untreated and treated Douglas fir timber sets in the large-scale gallery fire tests were measured to be 660 K and 770 K respectively, compared with values of 660 K and 760 K respectively obtained from the small-scale tests.

The U.S. Bureau of Mines ratings for untreated and treated styrene-butadiene, German-X and -Z conveyor belt samples were 16, 1, 0, and 0 respectively* (26,27), compared with IP values of 2.1×10^{-3}, 1.0×10^{-3}, 0.50×10^{-3}, and 0.50×10^{-3} m^2/kJ respectively. The U.S. Bureau of Mines ratings** for brattice cloth samples 1280A, 1620, 1688, and 1580 were 6, 5, 4, and 1, respectively (27), compared with IP values of 1.7×10^{-3}, 1.2×10^{-3}, 1.3×10^{-3}, and 1.0×10^{-3} m^2/kJ respectively.

Thus, IP values may be used for ranking of mine materials quantitatively for ignition/surface flame spread characteristics. For further verification, it is proposed that several samples of conveyor belt and brattice cloth, for which larger-scale fire tests data are available, be examined in the FM Small-Scale Apparatus to establish the validity of IP values and to rank the materials.

2. Vapor Generation Parameter (Appendix C)

Vapor generation parameter (VP) is defined as the ratio of generation rate of combustible vapors (g/m^2s) to external heat flux applied to the sample (kW/m^2). VP is the inverse of the heat of gasification of the sample for higher external heat flux values. The higher the value of VP, the higher is the generation rate of combustible vapors expected in large-scale fires and the higher is the fire hazard expected.

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* The rating values range from 33 for red oak to a zero value for highly fire resistant belt under the test conditions. The low values indicate that ignition is expected to be difficult and flame propagation is not expected (26,27).

** The brattice cloth ratings are based on the shortest time to flame extinction after removal of a torch held for 30 s to the full size sample. The flame of the lowest ranking sample, i.e., 1, extinguishes in less than 6 s; and the flame of the highest ranking sample, i.e., 6, remains sustained for >120 s.

VP values decrease with increase in the external heat flux for treated and untreated wood samples, because of enhancement of carbon formation in the solid phase. For pure cellulose, VP = 0.34 g/kJ, for external heat flux of 50 kW/m^2, whereas for untreated Douglas fir and red oak, VP = 0.33 and 0.38 for external heat flux values of 46 and 52 kW/m^2 respectively. Wood treatments decrease the VP values because of increased enhancement of carbon formation in the solid phase by the treatments. German-X and -Z belt samples have lower VP values than the styrene-butadiene conveyor belt samples. Brattice cloth samples show low VP values.

Thus, VP values may be used for ranking of mine materials based on their combustible vapor generation characteristics; however, flame radiation must be quantified. It is thus proposed that, for the continuation of the study, the flame radiation scaling technique described in Appendix C (3-6) be used to refine VP, such that mine materials would be ranked for large-scale fire conditions for self-propagating fires.

3. Heat Generation Parameter (Appendix D)

The heat generation parameter (HP) is defined as the ratio of actual heat release (kW/m^2) to the external heat flux applied to the sample (kW/m^2). The higher the value of HP, the higher is the actual heat release rate in fires and higher is the fire hazard. In this study HP values were obtained for overventilated fire conditions.

HP values decrease with increase in external heat flux for treated and untreated wood samples because of enhancement of carbon formation in the solid phase. For pure cellulose, HP = 5.8 for external heat flux of 50 kW/m^2, whereas for untreated Douglas fir and red oak, HP = 4.6 and 5.2 for external heat flux of 46 and 52 kW/m^2 respectively. Wood treatments decrease the HP values because of increased enhancement of carbon formation in the solid phase compared to the untreated samples. The ratio of HP values for NCX-treated and untreated Douglas fir is 0.51 compared with a value of 0.60 for the ratio of actual heat release for treated and untreated timber sets in large-scale fires. The combustion efficiencies of untreated red oak and Douglas fir are 0.76 and 0.85 respectively. For both oak and treated wood samples, the combustion efficiency is 0.48. Combustion efficiency is the ratio of actual heat release rate to heat release rate for complete combustion.

The HP values for German-X and -Z conveyor belt samples are about 1/4 the values for the styrene-butadiene conveyor belt samples. The fire retardant appears to be somewhat effective for the styrene-butadiene conveyor belt samples only at lower heat flux values. At 30 kW/m^2, the calculated HP values for untreated and treated styrene-butadiene conveyor belt samples from Ohio State Apparatus are 18.2 and 11.7 respectively (26), compared with values of 18.6 and 15.2 at 37 kW/m^2 respectively from this study. The HP value for research-grade polystyrene at 50 kW/m^2 is 19, compared with a value of 15.6 at 52 kW/m^2 for the untreated styrene-butadiene conveyor belt sample.

The HP value for the untreated jute brattice cloth sample (No. 1280A) at 52 kW/m^2 is 5.3 compared with a HP value of 5.8 for pure cellulose at 50 kW/m^2. The HP values for brattice cloth samples appear to follow the U.S. Bureau of Mines ratings (27).

Thus, HP values may be used to rank the mine materials for heat generation characteristics. The influence of ventilation on the HP values, especially underventilation, which was not investigated in this study, is proposed for the continuation such that mine materials would be rated for over- and underventilated fire conditions.

4. "Smoke", Toxic and Corrosive Chemical Compound Generation Parameter (Appendix D)

The chemical compound generation parameter (CP) is defined as the ratio of the generation rate of the compound (g/m^2s) to the external heat flux (kW/m^2). The higher the value of CP, the higher is the generation rate of "smoke," toxic and corrosive compounds in fires and the higher is the fire hazard expected. In this study CP values were obtained for CO_2, CO, and hydrocarbons only for overventilated fire conditions. (CO is considered to be a toxic compound in fires.)

For both untreated and treated wood samples the CP values for CO for flaming fire were less than 0.0008 and that for hydrocarbons was less than 0.0002, in agreement with values for pure cellulose for overventilated fires. The wood treatments are thus not expected to increase the hazard due to CO in overventilated fires. This result is in agreement with the tendency of treated wood samples to show enhancement of carbon formation in the solid phase and water

formation in the vapor phase.

For research grade polystyrene, CP values for CO_2, CO, and hydrocarbons at 50 kW/m^2 are 1.5, 0.066, and 0.032 g/kJ, compared with values of 0.94, 0.066, and 0.022 g/kJ for untreated styrene butadiene conveyor belt sample respectively. The CP values for CO_2, CO, and hydrocarbons for German-X and -Z belt samples are considerably smaller than the values for the styrene-butadiene conveyor belt samples.

Among brattice cloth samples, the CP value of CO for untreated jute samples (No. 1280A) is smallest (comparable to the value for pure cellulose).

CP values can be measured for major toxic and corrosive products and for "smoke" and relationships established between CP values and animal behavior, which can be used for ranking of mine materials for hazards associated with toxic and corrosive products and "smoke." For continuation of this study, it is proposed that CP values for major toxic and corrosive products and "smoke" be established as functions of ventilation and animal behavior, which can then be used for the assessment of hazard associated with various mine fire scenarios. For the assessment of corrosivity of fire products, a new technique has been developed at the Factory Mutual Research Corporation, which can be used for mine materials.

5. Light Obscuration Parameter (Appendix E)

The light obscuration parameter (LP) (m^2/kJ) is defined as the ratio of optical density per unit path length (m^{-1}) to external heat flux applied to the sample (kW/m^2), normalized with respect to the sample surface area (m^2) and volumetric flow rate of the fire products mixed with air (m^3/s). The higher the value of LP, the higher is the light obscuration by "smoke" (reduced visibility expected in mine fires.

Wood treatments, except Fireguard, reduce the LP values, which is expected on the basis of enrichment of the solid phase by carbon formation and the vapor phase by water formation. The LP value for research grade polystyrene is 0.21 m^2/kJ at 50 kW/m^2 compared with a value of 0.24 m^2/kJ for untreated styrene-butadiene conveyor belt sample. The LP values for German-X and -Z belt samples are about 1/10th the value for the styrene-butadiene sample. LP values for the brattice cloth samples, except untreated jute sample, are comparable to the values for untreated wood samples and German-X and -Z belt samples. The ratio of LP values for treated and untreated styrene-butadiene conveyor belt samples

is 1.0 compared with a value of 0.84 calculated from the Ohio State University Apparatus (26), whereas the U.S. Bureau of Mines smoke index ratio is 0.70 (26). The mass attenuation coefficient of "smoke," which depends on the physical and chemical properties of "smoke" (particle size, refractive index, carbon-hydrogen-nitrogen atom ratio, etc.), appears to vary between 3 and 4 m^2/g for a variety of generically different research samples and the mine materials. For these combustibles, a large fraction of "smoke" is present as soot*. It thus appears that, for these combustibles, "smoke" probably has similar physical and chemical properties. The mass attenuation coefficient increases as the soot fraction in "smoke" decreases, for example for untreated wood samples, which is an indication of decrease in the particle size and a change in the chemical structure of the compounds in "smoke."

Thus, LP values may be used for rating mine materials for "smoke" generation characteristics. LP values, however, need to be examined for underventilated fires and as functions of the wavelength of the light source for reliable assessment of hazard, and is proposed for the continuation of the study.

CONCLUSION

Wood treatments, except Fireguard, selected by the U.S. Bureau of Mines, for reducing the fire hazard, have been found to be effective based on predictions from the FM Small-Scale Combustibility Apparatus and from the large-scale fire tests in the simulated mine gallery.

For styrene-butadiene and German-X and -Z conveyor belt samples and four brattice cloth samples, reasonable correlations have been found between U.S. Bureau of Mines ratings and ratings based on the data from the FM Small-Scale Combustibility Apparatus.

Five separate parameters are proposed for rating of mine materials for the evaluations of hazards associated with 1) ignition/flame spread; 2) generation of combustible vapors; 3) generation of heat; 4) generation of "smoke," toxic and corrosive products; and 5) light obscuration by "smoke."

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*determined by the filter paper weighing technique (3-13)

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I

INTRODUCTION

Prevention of unwanted fires requires a knowledge of the combustibility behavior of materials likely to be encountered under various conditions of use (or misuse). The combustibility behavior of materials is generally examined under fixed conditions using "standard" or other tests under specified conditions with a "pass"/"fail" criteria. Since the test conditions used in standard tests are very different from actual fire conditions, materials often behave quite differently in actual fires than expected on the basis "standard" or other specified tests criteria.

The combustibility behavior of materials in fires is a result of the interactions of fire properties of the materials and the fire environments. The fire properties include: 1) heat flux required for the initiation of pyrolysis (generation of combustible vapors); 2) heat flux and energy required for ignition of combustible vapors; 3) heat required to generate a unit mass of combustible vapors or heat of gasification of the combustible; 4) yields of fire products which include heat and chemical compounds; 5) optical properties of fire products; and 6) fire suppression and extinguishment.

The fire environment consists of: 1) convective and radiative heat generated from flame and external heat sources; 2) natural air flow and ventilation in enclosed fires, including inflow of ambient air, accumulation, and mixing of fire products and air, and outflow of such mixtures. Overventilated fires are defined as fires with excess inflow of ambient air without significant accumulation of fire products, whereas underventilated fires are defined as fires with insufficient inflow of air, and recirculation of air contaminated with fire products.

As a result of the interactions of fire properties of the materials and fire environments, various types of hazards can be created due to hot corrosive and toxic compounds and "smoke" which reduces visibility; in some cases the hazards may exceed the threshold limits for life and property (1,2). It is thus essential that materials be examined under test conditions simulating the interactions of the fire properties of materials and actual fire environments.

This report presents a general review of progress which has been made in quantifying the combustibility behavior of mine materials under various conditions expected in mine fires.

II

EXPERIMENTAL APPROACH

The experimental approach taken in this study has been based on the concepts developed at the Factory Mutual Research Corporation (FMRC) (3-15). Fire environments are simulated by using: 1) external heat flux from radiant heaters and pool fires and radiative heat flux from the flame by using variable oxygen concentration in ambient air and size and arrangement of materials; and 2) natural air flow and forced air flow (variable flow rate, temperature, and contaminants in air). Experiments are performed in three apparatuses:

1) Factory Mutual Small-Scale Combustibility Apparatus, for materials ~0.1-m diameter, ~0.1-m high, and ~0.01 to 0.02-m thick. External heat source is simulated by using four coaxially placed quartz-tungsten radiant heaters (peak at 1.15 μ). Flame radiative heat flux is simulated by varying the mass fraction of oxygen in air. Ventilation is provided by introducing air at the bottom of the apparatus with variable flow rate, temperature, and contaminant. Experiments can also be performed under natural air flow. A very small pilot flame is provided for ignition (3-6).

2) Factory Mutual Intermediate-Scale Combustibility Apparatus for materials ~0.3 x 0.3 x 1-m high. External heat source is simulated by using liquid pool fires of methanol and heptane placed under the material. Flame radiation and ventilation are provided in a fashion very similar to that used in the Small-Scale Apparatus (3,5,6).

3) Factory Mutual Large-Scale Apparatus for materials ~3 x 3 x 3-m high. No external heat source is used and experiments are performed under natural air flow conditions (5,6).

In all three apparatuses, fire products are captured in the respective sampling ducts, are diluted with ambient air, and are well mixed before sampling. In the sampling ducts, measurements are made for total flow rate, gas temperature, concentrations of CO, CO_2, O_2, total gaseous hydrocarbons, "smoke" (defined as a mixture of soot and low vapor-pressure liquids), HCl, HCN, and NO_x, and optical transmission through fire products. Other measurements include time to ignition, generation rate of combustible vapors, and water application rate for fire suppression and extinguishment. Measurements where apparatuses are not used include elemental composition of the material and "smoke", heat of

complete combustion of the material, and "smoke," and corrosion property of the fire products (see Appendices for details).

In the apparatuses, measurements are made at an interval of ~1 s (or longer) for the entire fire duration. Computer data acquisition systems are used for measurement and analysis of the data.

In this study for mine materials, the FM Small-Scale Combustibility Apparatus was used in conjunction with the U.S. Bureau of Mines separate study at FMRC, where a large-scale mine gallery was used. The mine gallery has been described in detail previously (14,16-24).

The gallery is a T-shaped structure with two passageways (drifts), each about 47-m long and about 2.4 x 2.4 m in cross-sectional area. The north and east drifts are horizontal, and the west drift has a slope of about 13 degrees. Tests were performed with air pushed into the gallery by a fan or with air pulled out of the gallery by an air pollution control system.

2.1 DETAILED DESCRIPTION OF THE FM SMALL-SCALE COMBUSTIBILITY APPARATUS

Figure 1 is a sketch of the FM Small-Scale Combustibility Apparatus.

In the apparatus, the sample, ~0.008 m^2 in area, ~0.01-m to 0.02-m thick, contained in a dish made from two sheets of heavy-duty aluminum foil, is placed on top of four steel pins to reduce the effects of thermal inertia. The steel pins are attached to a water-cooled load-cell assembly. The load-cell output is monitored by a MINC, Model LS1-1103 analog-to-digital data acquisition system (Digital Equipment Corp., Northboro, Mass.).

For experiments with forced-air flow, a quartz tube is placed around the sample. Air is introduced at the bottom of the apparatus through a loosely packed bed of glass beads, for an even velocity profile around the sample. The maximum air flow rate that can be used is ~0.003 m^3/s. For experiments with preheated and contaminated air, an air heater is used (maximum air temperature ~400 K) and various contaminants (CO, CO_2, hydrocarbons, "smoke," etc.) can be added in different amounts. The air flow rate is measured by an electronic flow meter. The oxygen concentration of the inlet air is measured by an oxygen analyzer. The concentrations of the contaminants are measured by monitoring the respective flow rates of air and the contaminants. The inlet air temperature is measured by the thermocouples (7 and 8).

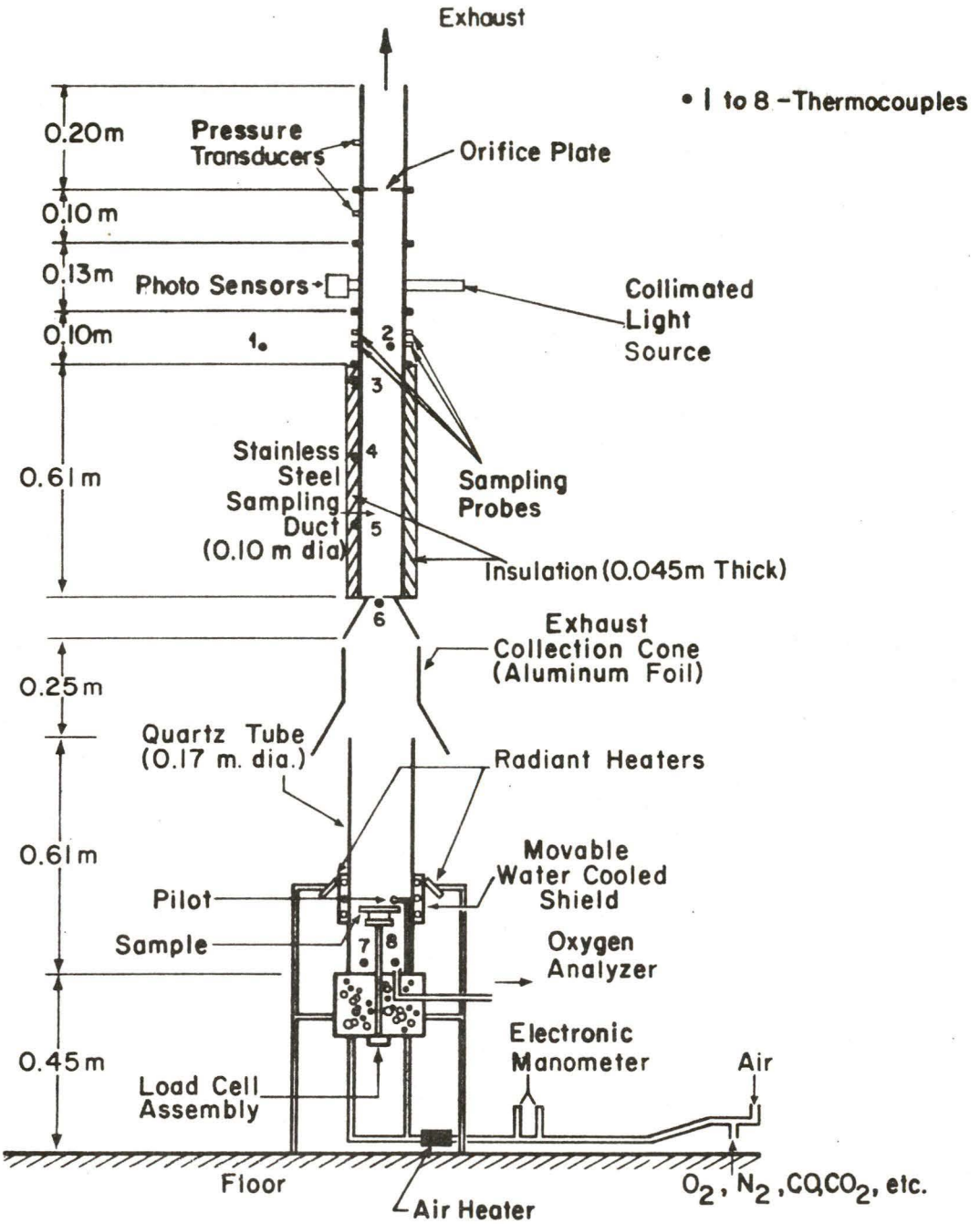

FIGURE 1 FM Small-Scale Combustibility Apparatus

For experiments under natural air flow, the quartz tube is not placed around the sample and the forced air flow is not introduced into the apparatus.

In order to ignite the combustible vapors, a small premixed ethylene-air pilot flame about 0.02 m in length and ~0.01 m above the sample surface is used; for autoignition, the pilot flame is not used.

The sample is exposed to external heat flux from four high-density radiant heaters (tungsten-quartz lamps) placed coaxially. All the radiant heaters are connected to a single controller, through which power supplied to the heaters can be changed. The heat flux to the sample as a function of the controller setting is calibrated by using a small Medtherm heat flux gage at various horizontal and vertical locations within the dimensions of the sample to be used. Because of the inertia of the radiant heaters, the heaters are allowed to stabilize for 180 s in the calibration and in every experiment. (The sample is protected by a water-cooled shield during the heater stabilization period.)

All the products generated from nonflaming fires (pyrolysis) or flaming fires (combustion) are captured in the sampling duct together with air where fire products and air become well mixed before reaching the sampling probes. Measurements are then made for 1) ambient temperature outside the duct (No. 1 in Figure 1), temperatures of product-air mixture inside the duct (No. 2 in Figure 1) and just before the mixture enters the duct (No. 6, three thermocouples), and duct skin temperatures (Nos. 3, 4, and 5); 2) concentrations* of CO, CO_2, O_2, total gaseous hydrocarbons, HCl, HCN, and NO_x; 3) optical transmission at three wavelengths; and 4) pressures before and after the orifice plate and ambient pressure.

The mixture of fire product and air is exhausted by a blower.

The experimental procedure consists of: 1) initializing the MINC with pertinent sample information, test number, date, experimental conditions, operator, etc.; 2) turning on the inlet air flow, exhaust blower and pilot flame; 3) weighing the sample and placing it in the apparatus; 4) raising the water-cooled shield around the sample; 5) turning on the radiant heaters 3 min before the test begins, with the controller set at the desired heat flux to the sample, and taking 1 min of background readings with the MINC during the

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*instruments and their ranges and accuracy of measurements are described in references 3-13.

middle minute; 6) starting the MINC to take test data; 7) at 60 s from the time the MINC began taking test data, lowering the shield to expose the sample to the external heat flux; 8) at 180 s from the time heaters are turned on, lowering the shield to expose the sample to external heat flux; 9) measuring time to ignition (other measurements are taken automatically by the MINC); and 10) measuring the corrosivity of fire products using a separate test setup. The experiment is terminated when the instrument outputs reach ambient conditions and the sample ceases to generate fuel vapors. After cooling the sample residue in the dish, it is weighed to determine the total amount of combustible vapors generated in the experiment.

The time to ignition, the amount of residue, and visual observations are entered into the MINC. The MINC is then instructed to analyze the data and within about 30 min the data are ready in tabular or graphical form for the following fire properties as functions of time (see Appendices):

1) generation rate of combustible vapors per unit surface area of material in g/m^2s (see Appendix C);

2) inlet air flow rate (m^3/s); concentration of oxygen in inlet air in volume percent, temperature in °C, and concentration of contaminants in volume percent;

3) generation rates of fire products per unit surface area of the material (see Appendix D);

   a) heat release rates (actual, convective, or radiative in kW/m^2). The convective heat release rate is corrected for the contribution by the radiant heaters;

   b) generation rates of chemical compounds in g/m^2s, where chemical compounds include CO, CO_2, total gaseous hydrocarbons, HCl, HCN, etc.;

4) optical transmission per unit optical path length for individual wave lengths expressed as $[\ell n(I_o/I)]/\ell$, where I/I_o is the fraction of light transmitted through the mixture of fire products and air, and ℓ is the optical path length (see Appendix E);

5) total mass flow rate of fire product-air mixture in kg/s and total volumetric flow rate of product-air mixture in m^3/s (see Appendix A);

6) heat losses to the duct skin in kW/m^2 and through the inlet region of the duct (kW/m^2);

7) most probable size and number density of particulates present in the fire products (32).

Pyrolysis and combustion experiments are performed under variable conditions of: 1) external heat flux; 2) inlet air flow rate; 3) inlet air temperature, and contaminants; 4) oxygen concentration; 5) water application rate for fire suppression/extinguishment; and 6) materials - solids, powders, liquids, and foams, used alone or in combinations with one another and with inerts such as glass fibers, copper (conductor in the cables). Separate experiments are performed for each condition. In this study for the U.S. Bureau of Mines, only the external heat flux was used as a variable.

III

SAMPLES USED IN THE STUDY

The following samples were used in the study:

1) Wood samples (~0.01 m thick)
   a) Red oak
      (1) untreated;
      (2) treated with: (a) Fyreprufe*; (b) intumescent paint*.
   b) Douglas fir
      (1) untreated;
      (2) treated with: (a) NCX*; (b) Fireguard*.
2) Conveyor belt samples (~0.01 m thick)
   a) Styrene butadiene rubber
      (1) untreated (NFRR);
      (2) treated (FRR).
   b) German X belt ~0.01 m thick (materials/treatment not identified).
   c) German Z belt ~0.02 m thick (materials/treatment not identified).
3) Brattice cloth samples (materials not identified)
   a) MSHA Lab No. 1280A (14 oz/yd^2, untreated jute);
   b) MSHA Lab No. 1580 (12 oz/yd^2 yellow);
   c) MSHA Lab No. 1620 (15 oz/yd^2 clear);
   d) MSHA Lab No. 1688 (12 oz/yd^2 clear).

For all the samples, a ~0.008 m^2 sample dish, made from two sheets of heavy duty aluminum foil, was used, with lip height adjusted for the thickness of the sample.

The wood samples were dried at 84°C for 168 hr in a vacuum oven at 0.5 atm and were kept inside a desiccator until the samples were placed in the apparatus. An example of the water absorption behavior, for treated and untreated fir samples exposed to ambient conditions, is shown in Figure 2. The data in Figure 2 indicate that a negligible amount of moisture will be absorbed by the sample in a few minutes prior to an experiment. Therefore, in the analysis of the results the influence of water absorption was neglected.

The brattice cloth samples were not dried but were kept in the desiccator

*Described in references 28 to 31.

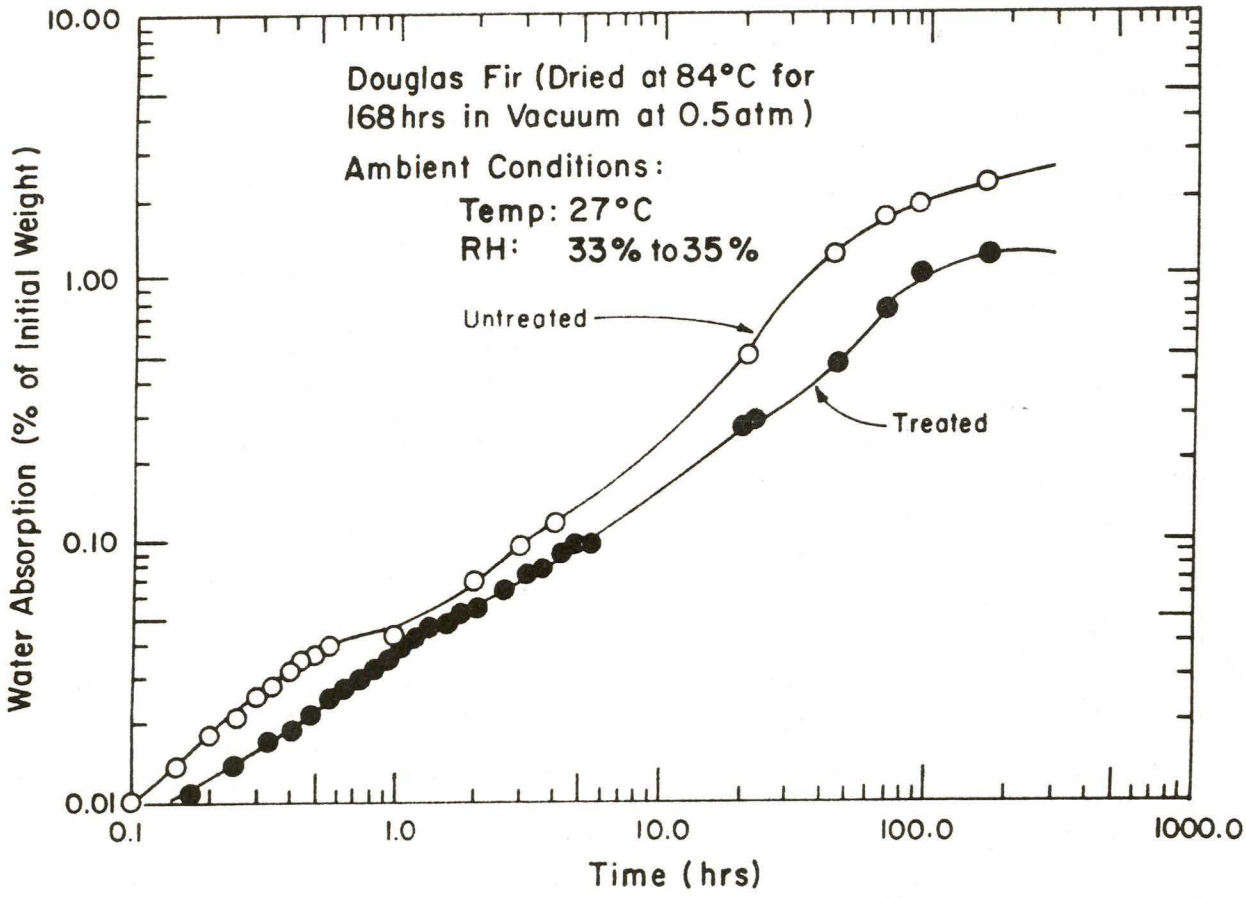

FIGURE 2 Water Absorption Behavior of NCX-Treated and Untreated Douglas Fir Exposed to Ambient Humidity Conditions

until used in the experiments. The conveyor belt samples were not dried; however, the surface was cleaned with isopropanol before the experiment.

3.1 SAMPLE PROPERTIES

The heat of complete combustion and elemental composition of wood samples measured in this study are listed in Table 1. Elemental composition data from reference 25 are also included in the table. These measurements were not made for conveyor belt and brattice cloth samples.

Tables 2 to 8 list the literature data available for the samples examined in this study (25,26,27).

From the data for elemental compositions given in Table 1, expected yields of C, O, H, N atoms in the vapors generated from the sample can be calculated. The calculated data are listed in Table 9. The yields of C, O, H, N atoms within a generic group of chemical compounds in the vapors can also be calculated from the data in Tables 2 to 6 and from the chemical formula of each compound present within a generic group. The data are listed in Tables 10 to 14. From the data in Tables 9 to 14, the atom transfer efficiency* from the solid to the vapor phase can be calculated. The calculated data are listed in Table 15. In addition, the chemical formula of the solid and vapor phase can be calculated from the data in Table 1 and Tables 10 to 14. The calculated formulas are listed in Table 16.

The atom transfer efficiency in Table 15 indicates the following:

1) Carbon Atom Transfer Efficiency from the Solid to Vapor Phase

In pyrolysis in N_2, transfer efficiency is low for treated and untreated samples (~11 to 19%). It increases for pyrolysis in air (~27 to 31%) and the preignition region, where NCX treatment appears to reduce the efficiency by about one-half.

2) Oxygen Atom Transfer Efficiency from the Solid to Vapor Phase

Oxygen is present in the sample and is also provided to the sample by air. In pyrolysis in N_2, where oxygen atoms are provided by the sample alone, the NCX

*The atom transfer efficiency is defined as the ratio of experimental to theoretical yield of the atom, where the theoretical yield is calculated on the basis of the original elemental composition of the sample.

TABLE 1

HEAT OF COMPLETE COMBUSTION AND ELEMENTAL COMPOSITION OF WOOD SAMPLES

Sample	Treatment	Heat of Complete Combustion (kJ/g)		Elemental Composition (wt %)				
		Gross	Net	C	H	O	N	Ash
Red Oak	Untreated	19.2	17.8	46.9	6.23	44.4	0.069	2.35
				46.1[a]	6.56[a]	N	<0.05[a]	N
	Fyrepruf	17.6	16.2	46.0	6.17	46.9	0.35	0.20
	Intumescent paint	17.2	15.8	44.8	6.24	47.2	1.09	0.70
	NCX	N	N	44.9[a]	6.39[a]	N	2.20[a]	N
Douglas fir	Untreated	18.3	16.4	47.1	6.55	46.3	0.13	0.27
				47.3[a]	6.65[a]	N	<0.05[a]	N
	NCX	16.8	15.4	44.2	6.46	45.9	3.42	1.04
				44.3[a]	6.31[a]	N	2.76[a]	N
Residue	Red oak/NCX	N	N	64.5[a]	4.01[a]	N	4.33[a]	N
	Douglas fir/NCX	N	N	65.7[a]	3.47[a]	N	4.32[a]	N

[a]Data taken from Reference 25; N - Not measured

TABLE 2

YIELDS OF VARIOUS CHEMICAL COMPOUNDS GENERATED FROM UNTREATED DOUGLAS FIR HEATED AT 773 K[a]

Chemical Compound[b]	Yield (mg/g of Combustible Vapors)		
	Pyrolysis (N_2)	Preign (Air)	After Flame Extinguishment[c] (Air)
H_2O	294	542	320
CO	30.0	29.6	44.7
CO_2	75.8	821	71.4
Hydrocarbons[d]	1.52	1.65	1.94
Σ Ethers	*d*	*d*	*d*
Σ Furans	3.47	0.289	5.19
Σ Alcohols	4.36	2.50	4.96
Σ Aldehydes	11.0	5.27	6.61
Σ Ketones	5.12	0.534	5.58
Σ Acids	4.64	3.15	6.99
Σ Esters	0.332	0.062	0.362
Σ Nitriles	*e*	*e*	*e*
Σ Cyanides	*e*	*e*	*e*
Residue	301	91.2	218

[a] from the data given in Reference 25

[b] Σ sum of the yields of all the compounds within each generic group

[c] flame extinguishment by N_2

[d] no data for CH_4

[e] data not reported

TABLE 3

YIELDS OF VARIOUS CHEMICAL COMPOUNDS GENERATED FROM NCX-TREATED DOUGLAS FIR HEATED AT 773 K[a]

Chemical Compounds[b]	Yield (mg/g of Combustible Vapors) Pyrolysis (N_2)	Pyrolysis (Air)	Preign[c] (Air)
H_2O	596	581	554
CO	28.7	86.8	>67.0
CO_2	140	246	241
Σ Hydrocarbons[d]	1.39	1.61	1.63
Σ Ethers	0.304	0.167	0.078
Σ Furans	2.84	2.03	1.79
Σ Alcohols	13.6	19.4	17.8
Σ Aldehydes	10.3	13.2	4.89
Σ Ketones	7.00	8.24	5.42
Σ Acids	10.2	11.1	1.41
Σ Esters	0.426	0.676	0.172
Σ Nitriles	2.98	4.95	5.53
Σ Cyanides	0.481	12.5	2.11
Residue	51.1	63.4	70.8

[a] from the data given in Reference 25

[b] Σ sum of the yields of all the compounds within each generic group

[c] heated to 923 K; no ignition at 773 K

[d] no data for CH_4

TABLE 4

YIELDS OF VARIOUS CHEMICAL COMPOUNDS GENERATED FROM UNTREATED RED OAK HEATED AT 773 K[a]

Chemical Compound[b]	Yield (mg/g of Combustible Vapors)	
	Preign (Air)	After Flame Extinguishment[c]
H_2O	417	341
CO	73.8	74.1
CO_2	469	136
Hydrocarbons[d]	4.02	1.65
Σ Ethers	*e*	0.022
Σ Furans	0.717	3.00
Σ Alcohols	12.8	18.7
Σ Aldehydes	27.2	23.2
Σ Ketones	3.17	11.6
Σ Acids	32.9	68.7
Σ Esters	1.08	9.71
Σ Nitriles	*e*	*e*
Σ Cyanides	*e*	*e*
Residue	118	146

[a] from the data given in Reference 25

[b] Σ sum of the yields of all the compounds within each generic group

[c] flame extinguishment by N_2

[d] no data for CH_4

[e] data not reported

TABLE 5

YIELDS OF VARIOUS CHEMICAL COMPOUNDS GENERATED FROM NCX-TREATED RED OAK HEATED AT 773 K[a]

Chemical Compounds[b]	Yield (mg/g of Combustible Vapors) Pyrolysis (N_2)	Pyrolysis (Air)
H_2O	546	514
CO	22.5	>63.9
CO_2	189	218
Σ Hydrocarbons[c]	1.09	1.83
Σ Ethers	0.072	0.075
Σ Furans	1.09	0.894
Σ Alcohols	15.9	17.3
Σ Aldehydes	4.95	11.1
Σ Ketones	3.66	4.74
Σ Acids	31.6	33.7
Σ Esters	2.91	4.50
Σ Nitriles	2.29	3.33
Σ Cyanides	0.75	5.76
Residue	57.9	31.8

[a] from the data given in Reference 25

[b] Σ sum of the yields of all the compounds within each generic group

[c] no data for CH_4

TABLE 6

YIELDS OF VARIOUS CHEMICAL COMPOUNDS GENERATED FROM UNTREATED AND FIRE RETARDANT TREATED STYRENE-BUTADIENE RUBBER (CONVEYOR BELT) HEATED IN AIR AT 773 K[a]

Chemical Compound[b]	Yield (mg/g of Combustible Vapors)	
	Untreated	Treated
H_2O	278	454
CO	>108	>117
CO_2	628	465
Σ Hydrocarbons[c]	208	120
Σ Alcohols	0.285	7.33
Σ Aldehydes	4.57	2.18
Σ Ketones	1.97	1.45
Σ Furans	0.189	0.376
Σ Acids	0.228	3.99
Σ Esters	0.0171	-
Σ Nitriles	0.142	0.296
Σ Sulfides	0.212	
HCl	0.221	13.7
COS	2.59	4.56
CS_2	0.450	-
HCN	3.14	3.22
Residue	130	143

[a] from the data given in Reference 25

[b] Σ sum of the yields of all the compounds within each generic group

[c] no data for CH_4

TABLE 7

US BUREAU OF MINES FLAMMABILITY INDEX DATA FOR RED OAK AND CONVEYOR BELT SAMPLES[a]

Sample	Critical Ignitor Input, (kJ/m^2)	Flame Spread Rate ($(m/s)x10^3$)	Heat Release Rate (kW/m^2)	Flammability Index
Red Oak	6067	3.5	160	33
Styrene-butadiene rubber (A)	6067	1.8	148	16
Neoprene (A)	10,042	1.8	115	7.3
PVC (A)	14,016	2.0	85	4.4
Styrene-butadiene rubber (A with fire retardant)	14,000	1.0	42	1.0
Neoprene (B)	34,300	1.2	53	0.7
PVC (B)	54,200	1.2	52	0.4
PVC (C)	>60,300;≥56,300	0(0.7)	NI(45)	0(0.2)
PVC (D)	>100,400;36,000	0(0.8)	NI(49)	0(0.4)
Neoprene (C)	>100,400	0	NI	0
German - X[b]	N	N	N	0
German - Z[b]	N	N	N	0

[a] data taken from Reference 26

[b] data taken from Reference 27

NI: no ignition

N: data not available

TABLE 8

US BUREAU OF MINES FLAMMABILITY RATINGS

OF BRATTICE CLOTHS[a]

Sample	Rating
MSHA Lab No. 1280A (untreated jute)	6
MSHA Lab No. 1580 (12 oz yellow)	1
MSHA Lab No. 1620 (15 oz clear)	5
MSHA Lab No. 1688 (12 oz clear)	4

[a]data taken from Reference 27

TABLE 9

C, O, H AND N ATOM YIELDS IN VAPORS EXPECTED FROM THE ELEMENTAL COMPOSITIONS OF THE ORIGINAL SAMPLE[a]

Sample	Treatment	Yield (mg/g of Combustible Vapors) Carbon	Oxygen	Hydrogen	Nitrogen
Douglas fir	Untreated	467	467	65.4	0.926
Douglas fir	NCX	454	448	65.5	31.8
Residue (Douglas fir/NCX)	-	709	208	37.2	46.3
Red Oak	Untreated	471	464	64.7	0.659
Red Oak	NCX	465	447	66.3	22.2
Residue (Red Oak/ NCX)	-	690	221	43.1	45.9

[a] assumed that vapors have the same elemental composition as the original solid sample

TABLE 10

C, O, AND H ATOM YIELDS IN VAPORS GENERATED FROM UNTREATED DOUGLAS FIR HEATED AT 773 K[a]

Compounds	Yield (mg/g of Combustible Vapors)								
	Carbon			Oxygen			Hydrogen		
	Pyrolysis (N_2)	Preign. (Air)	Flame Exting[a] (N_2)	Pyrolysis (N_2)	Preign. (Air)	Flame Exting[a] (N_2)	Pyrolysis (N_2)	Preign. (Air)	Flame Exting[a] (N_2)
H_2O	-	-	-	262	482	285	32.3	59.6	35.2
CO	12.9	12.7	19.2	17.1	16.9	25.5	-	-	-
CO_2	20.5	222	19.3	27.3	296	25.7	-	-	-
Hydrocarbons	1.31	1.42	1.67	-	-	-	0.213	0.231	0.272
Ethers	-	-	-	-	-	-	-	-	-
Furans	2.46	0.205	3.68	0.831	0.0694	1.25	0.201	0.0168	0.301
Alcohols	1.66	0.950	1.88	2.18	1.25	2.48	0.567	0.325	0.645
Aldehydes	6.88	3.29	4.13	3.63	1.74	2.18	0.506	0.242	0.304
Ketones	3.43	0.358	3.74	1.13	0.117	1.23	0.563	0.0587	0.614
Acids	1.86	1.26	2.80	2.46	1.67	3.70	0.311	0.211	0.468
Esters	0.133	0.0250	0.145	0.176	0.0329	0.192	0.0222	0.00415	0.0243
Nitriles	-	-	-	-	-	-	-	-	-
Cyanides	-	-	-	-	-	-	-	-	-
Total	51.1	242	56.5	317	800	347	34.7	60.7	37.8

[a] after flame extinguishment using N_2

TABLE 11

C, O, H AND N ATOM YIELDS IN VAPORS GENERATED FROM NCX-TREATED DOUGLAS FIR

Compound	Yield (mg/g of Combustible Vapors)											
	Carbon			Oxygen			Hydrogen			Nitrogen		
	Pyrolysis (773K)		Preign	Pyrolysis (773K)		Preign	Pyrolysis (773K)		Preign	Pyrolysis (773K)		Preig
	N_2	Air	(923K,Air)	N_2	Air	(923K,Air)	N_2	Air	(923K,Air)	N_2	Air	(923K,Air)
H_2O	-	-	-	530	517	493	65.6	63.9	60.9	-	-	-
CO	12.3	37.3	28.8	16.3	49.5	38.2	-	-	-	-	-	-
CO_2	37.8	66.4	65.1	50.4	88.6	86.8	-	-	-	-	-	-
Hydrocarbons	1.20	1.38	1.40	-	-	-	0.195	0.225	0.228	-	-	-
Ethers	0.158	0.0868	0.0406	0.106	0.0585	0.0273	0.0395	0.0217	0.0101	-	-	-
Furans	2.02	1.44	1.27	0.682	0.487	0.430	0.165	0.118	0.104	-	-	-
Alcohols	5.17	7.37	6.76	6.80	9.70	8.90	1.77	2.52	2.31	-	-	-
Aldehydes	6.44	8.25	3.06	3.40	4.36	1.61	0.474	0.607	0.225	-	-	-
Ketones	4.69	5.52	3.63	1.54	1.81	1.19	0.770	0.906	0.596	-	-	-
Acids	4.08	4.44	0.564	5.41	5.88	0.747	0.683	0.744	0.0945	-	-	-
Esters	0.170	0.270	0.0688	0.226	0.358	0.0912	0.0285	0.0453	0.0115	-	-	-
Nitriles	1.76	2.92	3.26	-	-	-	0.218	0.361	0.404	1.01	1.68	1.88
Cyanides	0.212	5.50	0.928	-	-	-	0.0118	0.463	0.0781	0.250	6.50	1.10
Total	76.0	141	115	615	678	631	70.0	69.9	65.0	1.26	8.18	2.98

TABLE 12

C, O, AND H ATOM YIELDS IN VAPORS GENERATED FROM UNTREATED RED OAK HEATED AT 773 K

Compound	Yield (mg/g of Combustible Vapors)					
	Carbon		Oxygen		Hydrogen	
	Preign. (Air)	Flame Exting(N_2)[a]	Preign. (Air)	Flame Exting(N_2)[a]	Preign. (Air)	Flame Exting(N_2)[a]
H_2O	-	-	371	303	45.9	37.5
CO	31.7	31.9	42.1	42.2	-	-
CO_2	127	36.7	169	49.0	-	-
Hydrocarbons	3.46	1.42	-	-	0.563	0.231
Ethers	-	0.0114	-	0.00770	-	0.00286
Furans	0.509	2.13	0.172	0.721	0.0416	0.174
Alcohols	4.86	7.11	6.41	9.35	1.66	2.43
Aldehydes	17.0	14.5	8.90	7.66	1.25	1.07
Ketones	2.12	7.77	0.697	2.55	0.349	1.28
Acids	13.2	27.5	17.4	36.4	2.20	4.60
Esters	0.432	3.88	0.572	5.15	0.0724	0.651
Nitriles	-	-	-	-	-	-
Cyanides	-	-	-	-	-	-
Total	200	133	616	456	52.0	47.9

[a] after flame extinguishment using N_2

TABLE 13

C, O, H AND N ATOM YIELDS IN VAPORS GENERATED FROM NCX-TREATED RED OAK HEATED AT 773 K

Compound	Yield (mg/g of Combustible Vapors)							
	Carbon		Oxygen		Hydrogen		Nitrogen	
	Pyrolysis (N_2)	Pyrolysis (Air)	Pyrolysis (N_2)	Pyrolysis (Air)	Pyrolysis (N_2)	Pyrolysis (Air)	Pyrolysis (N_2)	Pyrolysis (Air)
H_2O	-	-	486	457	60.1	56.5	-	-
CO	9.68	27.5	12.8	36.4	-	-	-	-
CO_2	51.0	58.9	68.0	78.5	-	-	-	-
Hydrocarbons	0.937	1.57	-	-	0.153	0.256	-	-
Ethers	0.037	0.039	0.0252	0.0263	0.00936	0.00975	-	-
Furans	0.774	0.635	0.262	0.215	0.0632	0.0519	-	-
Alcohols	6.04	6.57	7.95	8.65	2.07	2.25	-	-
Aldehydes	3.09	6.94	1.63	3.66	0.228	0.511	-	-
Ketones	2.45	3.18	0.805	1.04	0.403	0.521	-	-
Acids	12.6	13.5	16.7	17.9	2.12	2.26	-	-
Esters	1.16	1.80	1.54	2.39	0.195	0.302	-	-
Nitriles	1.35	1.96	-	-	0.167	0.243	0.779	1.13
Cyanides	0.33	2.53	-	-	0.0278	0.213	0.390	3.00
Total	89.4	125	596	606	65.5	63.1	1.17	4.13

TABLE 14

C, O, H, N, S AND Cl ATOM YIELDS IN VAPORS GENERATED FROM UNTREATED AND TREATED STYRENE-BUTADIENE RUBBER HEATED IN AIR AT 773 K

Compound	Yield (mg/g of Combustible Vapors)											
	Carbon		Oxygen		Hydrogen		Nitrogen		Sulfur		Chlorine	
	Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated
H_2O	-	-	164	404	30.6	49.9	-	-	-	-	-	-
CO	46.4	50.3	61.6	66.7	-	-	-	-	-	-	-	-
CO_2	170	126	226	167	-	-	-	-	-	-	-	-
Hydrocarbons	179	103	-	-	29.1	16.8	-	-	-	-	-	-
Alcohols	0.108	2.79	0.143	3.67	0.0371	0.953	-	-	-	-	-	-
Aldehydes	2.86	1.36	1.51	0.719	0.210	0.100	-	-	-	-	-	-
Ketones	1.32	0.972	0.433	0.319	0.217	0.160	-	-	-	-	-	-
Furans	0.134	0.267	0.0454	0.0902	0.0110	0.0218	-	-	-	-	-	-
Acids	0.0912	1.60	0.121	2.11	0.0153	0.267	-	-	-	-	-	-
Esters	0.00680	-	0.00901	-	0.00114	-	-	-	-	-	-	-
Nitriles	0.0838	0.175	-	-	0.0104	0.0216	0.0483	0.101	-	-	-	-
Cyanides	1.38	1.42	-	-	0.116	0.119	1.63	1.67	-	-	-	-
Chlorides (HCl)	-	-	-	-	0.00616	0.384	-	-	-	-	0.213	13.3
Sulfide (CS_2)	0.0711	-	-	-	-	-	-	-	0.189	-	-	-
COS	0.518	0.912	0.699	1.23	-	-	-	-	1.37	2.41	-	-
Total	402	289	455	646	60.3	69.6	1.68	1.77	1.56	2.41	0.213	13.3

TABLE 15

EFFICIENCY OF ATOM TRANSFER FROM SOLID TO VAPOR PHASE

FOR TREATED AND UNTREATED WOOD SAMPLES

Sample	Treatment	Atom Transfer Efficiency (%)															
		Carbon				Oxygen				Hydrogen				Nitrogen			
		Pyrolysis N_2	Pyrolysis Air	Preig (Air)	Flame Extinc	Pyrolysis N_2	Pyrolysis Air	Preign (Air)	Flame Extinc	Pyrolysis N_2	Pyrolysis Air	Preign (Air)	Flame Extinc	Pyrolysis N_2	Pyrolysis Air	Preign (Air)	Flame Extinc
Douglas fir	None	10.9	-	51.8	12.1	67.9	-	171	74.3	53.1	-	92.8	57.8	-	-	-	-
Douglas fir	NCX	16.7	31.1	25.3	-	137	151	141	-	107	107	99.2	-	3.96	25.7	9.37	-
Red oak	None	-	-	42.5	28.3	-	-	133	98.3	-	-	80.4	74.0	-	-	-	-
Red oak	NCX	19.2	26.9	-	-	133	136	-	-	98.8	95.2	-	-	5.27	18.6	-	-

TABLE 16

CHEMICAL FORMULAE CALCULATED FROM THE ELEMENTAL COMPOSITION OF THE ORIGINAL SAMPLE AND ATOM BALANCE AND AIR-TO-FUEL RATIO REQUIRED BY STOICHIOMETRY[a]

Sample	Treatment	Phase	Vapor Generation Conditions	Chemical Formula	Stoichiometric Air-to-Fuel Ratio
Douglas fir	None	Solid	Original sample	$C_{1.33}H_{2.24}O\ N_{0.002}$	5.6
		Vapor	Pyrolysis, N_2, 773 K	$C_{0.22}H_{1.75}O$	1.07
		Vapor	Preign, Air, 773 K	$C_{0.40}H_{1.21}O$	1.27
		Vapor	After flame extinc[b]	$C_{0.22}H_{1.74}O$	1.05
Douglas fir	NCX	Solid	Original sample	$C_{1.35}H_{2.34}O\ N_{0.082}$	5.87
		Vapor	Pyrolysis, N_2, 773 K	$C_{0.16}H_{1.82}O\ N_{0.002}$	0.82
		Vapor	Pyrolysis, Air, 773 K	$C_{0.28}H_{1.65}O\ N_{0.014}$	1.30
		Vapor	Preign, Air, 932 K	$C_{0.24}H_{1.65}O\ N_{0.005}$	1.06
		Solid	Residue	$C_{4.55}H_{2.86}O\ N_{0.255}$	8.99
Red oak	None	Solid	Original sample	$C_{1.35}H_{2.23}O\ N_{0.002}$	5.66
		Vapor	Preign, Air, 773 K	$C_{0.43}H_{1.35}O$	1.64
		Vapor	After flame extinc[b]	$C_{0.39}H_{1.68}O$	1.91
Red Oak	NCX	Solid	Original sample	$C_{1.39}H_{2.38}O\ N_{0.057}$	5.94
		Vapor	Pyrolysis, N_2, 773 K	$C_{0.20}H_{1.76}O\ N_{0.002}$	0.97
		Vapor	Pyrolysis, Air, 773 K	$C_{0.28}H_{1.67}O\ N_{0.008}$	1.34
		Solid	Residue	$C_{4.17}H_{3.13}O\ N_{0.24}$	8.93
Red oak	Fyrepruf	Solid	Original sample	$C_{1.31}H_{2.10}O\ N_{0.009}$	5.45
Red oak	Intumescent paint	Solid	Original sample	$C_{1.26}H_{2.11}O\ N_{0.026}$	5.42
Styrene-butadiene (conveyor belt)	None	Vapor	Preign, 773 K	$C_{1.18}H_{2.12}O\ N_{0.004}S_{0.002}Cl_{0.001}$	5.18
	Fire retardant	Vapor	Preign, 773 K	$C_{0.60}H_{1.72}O\ N_{0.003}S_{0.002}Cl_{0.001}$	2.94

[a] from data given in Table 1 and Tables 10 to 14

[b] flame extinction by N_2

treatment appears to double the transfer efficiency; for the treated samples, presence of air appears to show insignificant affect on the transfer efficiency. For the untreated sample, presence of air increases the transfer efficiency by about two and a half times the efficiency in pyrolysis in N_2.

3) Hydrogen Atom Transfer Efficiency from the Solid to Vapor Phase

The hydrogen atoms, which are provided by the sample alone, are transferred very efficiently (~100%) for the NCX treated samples. For untreated samples, the efficiency is about 53% in N_2 and increases to about 93% in air.

4) Nitrogen Atom Transfer Efficiency from the Solid to Vapor Phase

NCX treatment increases the nitrogen atoms in the sample. The nitrogen atom transfer efficiency is low in pyrolysis in N_2 (~4 to 5%), but increases to ~19 to 26% in air.

The atom transfer efficiency data thus indicate that in the solid phase carbon formation is enhanced and in the vapor phase water formation is enhanced in the thermal decomposition of the treated samples. This is indicated by the chemical formulae and stoichiometric air to fuel ratios in Table 16.

The enhancement of carbon formation in the solid phase and water formation in the vapor phase is beneficial in two ways: 1) carbon at the surface presents resistance to vapors and thus ignition would be expected to be difficult and the generation rate of combustible vapors would be decreased; and 2) the air requirement for the combustion of vapors would be reduced as indicated by the stoichiometric air to fuel ratio in Table 16; thus the air entrained in the fire plume would be expected to be sufficient to maintain overventilated conditions, i.e., high combustion efficiency or lower rates of generation of fire products associated with incomplete combustion i.e., CO, "smoke," hydrocarbons, etc. These beneficial effects of the wood treatments as well as the behavior of conveyor belt and brattice cloth samples have been examined on the basis of data measured directly as presented in the following section.

IV

EXPERIMENTAL RESULTS

4.1 IGNITION

The ignition concepts used in this study are described in Appendix B. The data for time to ignition (t_{ig}) as a function of external heat flux ($\dot{q}''_e$) are listed in Table 17.

Figures 3, 4, and 5 show data for $1/E_{ig}$, defined as the ignition parameter (IP), as a function of $\dot{q}''_e$; E_{ig} is the ignition energy equal to $t_{ig}\ \dot{q}''_e$ (see eq (B-1) in Appendix B). By extrapolating the data for $\dot{q}''_e$ where $1/E_{ig} \approx 0$, the critical heat flux ($\dot{q}''_{cr}$) for the samples can be determined. IP increases as $\dot{q}''_e$ is increased and approaches an asymptotic value. The data for $\dot{q}''_{cr}$, critical temperature, T_{cr}, and asymptotic values of IP are listed in Table 18 for wood, conveyor belt and brattice cloth samples. The smaller the value of $\dot{q}''_{cr}$ and the larger the value of IP, the shorter is the time to ignition and the faster is the surface flame spread expected in fires. Data in Table 18 suggest that intumescent paint, Fyreprufe and NCX treatments of red oak and Douglas fir are expected to be beneficial in 1) increasing the critical flux (or critical temperature) and 2) reducing the ignition parameter. Thus, treated samples would be expected to show a lower surface flame spread rate than untreated samples. This performance is expected on the basis of enhancement of carbon formation in the solid phase and enhancement of water formation in the vapor phase by the treatments enumerated in Section 3.1.

This behavior is further confirmed by the large-scale timber fire tests performed in the mine gallery (14). The minimum critical value of the temperature in the gallery for fire propagation in untreated and NCX-treated Douglas fir timber sets was found to be about 660 K and 770 K respectively compared with 660 K and 760 K respectively in Table 18. The stagnation burner experiments (25) also show a longer time to ignition and higher temperature required for ignition for NCX-treated red oak and Douglas fir than for the untreated samples.

For the conveyor belt samples, the IP values from Table 18 for untreated and treated styrene-butadiene rubber and German-X and German-Z belts are 2.1, 1.0, 0.50, and 0.5 x 10^{-3} m^2/kJ respectively. From Table 7 and Figure 6, the U.S. Bureau of Mines' ratings for these belts are 16, 1, 0, and 0 respectively.

TABLE 17

TIME TO IGNITION AS A FUNCTION OF EXTERNAL HEAT FLUX FOR SAMPLES OF WOOD, CONVEYOR BELTS AND BRATTICE CLOTH[a]

Sample	Treatment	External Heat Flux (kW/m^2)										
		14	20	25	31	37	42	46	52	60	66	71
		Time to Ignition (s)										
Wood												
Red oak	Untreated	-	106	47	28	20	16	14	12	10	-	8
	Intumescent paint	-	507	225	135	96	78	68	56	46	-	37
	Fyreprufe	-	287	143	90	65	53	46	39	32	-	26
Douglas fir	Untreated	215	72	46	32	25	21	18	16	13	-	11
	NCX	-	-	241	110	71	55	46	38	30	-	24
	Fireguard	-	-	-	99	45	31	25	19	15	-	11
Conveyor Belt												
Styrene-Butadiene	Untreated	-	-	-	47	25	18	15	12	9	-	7
	Fire retardant	-	-	125	63	42	33	28	23	18	-	14
German-X	Unknown	-	-	-	191	-	-	96	-	49	31	-
German-Z	Unknown	-	-	-	225	-	-	86	-	49	30	-
Brattice Cloth												
MSHA Lab No. 1280A	-	-	286	-	32	-	16	-	12	10		-
MSHA Lab No. 1580	-	-	289	-	82	-	31	-	21	17		-
MSHA Lab No. 1620	-	-	142	-	42	-	22	-	16	13		-
MSHA Lab No. 1688	-	-	168	-	54	-	29	-	19	15		-

[a] forced air flow ~0.003 m^3/s; area ~0.008 m^2; surface coated with a small amount of fine graphite powder

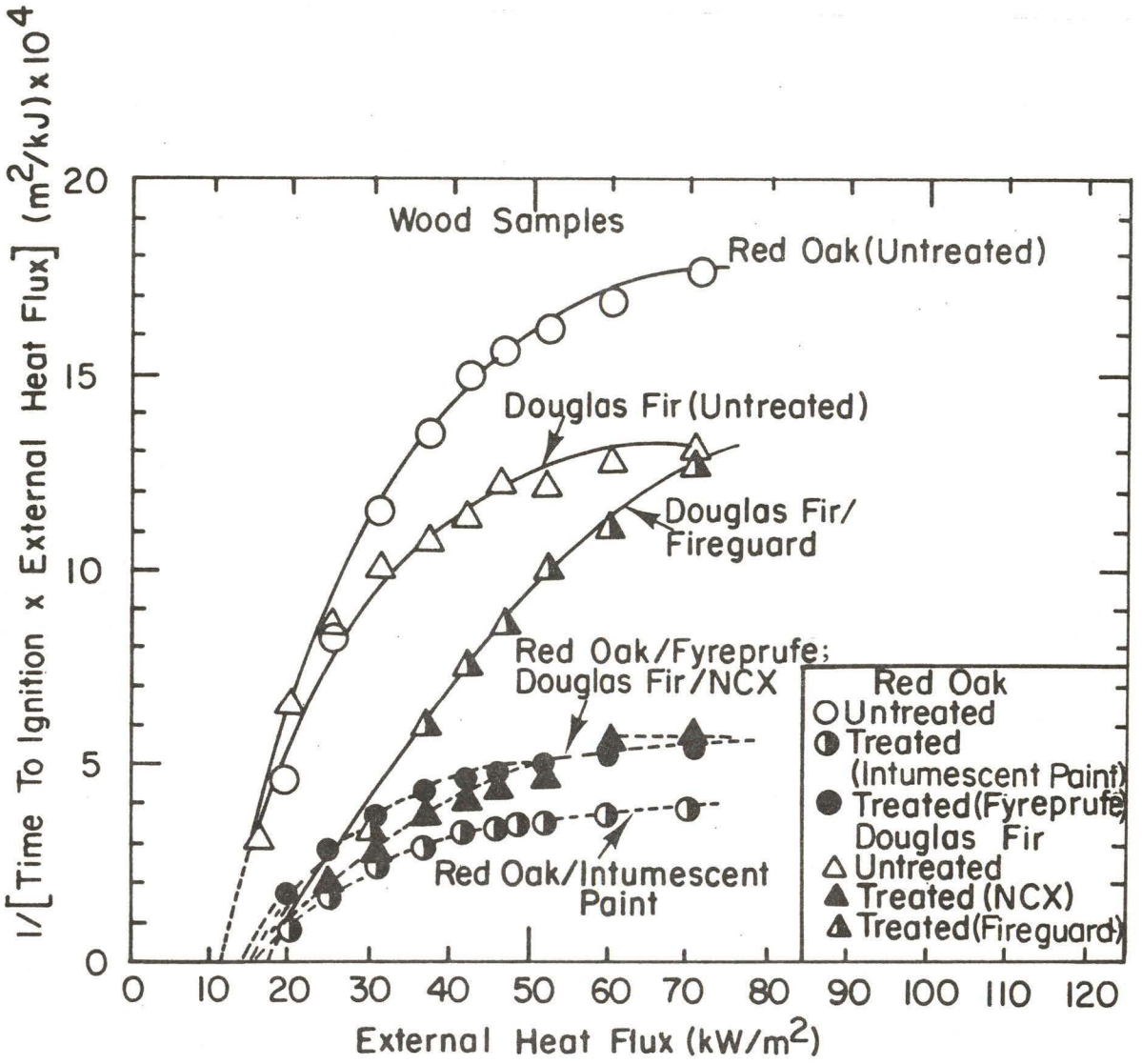

FIGURE 3. Inverse of the piloted ignition energy as a function of the external heat flux for wood samples

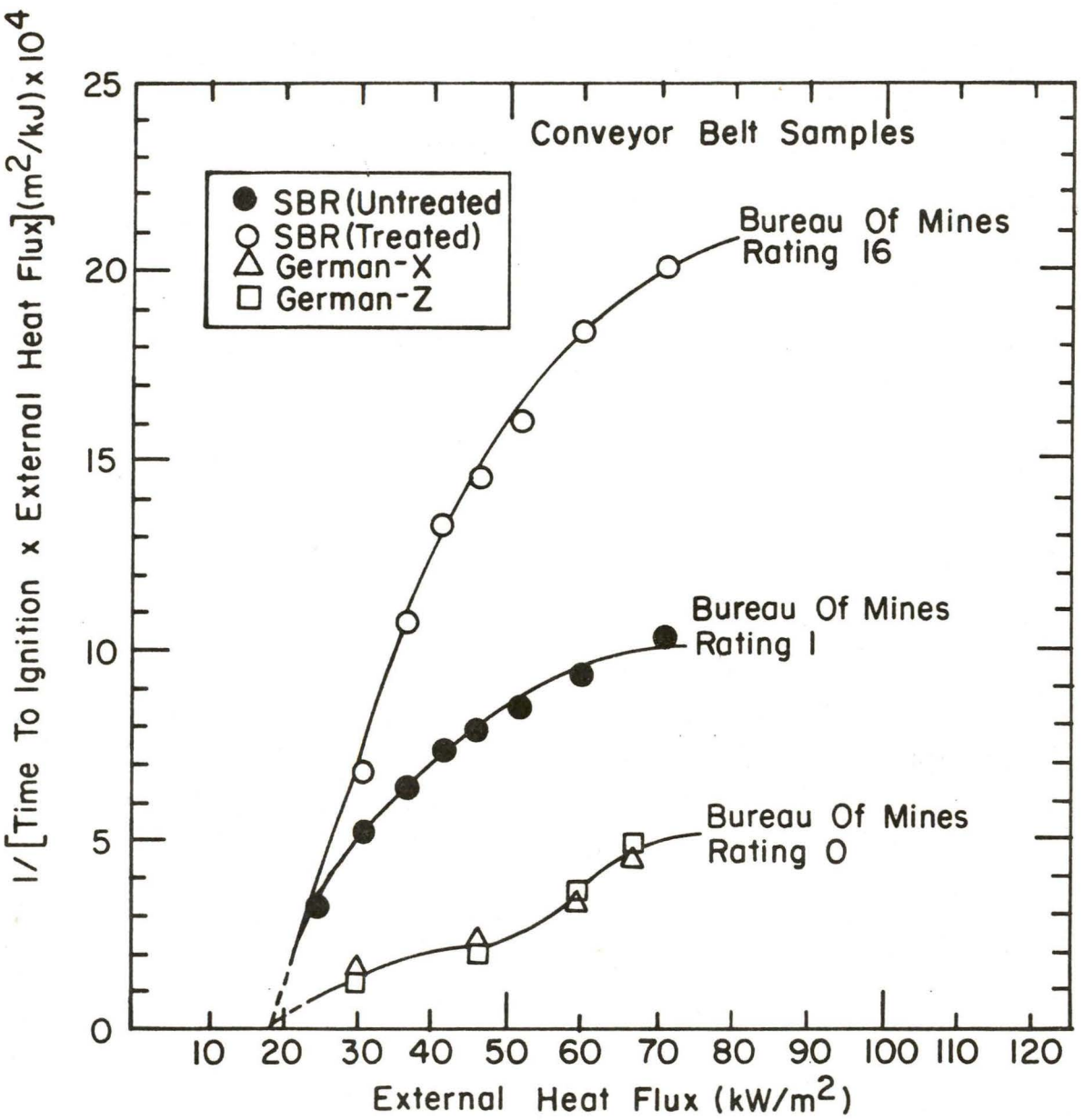

FIGURE 4. Inverse of the piloted ignition energy as a function of the external heat flux for conveyor belt samples. Bureau of Mines ratings from ref 26 and 27.

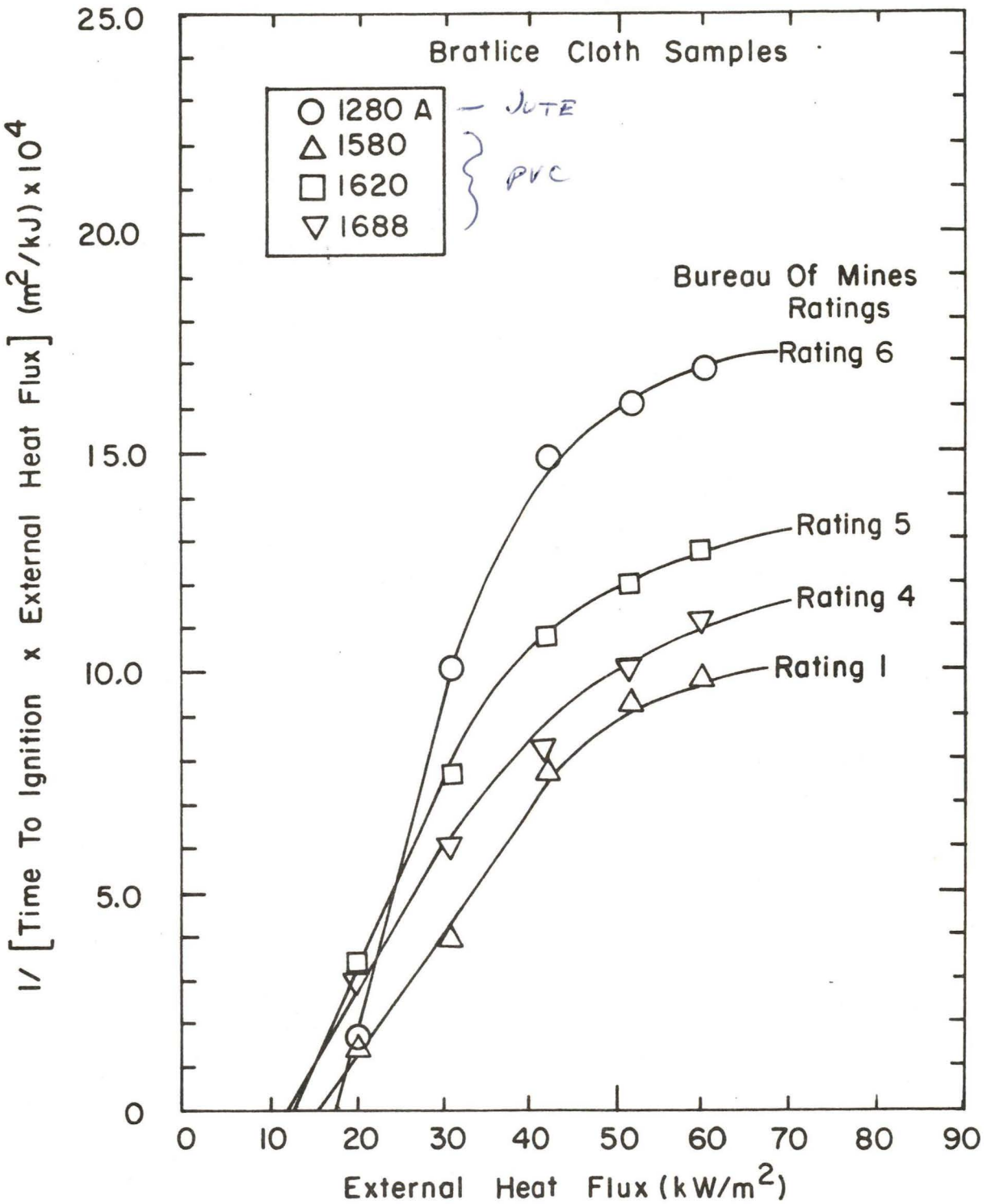

FIGURE 5. Inverse of the piloted ignition energy as a function of the external heat flux for brattice cloth samples. U.S. Bureau of Mines ratings from ref 27.

TABLE 18

CRITICAL HEAT FLUX AND ASYMPTOTIC VALUE OF IGNITION PARAMETER FOR MINE MATERIALS[a]

Sample	Treatment	$\dot{q}''_{cr}$ (kW/m^2)	T_{cr}[b] (K)	IPx10^6[c] (m^2/kJ)
Wood				
Red oak	Untreated	11	660	1750
	Intumescent paint	16	730	400
	Fyrepruf	15	720	560
Douglas fir	Untreated	11	660	1300
	NCX	19	760	560
	Fireguard	15	720	1350
Conveyor Belt				
Styrene-butadiene Rubber	Untreated	17	740	2100
	Fire retardant	17	740	1000
German-X	Unknown	18	750	500
German-Z	Unknown	18	750	500
Brattice Cloth				
MSHA Lab No. 1280A	Unknown	18	750	1700
MSHA Lab No. 1580	Unknown	15	720	1000
MSHA Lab No. 1620	Unknown	12	680	1300
MSHA Lab No. 1688	Unknown	12	680	1200

[a] piloted ignition; forced air flow ~0.003 m^3/s; samples ~ 0.008 m^2 in surface area; ~0.01 to 0.02 m thickness

[b] calculated from $\dot{q}''_{cr} = \sigma T^4_{cr}$, $\sigma = 56.7 \times 10^{-12} \left(\frac{kW}{m^2 K}\right)^4$

[c] asymptotic value of IP or $1/E_{ig}$, where $E_{ig} = t_{ig}\dot{q}''_e$

It thus appears that IP values follow the U.S. Bureau of Mines' rating and when IP values are about 0.50×10^{-3} m^2/kJ or less, the Bureau of Mines ratings are close to zero.

For brattice cloth, a comparison of IP values from Table 18 and U.S. Bureau of Mines ratings from Table 8 and Figure 7 show a reasonable correlation.

From the above comparisons for wood, conveyor belt and brattice cloth samples, it appears that critical heat flux (critical temperature) and ignition parameters measured for a variety of combustibles in the FM Small-Scale Combustibility Apparatus can be used as quantified ignition/flame spread criteria for ratings of various mine materials.

4.2 GENERATION RATE OF COMBUSTIBLE VAPORS

The concepts used for quantifying the generation rate of combustible vapors are discussed in Appendix C. Data for the ratio of generation rate of combustible vapors to external heat flux which is defined as the combustible vapor generation parameters (VP) are listed in Table 19. It should be noted that the inverse of VP is equal to the heat of gasification. The larger the value of VP, the higher is the generation rate of combustible vapors expected in fires.

The data in Table 19 show that wood treatments decrease the VP values, as expected on the basis of enrichment of solid phase by carbon, discussed in Section 3.1. Further, as external heat flux is increased, VP decreases for treated as well as untreated samples. The decrease in VP values indicates increased enrichment of the solid phase by carbon. For untreated Douglas fir and red oak, $-VP = 0.33$ and 0.38 g/kJ for external heat flux of 46 and 52 kW/m^2 respectively, compared with a value of 0.34 g/kJ for pure cellulose at 50 kW/m^2.

For conveyor belt samples, German-X and Z belts show lower VP values at higher heat fluxes than the styrene-butadiene belt samples at lower heat fluxes. The VP values for brattice cloth samples are smallest.

VP values can be used for ratings of mine materials for the generation of combustible vapors. For larger-scale fire simulation, flame radiation should be incorporated into the VP values, where radiation-scaling techniques (3-6) can be used. The quantification of flame radiation would also be helpful in a better definition of self-propagating fires in mine materials.

TABLE 19

COMBUSTIBLE VAPOR GENERATION PARAMETER FOR MINE MATERIALS[a]

Sample	Treatment	External Heat Flux (kW/m^2)					
		31	37	46	52	60	67
		VP (g/kJ)					
Wood							
Red oak	Untreated	0.55	0.58	0.49	0.38	0.34	-
	Fyrepruf	0.48	0.42	0.35	0.34	0.30	-
	Intumescent paint	0.39	0.34	0.28	0.28	0.25	-
Douglas fir	Untreated	0.46	0.40	0.33	-	0.29	-
	NCX	0.38	0.34	0.33	-	0.31	-
	Fireguard	0.40	0.35	0.32	-	0.26	-
Conveyor Belt							
Styrene-butadiene	Untreated	-	-	-	0.46	0.32	-
	Fire retardant	-	-	-	-	-	-
German-X	Unknown	-	-	-	-	-	0.23
German-Z	Unknown	-	-	-	-	-	0.23
Brattice Cloth							
MSHA Lab No. 1280A	Unknown	-	-	-	0.14	-	-
MSHA Lab No. 1580	Unknown	-	-	-	0.13	-	-
MSHA Lab No. 1620	Unknown	-	-	-	0.14	-	-
MSHA Lab No. 1688	Unknown	-	-	-	0.12	-	-

[a] forced air flow ~0.003 m^3s; area ~0.008 m^2; piloted ignition; combustible vapor generation parameter (VP) = $\dot{G}''_{comb}/\dot{q}''_e$;

$\dot{G}''_{comb}$ = generation rate of combustible vapors (g/m^2s)

$\dot{q}''_e$ = external heat flux (kW/m^2)

4.3 GENERATION RATE OF FIRE PRODUCTS (HEAT AND CHEMICAL COMPOUNDS)

The concepts used in this study for quantifying the generation rate of fire products are described in Appendix D.

4.3.1 Actual Heat Release Rate

Data for the ratios of actual heat release rate to external heat flux, defined as the heat generation parameter, HP, are listed in Table 20. The larger the value of HP, the higher is the actual heat release rate expected in fires.

The average HP values for untreated red oak and Douglas fir at 52 and 46 kW/m^2 from Table 20 are 5.2 and 4.6 respectively compared with a value of 5.8; for pure cellulose at 50 kW/m^2. Data in Table 20 indicate that wood treatments, except Fireguard, decrease HP values; for example, the average ratio of HP values for NCX-treated Douglas fir to untreated fir is 0.51. The ratio of the actual heat release rate for treated and untreated Douglas fir timber sets from large-scale fire tests in the gallery is about 0.65 (14), showing that HP values obtained from the small-scale tests are reasonable.

If HP values are plotted as functions of the ratio of heat release rate for complete combustion to external heat flux, as shown in Figure 6 for wood samples, then the slope is the combustion efficiency. It can be noted in Figure 6 that combustion efficiency of untreated wood samples is less than unity (0.85 for Douglas fir and 0.75 for red oak), an indication of some carbon enrichment in the solid phase. For the treated samples, the combustion efficiency is much smaller than for the untreated samples (0.48), which is an indication of enhancement of carbon formation in the solid phase, which has been discussed previously in Section 3.1.

The HP value for research grade polystyrene, for overventilated fires at 50 kW/m^2, is 19, whereas for untreated styrene-butadiene conveyor belt sample it is 15.6 at 52 kW/m^2. HP values for conveyor belt samples decrease with increase in the external heat flux which is an indication of change toward underventilated conditions. The HP value for the treated styrene-butadiene conveyor belt sample is in the range of 15.2 to 11.0 compared with a range of 18.6 to 11.6 for the untreated sample; thus, the treatment appears to be effective to a limited extent.

HP values calculated from data from the Ohio State University apparatus for similar untreated and treated styrene-butadiene conveyor belt samples are 18.2 and 11.7 respectively at 30 kW/m^2 (26), compared with our values of 18.6 and 15.2 at 37 kW/m^2 respectively.

TABLE 20

HEAT GENERATION PARAMETER FOR MINE MATERIALS[a]

Sample	Treatment	External Heat Flux (kW/m^2)					
		31	37	46	52	60	67
		HP					
Wood							
Red oak	Untreated	6.7	6.7	5.2	4.6	4.7	-
	Fyrepruf	3.6	3.3	2.7	2.3	2.4	-
	Intumescent paint	2.3	2.4	1.7	2.0	1.9	-
Douglas fir	Untreated	6.4	5.8	4.6	-	3.7	-
	NCX	2.6	2.5	2.7	-	2.3	-
	Fireguard	4.6	4.4	4.8	-	3.7	-
Conveyor Belt							
Styrene-butadiene	Untreated	-	18.6	15.6	14.6	11.6	-
	Fire retardant	-	15.2	10.6	11.8	11.0	-
German-X	Unknown	-	-	-	-	-	2.8
German-Z	Unknown	-	-	-	-	-	3.2
Brattice Cloth							
MSHA Lab No. 1280A	Unknown	-	-	-	5.3	-	-
MSHA Lab No. 1580	Unknown	-	-	-	3.2	-	-
MSHA Lab No. 1620	Unknown	-	-	-	3.6	-	-
MSHA Lab No. 1688	Unknown	-	-	-	4.1	-	-

[a] piloted ignition, forced air flow ~0.003 m^3/s; sample ~0.008 m^2 in area; ~0.02 m in thickness; heat generation parameter, HP = $\dot{Q}''_A/\dot{q}''_e$; $\dot{Q}''_A$ = actual heat release rate (kW/m^2); $\dot{q}''_e$ = external heat flux (kW/m^2)

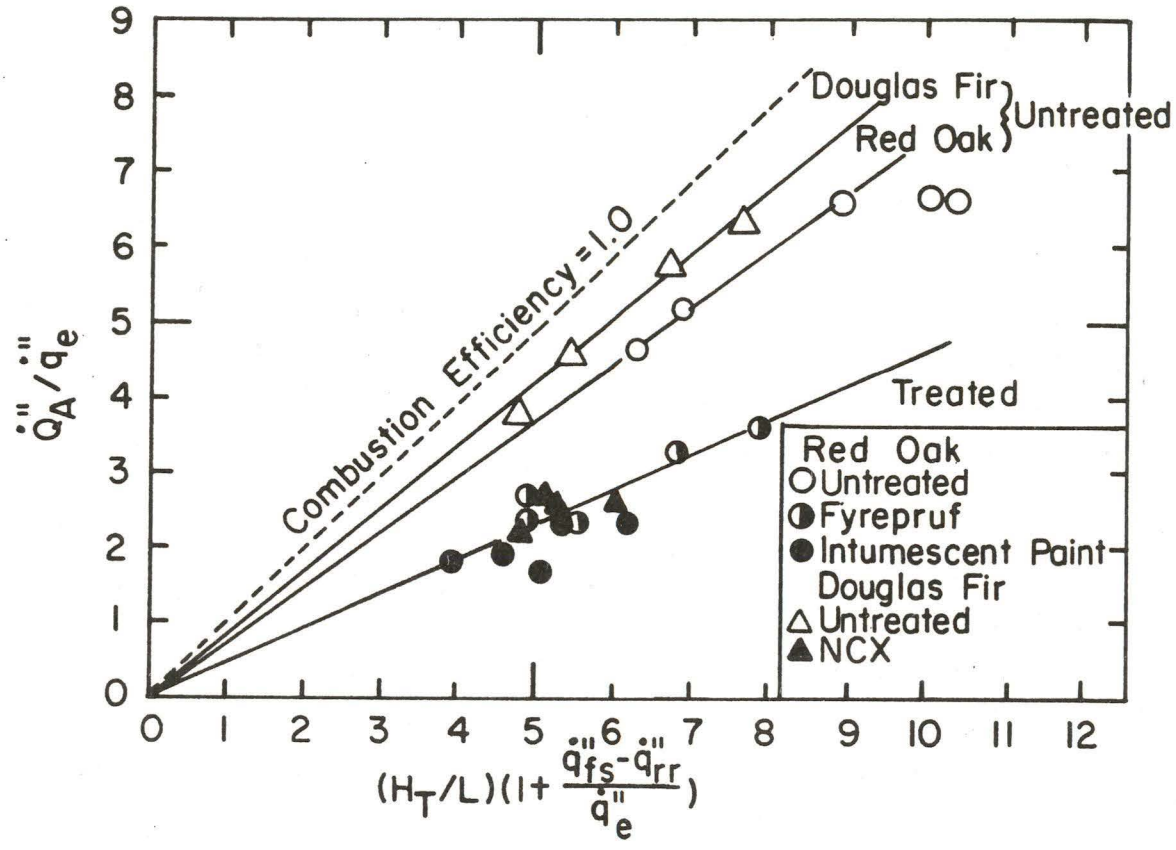

FIGURE 6. Ratio of actual heat release rate to external heat flux as a function of the ratio of heat release rate for complete combustion to external heat flux for treated and untreated wood samples

The HP values for German-X and German-Z conveyor belt samples are significantly smaller than the values for the styrene-butadiene conveyor belt sample. The heat release rate in fires thus would be expected to be much smaller for the German belt samples than for the styrene-butadiene samples, in agreement with the results expected on the basis of the U.S. Bureau of Mines larger-scale testing efforts.

From Table 20, the HP value for untreated jute sample (MSHA Lab No. 1280A), which is a cellulosic material, is 5.3 at 52 kW/m^2 compared with a value of 5.8 for pure cellulose at 50 kW/m^2. The HP values for the brattice cloth samples in Table 20 appear to follow U.S. Bureau of Mines ratings listed in Table 8.

From the data for the limited number of mine materials, it appears that HP values can be used for rating various mine materials for hazards associated with heat release rates. In addition, HP values can be used to estimate heat release rates in various mine fire scenarios. For the estimation of heat release rate, one would multiply HP values with the heat flux values expected in various mine scenarios.

4.3.2 Generation Rates of Chemical Compounds (CO, CO_2, and Hydrocarbons)

Tables 21 and 22 list the data for the ratios of generation rates of chemical compounds to external heat flux, defined as the chemical compound generation parameter, CP. The larger the value of CP, the higher the generation rate of chemical compounds expected in mine fires.

The values of $(CP)_{CO_2}$ from Table 21 for untreated red oak and Douglas fir are 0.57 and 0.45 for external heat flux values of 52 and 46 kW/m^2 respectively compared with a value of 0.60 for pure cellulose; at 50 kW/m^2, the value of $(CP)_{CO_2}$ decreases with increasing in external heat flux, because of increased amounts of carbon being retained in the solid phase. Data in Table 21 indicate that treatments, except Fireguard, reduce the values of $(CP)_{CO_2}$.

If the $(CP)_{CO_2}$ values are plotted as functions of $(CP)_{CO_2}$ values with all the carbon in the sample converted to CO_2, as shown in Figure 7, then the slope gives the generation efficiency of CO_2. It can be noted that CO_2 generation efficiency is less than unity for the untreated samples, indicating some enhancement of carbon formation of the solid phase. CO_2 generation efficiency shows a significant decrease for the treated samples, i.e., significant enhancement of carbon formation of the solid phase, supporting the conclusions derived in Section 3.1.

TABLE 21

CO_2 GENERATION PARAMETER FOR MINE MATERIALS[a]

Sample	Treatment	External Heat Flux (kW/m^2)					
		31	37	46	52	60	67
		$(CP)_{CO_2}$ (g/kJ)					
Wood							
Red oak	Untreated	0.69	0.72	0.66	0.57	0.47	-
	Fyrepruf	0.35	0.33	0.25	0.22	0.23	-
	Intumescent paint	0.22	0.20	0.18	0.19	0.18	-
Douglas fir	Untreated	0.59	0.51	0.45	-	0.38	-
	NCX	0.27	0.23	0.26	-	0.23	-
	Fireguard	0.40	0.39	0.33	-	0.31	-
Conveyor Belt							
Styrene-Butadiene	Untreated	-	1.10	0.86	0.94	0.70	-
	Fire retardant	-	0.53	0.72	0.76	0.70	-
German-X	Unknown	-	-	-	-	-	0.17
German-Z	Unknown	-	-	-	-	-	0.18
Brattice Cloth							
MSHA Lab No. 1280A	Unknown	-	-	-	0.37	-	-
MSHA Lab No. 1580	Unknown	-	-	-	0.19	-	-
MSHA Lab No. 1620	Unknown	-	-	-	0.22	-	-
MSHA Lab No. 1688	Unknown	-	-	-	0.25	-	-

[a] piloted ignition; forced air flow ~0.003 m^3/s; sample ~0.008 m^2 in area; ~0.01 to 0.02 m in thickness; CO_2 generation parameter $(CP)_{CO_2} = \dot{G}''_{CO_2}/\dot{q}''_e$;
$\dot{G}''_{CO_2}$ = generation rate of CO_2 (g/m^2s);
$\dot{q}''_e$ = external heat flux (kW/m^2)

TABLE 22

GENERATION PARAMETER FOR CO AND TOTAL GASEOUS HYDROCARBONS FOR MINE MATERIALS[a]

Sample	Treatment	External Heat Flux (kW/m^2)									
		37		46		52		60		67	
		CO	HC[b]	CO	HC[b]	CO	HC[b]	CO	HC[b]	CO	HC[b]
Conveyor Belt	Untreated	0.070	0.015	0.056	0.011	0.066	0.022	0.046	0.012	-	-
	Fire retardant	0.040	0.0038	0.028	0.0040	0.028	0.0038	0.026	0.003	-	-
German-X	Unknown	-	-	-	-	-	-	-	-	0.021	0.0015
German-Z	Unknown	-	-	-	-	-	-	-	-	0.030	0.0094
Brattice Cloth											
MSHA Lab No. 1280A	Unknown	-	-	-	-	0.00056	-	-	-	-	-
MSHA Lab No. 1580	Unknown	-	-	-	-	0.036	0.0025	-	-	-	-
MSHA Lab No. 1620	Unknown	-	-	-	-	0.040	0.0054	-	-	-	-
MSHA Lab No. 1688	Unknown	-	-	-	-	0.027	0.0055	-	-	-	-

[a] piloted ignition; forced air flow, ~0.003 m^3/s; sample ~0.008 m^2 in area; ~0.01 to 0.02 m in thickness. In the table, data for wood samples are not presented; $(CP)_{CO}$ and $(CP)_{hydrocarbons}$ are less than 0.0008 and 0.0002 respectively, due to excess air used in the experiments (overventilated conditions). Experiments were not performed for underventilated conditions.

Chemical compound generation parameter, $(CP)_j = \dot{G}''_j/\dot{q}''_e$;

$\dot{G}''_j$ = generation rate of compound j (CO or hydrocarbons in $g/m^2/s$);

$\dot{q}''_e$ = external heat flux (kW/m^2)

[b] total gaseous hydrocarbons

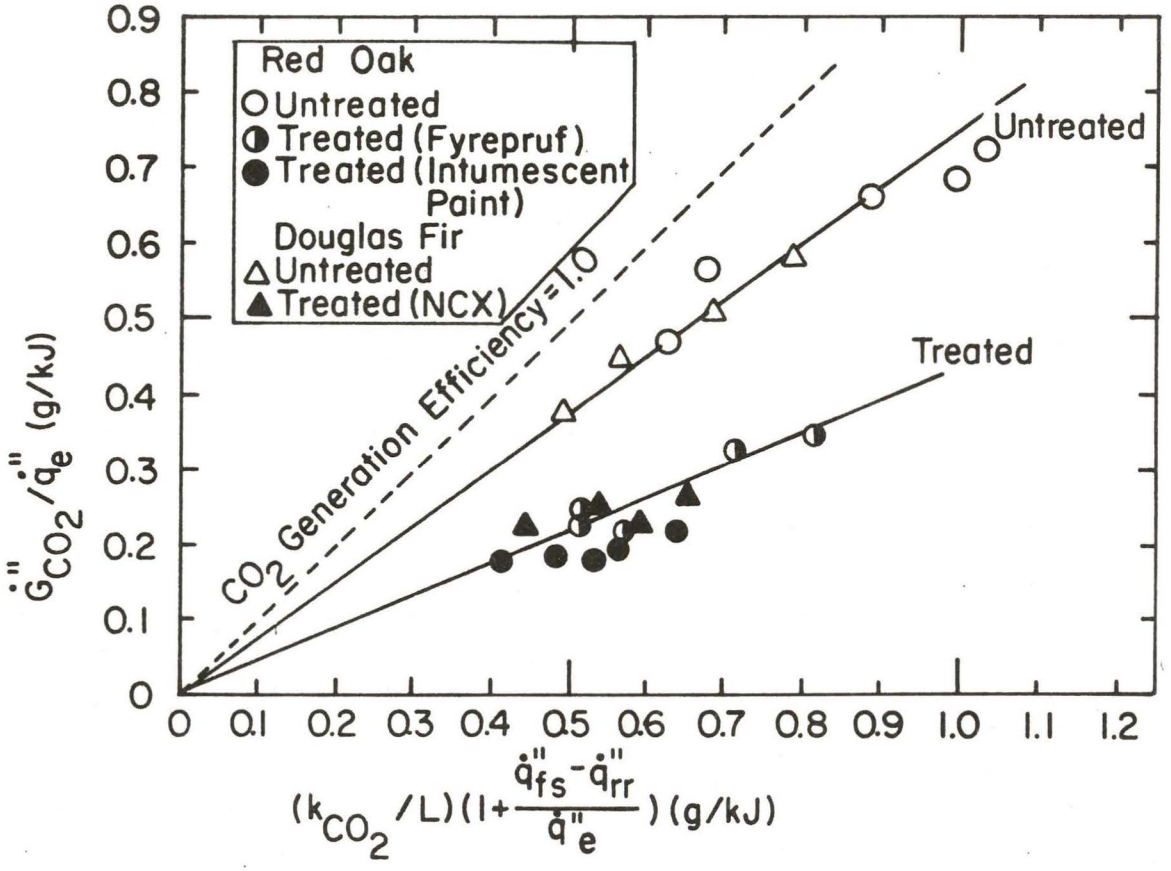

FIGURE 7. Ratio of generation rate of CO_2 to external heat flux as a function of the ratio of generation rate of CO_2, for complete conversion of carbon in the sample to CO_2, to external heat flux for treated and untreated wood samples

The $(CP)_{CO_2}$ values for styrene-butadiene conveyor belt samples are significantly higher than the values for German-X and -Z belt samples.

Values of $(CP)_{CO_2}$ for brattice cloth samples appear to follow U.S. Bureau of Mines ratings listed in Table 8. The $(CP)_{CO_2}$ value for untreated jute sample (MSHA Lab No. 1280A), which is cellulosic in nature, is 0.37, compared with a value of 0.60 for pure cellulose and an average value of 0.57 for red oak and Douglas fir.

In Table 22, the values of $(CP)_{CO}$ and $(CP)_{hydrocarbons}$ for wood samples are not included, because overventilated fire conditions were used and the values were less than 0.0008 and 0.0002 respectively, in agreement with the values for pure cellulose. The $(CP)_{CO}$ and $(CP)_{hydrocarbon}$ values are considerably higher for styrene-butadiene conveyor belt samples than the German-X and -Z samples. For research grade polystyrene, CP values for CO_2, CO, and hydrocarbons at 50 kW/m^2 are 1.5, 0.066, and 0.032 g/kJ respectively, compared with values of 0.94, 0.066, and 0.022 g/kJ for untreated styrene-butadiene conveyor belt sample at 52 kW/m^2 respectively.

The $(CP)_{CO}$ value for untreated jute sample (MSHA Lab No. 1280A), which is a cellulosic material, is 0.00056, compared with a value of $\lesssim$0.00080 for pure cellulose and the untreated wood samples. The $(CP)_{CO}$ and $(CP)_{hydrocarbon}$ values for brattice cloth samples other than the jute sample are comparable to the values for German-X and -Z belt samples.

It thus appears that for overventilated fire conditions, conveyor belt and brattice cloth samples may present a higher fire hazard than the wood samples. For underventilated fire conditions, the results may be similar or different. Fires in enclosures, such as mine passageways, may be underventilated in many cases; thus it is important that combustibility data for mine materials for underventilated conditions be quantified in future studies.

Quantified CP values for various toxic and corrosive products for over- and underventilated fires can be used for ratings of mine materials as well as for fire hazard analysis in various mine fire scenarios.

4.3.3 Light Obscuration by "Smoke"

The concepts used in quantifying light obscuration by "smoke" are described in Appendix E. Data for the light obscuration parameter (LP) are listed in Table 23. The higher the value of LP, the higher is the light obscuration by

TABLE 23

LIGHT OBSCURATION PARAMETER FOR MINE MATERIALS[a]

Sample	Treatment	External Heat Flux (kW/m^2)					
		31	37	46	52	60	67
		LP (m^2/kJ)[b]					
Wood							
Red Oak	Untreated	0.044	0.038	0.027	0.037	0.043	-
	Fyrepruf	0.0036	0.0069	0.0039	0.010	0.011	-
	Intumescent paint	0.0029	0.0056	0.0054	0.010	0.0065	-
Douglas fir	Untreated	0.025	0.022	0.025	-	0.043	-
	NCX	-	0.0014	0.0021	-	0.0033	-
	Fireguard	0.023	0.027	0.025	-	0.032	-
Conveyor Belt							
Styrene-butadiene	Untreated	-	0.28	0.20	0.24	0.21	-
	Fire retardant	-	0.28	0.24	0.22	0.21	-
German-X	Unknown	-	-	-	-	-	0.014
German-Z	Unknown	-	-	-	-	-	0.027
Brattice Cloth							
MSHA Lab No. 1280A	Unknown	-	-	-	0.0024	-	-
MSHA Lab No. 1580	Unknown	-	-	-	0.027	-	-
MSHA Lab No. 1620	Unknown	-	-	-	0.037	-	-
MSHA Lab No. 1688	Unknown	-	-	-	0.039	-	-

[a] light obscuration parameter, LP, is defined in eq (E-9) in Appendix E and is equal to $\sigma Y_{smoke}/L$, where σ = mass attenuation coefficient (m^2/g); Y_{smoke} = yield of "smoke" (g/g) and L = heat of gasification of the sample (kJ/g)

[b] for wave-length of 0.458 μ of the light-source

"smoke." Data in Table 23 indicate that wood treatments, except Fireguard, reduce the LP values. This is indicative of enrichment of the solid phase by carbon atoms for the treated samples, as discussed in Section 3.1. German-X and -Z belts as well as brattice cloth samples (except sample 1280A) show LP values similar to the values for untreated wood samples. However, the styrene-butadiene conveyor belt samples show that LP values are about 6 to 10 times the LP values for untreated wood samples; thus, the LP values for styrene-butadiene conveyor belt samples indicate that the hazard due to "smoke" is expected to be higher from these samples than from the wood, brattice cloth, and German-X and -Z belt samples. The LP value for research grade polystyrene at 50 kW/m^2 is 0.21 m^2/kJ compared with a value of 0.24 m^2/kJ for untreated styrene-butadiene conveyor belt sample at 52 kW/m^2.

It should be pointed out that LP values are sensitive to the wavelength of the light source as shown by the data in Table 24. A comparison of "smoke" data, thus, cannot be made on a quantitative basis with the data from other apparatuses such as U.S. Bureau of Mines conveyor belt test apparatus (26) and the Ohio State University Apparatus (26), because for these apparatuses, wavelength of light, volumetric flow rate of fire products, etc., are not reported. A comparison, on a relative basis, however, is possible for the fire retardant treated and untreated styrene-butadiene conveyor belt samples, which were common to all three studies: the ratio of the U.S. Bureau of Mines smoke index for treated and untreated sample is 0.70; the ratio of Ohio State smoke release rate for treated and untreated sample is 0.84; and the ratio of the light obscuration parameter for treated and untreated sample is 1.0 for a wavelength of 0.458 μ of the light source from this study.

In the light obscuration parameter (LP), the yield of smoke (Y_{smoke}) can be obtained from the ratio of the generation rate of "smoke" to the generation rate of the combustible vapors. 1/L can be obtained from the vapor generation parameter (VP) discussed in Section 4.2 and A, ℓ, and $\dot{V}$ are known; thus, the value of σ can be calculated from the LP values. Data for some selected samples are listed in Table 25, where data for measured soot fractions are also included.

The yield of "smoke" is high for polystyrene, styrene, and styrene-butadiene conveyor belt samples, all of which are aromatic type materials. The yield of "smoke" is small for the treated wood samples, except for Fireguard treated sample. It is interesting to note that the mass attenuation coefficient

TABLE 24

LIGHT OBSCURATION PARAMETER FOR THREE WAVELENGTHS OF LIGHT SOURCE[a]

Sample	Wavelength of Light Source (μ)		
	0.458	0.624	1.06
	LP (m^2/kJ)		
Conveyor Belt			
German-X	0.014	0.019	0.0074
German-Z	0.027	0.035	0.014
Brattice Cloth			
MSHA Lab No. 1280A	0.0024	0.0027	0.0018
MSHA Lab No. 1580	0.027	0.034	0.015
MSHA Lab No. 1620	0.037	0.048	0.020
MSHA Lab No. 1688	0.039	0.049	0.021

[a]light obscuration parameter, LP is defined in Table 23

TABLE 25

AVERAGE VALUES OF Y_S, σY_s, σ, AND SOOT FRACTION IN "SMOKE"

Sample	Treatment	Y_s[a] (g/g)	σY_s[b] (m^2/g)	σ[b] (m^2/g)	Soot Fraction in "Smoke"
Research Samples					
Polymethylmethacrylate	None	0.022	0.25	11	0.17
Polypropylene	None	0.095	0.38	4	0.78
Polystyrene	None	0.19	0.73	4	0.75
Styrene	None	0.20	0.78	4	-
Wood					
Red oak	Untreated	0.014	0.086	6	0.55
	Fyrepruf	0.006	0.020	3	-
	Intumescent Paint	0.010	0.021	2	-
Douglas fir	Untreated	0.013	0.084	6	0.55
	NCX	0.008	0.019	2	-
	Fireguard	0.023	0.083	4	-
Conveyor Belt					
Styrene-butadiene	Untreated	0.18	0.59	3	0.83
	Fire retardant	0.15	-	-	0.93
German-X	Unknown	-	0.061	-	-
German-Z	Unknown	-	0.12	-	-
Brattice Cloth					
MSHA Lab No. 1280A	Unknown	-	0.017	-	-
MSHA Lab No. 1580	Unknown	-	0.21	-	-
MSHA Lab No. 1620	Unknown	-	0.26	-	-
MSHA Lab No. 1688	Unknown	-	0.33	-	-

[a] Y_s = yield of "smoke" (g/g);

[b] σ = mass attenuation coefficient (m^2/g) for a wavelength of 0.476 μ for the light source

(σ) is between 3 to 4 m^2/g for polypropylene, polystyrene, styrene, Douglas fir with Fireguard, and styrene-butadiene, where about 78% of "smoke" consists of soot, suggesting that soot particles for these materials probably have similar physical and chemical properties (particle size, refractive index, etc.). For polymethylmethacrylate σ = 11, where soot fraction in "smoke" is 0.17; for untreated red oak and Douglas fir σ = 6, where soot fraction in "smoke" is 0.55. This appears to suggest that for these materials, the optical properties of "smoke" are governed by products other than soot particles, with particle sizes smaller than soot particles. By determining the value of σ as a function of the wavelength of the light source, it is possible to characterize the physical and chemical properties of "smoke," which is expected to be very useful in fire hazard evaluations in terms of visibility through "smoke," as well as for the evaluations of the fire detectors.

It thus appears that the light obscuration parameter, LP, is a useful parameter for rating of mine materials for "smoke" hazard evaluations and protection from such hazards in various mine fire scenarios.

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APPENDIX A

TOTAL VOLUMETRIC AND MASS FLOW RATES OF PRODUCT-AIR MIXTURE THROUGH THE SAMPLING DUCT.

The flow rates are calculated from measurements of: 1) pressure drop across the measuring orifice plate, Δp_m; 2) pressure inside the sampling duct p_d; and 3) bulk gas temperature in the duct, T_d. Using these measurements, the flow rates are calculated from the following relationship:

$$\dot{m} = 34.783\ K\ y\ d^2\ F_a(\Delta p_m \rho)^{1/2} \qquad \text{(A-1)}$$

where $\dot{m}$ is the mass flow rate (g/s); K = flow coefficient of the orifice in the duct; y = expansion factor (assumed to be unity); d = orifice opening diamter (cm); F_a = thermal expansion factor of metal (assumed to be unity); Δp_m = pressure drop across the orifice (g/cm^2); and ρ = density of the gaseous mixture flowing through the duct (g/cm^3).

The density of the gaseous mixture, assumed to be ideal, can be expressed as follows:

$$\rho = 11.798\ (p_d/T_d)\ MW \qquad \text{(A-2)}$$

where p_d = pressure of the gaseous mixtures in the duct (g/cm^2); T_d = bulk gas temperature (K); and MW = molecular weight of the gaseous mixture.

From Eqs. (A-1) and (A-2)

$$\dot{m} = 119.48\ K\ d^2\ [\Delta p_m\ (p_d/T_d)\ MW]^{1/2} \qquad \text{(A-3)}$$

If the products are diluted by large amounts of air, the molecular weight is approximately equal to 28.93 (i.e., the molecular weight of air) and Eq. (A-3) can be written as:

$$\dot{m}\ (kg/s) = 0.6426\ Kd^2\ [\Delta p_m\ (p_d/T_d)]^{1/2}. \qquad \text{(A-4)}$$

In the FM Small-Scale Apparatus the orifice plate diameter, d, is 5.08 cm. To determine the value of the flow coefficient K, the funnel (see Figure 3) was replaced by a calibration orifice plate. Experiments were performed with ambient air to measure the pressure drop across both plates (the calibration orifice plate and the orifice plate in the duct) simultaneously. The flow coefficient was calculated using the following equation:

$$K_m = K_c d_c^2 \, (\Delta p_c)^{1/2} / d_m^2 (\Delta p_m)^{1/2} \qquad \text{(A-5)}$$

where the subscript c refers to the calibration orifice plate and the subscript m refers to the measuring orifice plate in the duct. For this calculation, K_c was assumed to be equal to 0.61 and d_c was 4.06 cm. Using d_m equal to 5.08 cm, the average value of K_m was 0.62.

In the experiments, Δp_m is measured in cm H_2O and p_d is measured in kg/cm^2. Using these units and the values of K_m and d_m in Eq. (A-4), the mass flow rate can be expressed as:

$$\dot{m} \text{ (kg/s)} = 0.02032 \, K_m d_m^2 \, (\Delta p_m)^{1/2} \, (p_d/T_d)^{1/2} \qquad \text{(A-6)}$$

and the volumetric flow rate from Eqs. (A-2) and (A-6) is:

$$\dot{v} \text{ } (m^3/s) = \dot{m}/\rho = 0.00005953 \, K_m d_m^2 \, (\Delta p_m^{1/2} (T_d/p_d)^{1/2}. \qquad \text{(A-7)}$$

In the experiments, Δp_m, p_d and T_d are measured at one second (or longer) intervals. The mass and volumetric flow rates are calculated by substituting measured values into Eqs. (A-6) and (A-7), together with the values of K_m and d_m.

APPENDIX B

IGNITION

The time to ignition (t_{ig}) as a function of external heat flux ($\dot{q}''_e$) can be expressed as:

$$E_{ig} = \alpha \, t_{ig} \, \dot{q}''_e \qquad \text{(B-1)}$$

where E_{ig} = ignition energy (kJ/m^2), defined as the energy required to maintain a combustible vapor-air mixture near the surface; α = surface absorptivity; Figure B-1 shows $1/E_{ig}$ as a function of $\alpha\dot{q}''_e$ for piloted ignition of research grade polymers under forced air flow, with samples in a horizontal pool-like configuration, contained in a sample dish, made from two sheets of heavy duty aluminum foil. It can be noted in Figure B-1 that $1/E_{ig}$ is not a linear function of $\alpha\dot{q}''_e$. From the data shown in Figure B-1, the functional relationship between t_{ig} and $\dot{q}''_e$ can be derived. Also by data extrapolation, it is possible to obtain: 1) a value of $\dot{q}''_e$ at which $1/E_{ig}$ approaches zero, which can be defined as the critical heat flux ($\dot{q}''_{cr}$), which is a flux at or below which ignition is not expected to occur; and 2) the asymptotic value of $1/E_{ig}$ at higher external heat flux values where $1/E_{ig}$ is a constant or where t_{ig} is proportional to $1/\dot{q}''_e$. The larger the value of $1/E_{ig}$, the shorter is the ignition time and higher is the surface flame spread rate expected in fires. $1/E_{ig}$ thus can be defined as the ignition parameter (IP). In Figure B-1, the data indicate that IP for flexible polyurethane foam >>IP for polymethylmethacrylate >IP for polyethylene. Thus, in fires the surface flame spread rate is expected to be much faster for the flexible polyurethane foam than for polymethylmethacrylate; the rate for polymethylmethacrylate is expected to be faster than for polyethylene.

IP is a function of generic nature of the sample, sample orientation, local aerodynamic conditions (forced or natural air flow), mode of ignition (piloted or autoignition), and surface absorptivity.

In this study, we have used the above concept for the mine materials where samples were used in a horizontal pool-like configuration under forced air flow

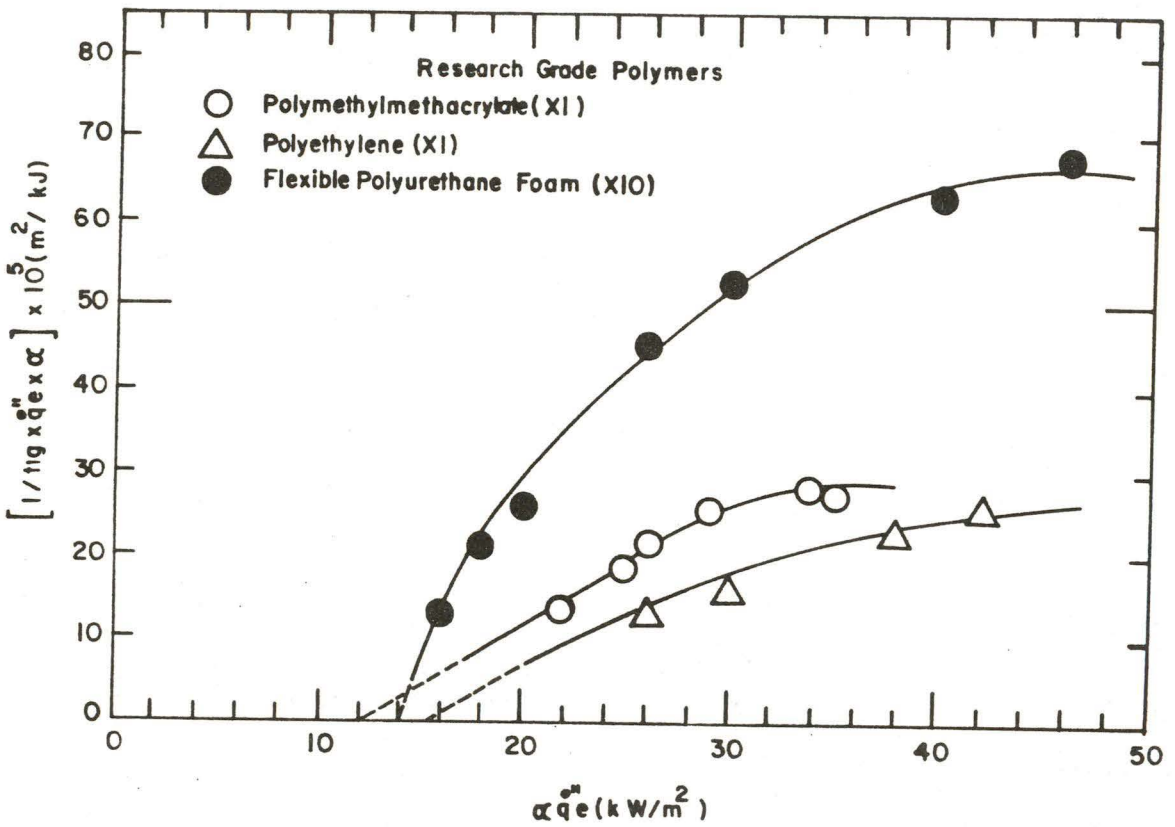

FIGURE B-1 PILOTED IGNITION PARAMETER AS A FUNCTION OF EXTERNAL HEAT FLUX

conditions and surface was coated with small amounts of fine graphite powder (i.e. $\alpha \approx 1$ in Eq. (B-1)). By measuring the IP values of the mine materials in this fashion the differenes in the IP values would be expected to show differences in the surface flame spread rate expected in fires.

In order to evaluate the self propagating surface flame characteristics of the mine materials, the heat flux from the burning samples need to be quantified. In this study no attempt was made to quantify the flame heat flux but this is recommended for future studies.

APPENDIX C

GENERATION RATE OF COMBUSTIBLE VAPORS PER UNIT SAMPLE SURFACE AREA

The generation rate of combustible vapors per unit sample surface area in flaming fires, $\dot{G}''_{comb}$, can be expressed as follows:

$$\dot{G}''_{comb} = (\dot{q}''_e + \dot{q}''_{fs} - \dot{q}''_{rr})/L \qquad (C\text{-}1)$$

where $\dot{G}''_{comb}$ is in g/m^2s; $\dot{q}''_e$ = external heat flux (kW/m^2); $\dot{q}''_{fs}$ = flame heat flux received by the sample (kW/m^2); $\dot{q}''_{rr}$ = surface reradiation loss (kW/m^2); and L = heat of gasification of the sample (kJ/g). In large fires, $\dot{q}''_{fs}$ is predominately due to flame radiation and in small fires $\dot{q}''_{fs}$ is predominantly due to flame convection. For small samples thus oxygen concentration in the inlet air is increased for radiation-scaling[3-6]. In this study radiation-scaling was not performed, but is recommended for future studies.

Dividing Eq. (C-1) by $\dot{q}''_e$,

$$\dot{G}''_{comb}/\dot{q}''_e = [1 + (\dot{q}''_{fs} - \dot{q}''_{rr})/\dot{q}''_e]/L \qquad (C\text{-}2)$$

For higher $\dot{q}''_e$ values for small samples in normal air, $(\dot{q}''_{fs} - \dot{q}''_{rr})/\dot{q}''_e << 1.0$ and hence:

$$\dot{G}''_{comb}/\dot{q}''_e \approx 1/L \qquad (C\text{-}3)$$

The larger the value of 1/L, the higher is the generation rate of the combustible vapors and thus 1/L can be defined as the combustible vapor generation parameter (VP) for mine materials; VP (g/kJ) is the amount of combustible vapors generated per unit of heat received by the sample.

This concept has been used to determine VP values for the mine materials.

For better definition of VP, it is necessary to include the heat flux from the flame, especially the flame radiative heat flux for simulating large-scale fires.

If the flame heat flux is quantified, it would also be possible to better define the ignition parameter (IP) discussed in Appendix B, especially for the self propagating fires for the mine materials. It is thus recommended that, for mine materials, $\dot{q}''_{fs}$ be quantified using radiation-scaling techniques[3-6].

In the experiments, the generation rate of combustible vapors is measured by a load-cell assembly. When the combustible vapors are generated from the sample the load-cell plate deflects a strainguage, which forms one leg of a wheatstone bridge. The voltage required to balance the bridge circuit is proprtional to the change of the mass of the sample. This voltage is monitored at one (or longer) second intervals by the MINC data acquisition system.

The generation rate of the combustible vapors is the instaneous slope or the derivative of the voltage (or mass) versus time curve. Because the electrical signal is somewhat noisy, a moving average is used by summing a specified number of points (p) adjacent to each other and dividing the sum by the total number of points involved. The average mass $\dot{m}_i$ (in volts) at scan, i is thus:

$$\bar{m}_i = \left(\sum_{j=-p}^{p} m_{i+j} \right)/n \qquad \text{(C-4)}$$

where n = number of points in the regression set (2p+1).

Early scan (i.e., scans before p+1) and late scans (i.e., scans after s-(p+1), where s is the total number of scans) are treated separately, since data cannot be averaged before or after the test. Early values of the mass loss are set equal to m_p, and late values are set equal to m_{s-p}.

The slope, a, then is calculated as follows:

$$a = \frac{n \sum_{i=1}^{n} t_i \bar{m}(t_i) - \sum_{i=1}^{n} t_i \sum_{i=1}^{n} \bar{m}(t_i)}{n \sum_{i=1}^{n} t_i^2 - \sum_{i=1}^{n} t_i \sum_{i=1}^{n} t_i} \qquad \text{(C-5)}$$

where, t is the time in seconds.

The generation of combustible vapors per unit surface area of the combustible at time, t, thus is:

$$\dot{G}''_{comb}(t) = a\ K\ A, \qquad \text{(C-6)}$$

where K = calibration constant of the load-cell assembly determined before each experiment (g/volt); and A = surface area of the sample (m^2).

APPENDIX D

GENERATION RATES OF FIRE PRODUCTS - HEAT AND CHEMICAL COMPOUNDS

D.1 GENERATION RATES OF FIRE PRODUCTS

Fire products consist of heat and various chemical compounds such as "smoke" toxic and corrosive products. The generation rate of heat actually released in flaming fires is defined as the actual heat release rate per unit sample surface, $\dot{Q}''_A$, and can be expressed as:

$$\dot{Q}''_A = \dot{Q}''_c + \dot{Q}''_R \qquad \text{(D-1)}$$

where $\dot{Q}''_A$ is in kW/m^2; $\dot{Q}''_c$ = convective heat release rate per unit sample surface area (kW/m^2); and $\dot{Q}''_R$ = radiative heat release per unit sample surface area (kW/m^2).

The chemical compounds can be generated in both nonflaming and flaming fires. In this study the mass generation rates per unit sample surface area of only CO, CO_2, and total gaseous hydrocarbons were determined in flaming fires.

D.2 MASS GENERATION RATES OF CHEMICAL COMPOUNDS PER UNIT SAMPLE SURFACE AREA

The mass generation rate of a chemical compound per unit sample surface area, $\dot{G}''_j$, can be expressed as:

$$\dot{G}''_j = \dot{v} c_j \rho_j / A \qquad \text{(D-2)}$$

where $\dot{G}''_j$ is in $g/m^2 s$; $\dot{v}$ is given by Eq. (A-7); c_j is the measured concentration of compound, j; and ρ_j is the density of the compound, j, given by Eq. (A-2); and A is the surface area of the sample (m^2).

From Eqs. (A-2), (A-7) and (D-2), if c_j is expressed in ppm,

$$\dot{G}''_j = 0.07025 \times 10^{-5} K_m (d_m)^2 (c_j (MW)(\Delta p_m)^{1/2} (p_d/T_d)^{1/2} \qquad \text{(D-3)}$$

The molecular weights for CO_2, CO, and total gaseous hydrocarbons (assumed to be CH_4) are 44, 28 and 16 respectively.

In the experiments, concentrations of CO_2, CO, and total gaseous hydrocarbons, as well as Δp_m, p_d and T_d, are monitored at one second interval (or longer). The generation rates are calculated from Eq. (D-3). The data for the generate rates are time shifted to account for delays with the gas sampling lines and respective instrument response. The generation rates of chemical compounds are functions of the generation rate of combustible vapors:

$$\dot{G}''_j = Y_j \dot{G}''_{comb} \tag{D-4}$$

where Y_j is the yield of compound j (g/g). From Eqs. (C-1) and (D-4):

$$\dot{G}''_j = Y_j (\dot{q}''_e + \dot{q}''_{fs} - \dot{q}''_{rr})/L \ . \tag{D-5}$$

Dividing Eq. (D-5) by $\dot{q}''_e$,

$$\dot{G}''_j/\dot{q}''_e = (Y_j/L) \left[1 + \frac{\dot{q}''_{fs} - \dot{q}''_{rr}}{q_e} \right] . \tag{D-6}$$

For higher $\dot{q}''_e$ values for small samples in normal air, $(\dot{q}''_{fs} - \dot{q}''_{rr})/\dot{q}''_e << 1$, and thus,

$$\dot{G}''_j/\dot{q}''_e \approx Y_j/L \ . \tag{D-7}$$

Y_j/L is the amount of compound j produced per unit amount of heat received by the sample; Y_j/L thus can be defined as the chemical compound generation parameter (CP).

D.3 HEAT RELEASE RATES

In the experiments, actual heat release rate, $\dot{Q}''_A$, and convective heat release rate, $\dot{Q}''_C$, per unit sample surface area are obtained directly from the measured data. The difference between $\dot{Q}''_A$ and $\dot{Q}''_C$, from Eq. (D-1), is the radiative heat release rate, $\dot{Q}''_R$.

D.4 ACTUAL HEAT RELEASE RATE PER UNIT SAMPLE SURFACE AREA

The actual heat release rate per unit sample surface area, $\dot{Q}''_A$, is calculated from the following equation:

$$\dot{Q}''_A = (H_T/k_{CO_2})\ \dot{G}''_{CO_2} + \left[\frac{H_T - H_{CO}}{k_{CO}}\right] \dot{G}''_{CO} \qquad \text{(D-8)}$$

where H_T is the net heat of complete combustion (kJ/g); H_{CO} is the heat of combustion of CO (10.1 kJ/g); and k_{CO} and k_{CO_2} are the maximum yields of CO and CO_2, calculated on the basis of complete conversion of carbon in the sample to CO without any CO_2 and CO_2 without any CO, respectively. $\dot{G}''_{CO_2}$ and $\dot{G}''_{CO}$ are calculated from Eq. (D-3). From the data for a variety of common combustibles with known H_T, k_{CO} and k_{CO_2}, it has been shown[4,6] that H_T/k_{CO_2} and $(H_T - H_{CO})/k_{CO}$ are approximately constant (average values 15 and 16 kJ/g respectively). Thus in this study for mine materials, the average values of H_T/k_{CO_2} and $(H_T - H_{CO})/k_{CO}$ were used to calculate $\dot{Q}''_A$.

D.5 CONVECTIVE HEAT RELEASE RATE PER UNIT SAMPLE SURFACE AREA

The convective heat release rate per unit sample surface are, $\dot{Q}''_{conv}$, is calculated from the following equation:

$$\dot{Q}''_{conv} = 4.184\ \frac{\dot{m}}{A}\ c_p\ (T_g - T_a) \qquad \text{(D-9)}$$

where $\dot{m}$ is the total mass flow rate of the gaseous mixture flowing through the sampling duct calculated from Eq. (A-6) as a function of time by the MINC; c_p is the specific heat of air (cal/g K); T_g is the gas temperature in the duct (K); and T_a is the ambient temperature (K). The specific heat, C_p, is corrected for temperature:

$$c_p = 0.2392 + 3.19 \times 10^{-5}\ T_g - 619/T_g^2 \qquad \text{(D-10)}$$

In the experiments, T_a and T_g are recorded at one second intervals (or longer) by the MINC and $\dot{Q}''_C$ is calculated from Eq. (D-9) and (D-10) using values of T_a and T_g and Eq. (A-6).

D.6 RADIATIVE HEAT RELEASE RATE PER UNIT SAMPLE SURFACE AREA

The radiative heat release rate, $\dot{Q}''_R$, is calculated as a function of time by the MINC by using Eqs. (D-1), (D-8) and (D-9) and stored with the disc for analysis. $\dot{Q}''_A$, $\dot{Q}''_C$ and $\dot{Q}''_R$ are functions of the generation rate of the combustible vapors, $\dot{G}''_{comb}$,

$$\dot{Q}''_A = H_A \dot{G}''_{comb} \tag{D-11}$$

$$\dot{Q}''_C = H_C \dot{G}''_{comb} \tag{D-12}$$

$$\dot{Q}''_R = H_R \dot{G}''_{comb} \tag{D-13}$$

where H_A, H_C and H_R are the actual, convective, and radiative heat of combustion respectively in kJ/g. From Eqs. (C-1) and (D-11 to 13),

$$\dot{Q}''_A = (H_A/L)\ (\dot{q}''_e + \dot{q}''_{fs} - \dot{q}''_{rr}) \tag{D-14}$$

$$\dot{Q}''_C = (H_C/L)\ (\dot{q}''_e + \dot{q}''_{fs} - \dot{q}''_{rr}) \tag{D-15}$$

$$\dot{Q}''_R = (H_R/L)\ (\dot{q}''_e + \dot{q}''_{fs} - \dot{q}''_{rr}) \tag{D-16}$$

and,

$$\frac{H_A}{L} = \frac{H_C}{L} + \frac{H_R}{L}\ . \tag{D-17}$$

Dividing Eq. (D-14) by $\dot{q}''_e$

$$\dot{Q}''_A/\dot{q}''_e = (H_A/L)\ \left[1 + \frac{\dot{q}''_{fs} - \dot{q}''_{rr}}{\dot{q}''_e}\right] \tag{D-18}$$

For higher $\dot{q}''_e$ values for small samples in normal air, $(\dot{q}''_{fs} - \dot{q}''_{rr})/\dot{q}''_e << 1$, and

$$\dot{Q}''_A/\dot{q}''_e \approx H_A/L\ . \tag{D-19}$$

In a similar fashion, it can be shown that

$$\dot{Q}''_C/\dot{q}''_e \approx H_C/L \quad \text{and} \tag{D-20}$$

$$\dot{Q}''_R/\dot{q}''_e \approx H_R/L \quad . \tag{D-21}$$

H_A/L, H_C/L and H_R/L are the amounts of actual, convective and radiative heat produced per unit amount of heat received by the sample respectively and, thus, can be defined as the heat generation parameter, HP (actual, convective or radiative).

The higher the values of the chemical compound and heat generation parameters, (CP and HP respectively), the higher are the generation rates of chemical compounds and heat expected in fires; thus, CP and HP can be used as indicators of the relative rankings of the combustibles. We have used these concepts in this study for the mine materials.

For better definition of CP and HP, the contribution of flame heat flux, especially flame radiation, simulated for large-scale fires, should be considered. It is recommended that flame heat flux be quantified by using the radiation-scaling technique[3-6] in future studies for mine materials.

APPENDIX E

OPTICAL TRANSMISSION THROUGH "SMOKE"

The fraction of light transmitted through "smoke", I/I_o, can be expressed as,

$$\ell n(I_o/I) = \ell \sigma c \qquad \text{(E-1)}$$

where ℓ is the optical path length (m); σ is the mass attenuation coefficient of "smoke" (m^2/g); and c is the mass concentration of "smoke" (g/m^3). $\ell n(I_o/I)$ is defined as the optical density, D (commonly expressed as log rather than ℓn).

In the experiments, I and I_o are recorded by the MINC at one-second intervals (or longer) and D is calculated, for 0.10 m optical path length, by the MINC as a function of time for the three wave-lengths: 0.458 μ, 0.624 μ, and 1.06 μ.

The concentration of "smoke" in Eq. (E-1) can be expressed as:

$$c = Y_{smoke}\, \dot{G}''_{comb}\, A/\dot{v}, \qquad \text{(E-2)}$$

where $\dot{G}''_{comb}$ = generation rate of combustible vapors per unit sample surface area ($g/m^2 s$); A = sample surface area (m^2); Y_{smoke} = yield of "smoke" (g/g) and $\dot{v}$ = volumetric flow rate of fire product-air mixture (m^3/s), calculated from Eq. (A-7) as a function of time by the MINC.

From Eqs. (E-1) and (E-2):

$$D = \sigma\, Y_{smoke}\, \dot{G}''_{comb}\, A\ell/\dot{v} \qquad \text{(E-3)}$$

For a closed system, such as the NBS Smoke Chamber, Eq. (E-3) can be expressed as:

$$\sigma\, Y_{smoke} = \frac{DV}{W\ell} \qquad \text{(E-4)}$$

where D is expressed as $\log_{10}(I_o/I)$, V is the volume of the chamber (m^3); and W is the weight of sample vaporized (g). The specific optical density, D_s, in the NBS Smoke Chamber is defined as:

$$D_s = DV/A\ell \tag{E-5}$$

From Eqs. (E-4) and (E-5),

$$\sigma Y_{smoke} = D_s A/W. \tag{E-6}$$

The mass attenuation coefficient, σ, is a function of the chemical and physical properties of the "smoke"; Y_{smoke} is a function of the chemical and physical properties of the combustible. Thus, the value of σY_{smoke} for a material is expected to be similar in different types of experiments, as long as the combustion/pyrolysis chemistry remains invariant.

From Eqs. (C-1) and (E-3),

$$D = \left[\frac{\sigma Y_{smoke}}{L}\right]\left[\left(\frac{A\ell}{\dot{v}}\right)\right](\dot{q}''_e + \dot{q}''_{fs} - \dot{q}''_{rr}). \tag{E-7}$$

Dividing Eq. (E-7) by $\dot{q}''_e$

$$D/\dot{q}''_e = \left[\frac{\sigma Y_{smoke}}{L}\right]\left[\left(\frac{A\ell}{\dot{v}}\right)\right]\ 1 + \frac{\dot{q}''_{fs} - \dot{q}''_{rr}}{\dot{q}''_e} \quad . \tag{E-8}$$

For higher $\dot{q}''_e$ values for small samples in normal air, $(\dot{q}''_{fs} - \dot{q}''_{rr})/\dot{q}''_e << 1$ and from Eq. (E-9).

$$D/\dot{q}''_e \approx \left[\frac{\sigma Y_{smoke}}{L}\right]\left[(A\ell/\dot{v})\right] \quad . \tag{E-9}$$

Since A, ℓ, and $\dot{v}$ are known, from $D/\dot{q}''_e$ values, $\sigma Y_{smoke}/L$ can be calculated. σ is a characteristic property of the "smoke"; Y_{smoke}/L is the amount "smoke" in gram generated per unit of heat received by the sample. $\sigma Y_{smoke}/L$ thus can be defined as the light obscuration parameter (LP) of "smoke".