Threshold powers and delays for igniting propane and butane-air mixtures by cw laser-heated small particles

Thomas H. Dubaniewicz, Jr.¹
National Institute for Occupational Safety and Health, Pittsburgh Research Laboratory, 626 Cochrans Mill Road, Pittsburgh, Pennsylvania 15236

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The National Institute for Occupational Safety and Health, Pittsburgh Research Laboratory conducted a study of laser safety in potentially flammable environments. Researchers measured threshold igniting powers as a function of beam diameter for butane and propane-air mixtures by laser-heating targets placed on optical fiber tips using a 1064 nm laser. The minimum igniting powers for propane-air and butane-air were about 250 and 300 mW, respectively. Threshold igniting powers for propane-air were approximately proportional to beam diameter for beam diameters from 0.1 to 2.0 mm. Results suggest that relatively powerful beams may be used in these atmospheres without causing ignition, provided the beam diameter is controlled. Threshold ignition delay times using 9/125 and 62.5/125 µm fibers were approximately proportional to the inverse square of the laser power. Ignition delays were about 45 ms or longer for laser powers up to 800 mW. Preproduction samples of a commercial optical fuse prevented ignitions under selected test conditions. A self-healing effect was observed for one sample. Comparisons are made with the results of other researchers. © 2006 Laser Institute of America.

Key words: propane ignition, butane ignition, laser ignition, nonbeam hazards, fiber optic fuse

I. INTRODUCTION

The National Institute for Occupational Safety and Health, Pittsburgh Research Laboratory (NIOSH, PRL) conducted a study of laser safety in potentially flammable environments (The findings and conclusions in this report are those of the author and do not necessarily represent the views of the National Institute for Occupational Safety and Health.) Fiber optic systems are being deployed in locations where explosive gas atmospheres are normally present or are present under fault conditions. For example, fiber deployment through sewer systems and natural gas lines is occurring to overcome the "last mile" hurdle for metro fiber optic systems.¹ Montgomery² suggests large core optical fibers up to 1 mm in diameter may be more suitable than small core fibers in many hazardous (classified) industrial environments due to enhanced ruggedness, ease of use, and maintenance issues. Research of high power fiber optic sensors for hostile environments such as fuel storage tanks continues.³

Propane and butane are found in natural gas and found in, or produced from, petroleum. Propane and butane are included with the Class I Group D or Group IIA flammable materials.⁴ Propane is typically used for purposes of testing and approval of electrical equipment for use in Class I Group D or Group IIA hazardous (classified) locations.⁵ Propane generally ignites more easily than methane, the primary component of natural gas. Natural gas consists mostly of methane gas (typically greater than 85%), with variable and much smaller amounts of ethane, propane, other hydrocarbons, and hydrogen. Testing with propane may be preferable to natural gas for safety evaluations in situations where natural gas contains variable or significant amounts of hydrocarbons heavier than methane. Propane may not be a conservative test gas for process gas containing significant amounts of hydrogen.⁶

The optical radiation guided by fiber optic systems can, under certain conditions, be considered a potential ignition source for explosive gas atmospheres. For wavelengths in the visible through mid infrared spectrum, optical ignitions occur with the lowest powers when a target contacts the beam and converts the optical energy to thermal energy.⁷ The best targets for causing ignition absorb most of the optical radiation and do not disintegrate before they become hot enough to ignite the gas. An optical fiber tip that becomes dirty (obstructed) can form a target approximating these conditions. Experiments reported here used obstructed fiber tips to simulate a worst case situation where a near infrared continuous wave (cw) beam is exposed to the flammable mixtures and potential targets are unknown.

Fiber optic power limiters can prevent excessive powers from propagating through the fiber and into hazardous environments. Where the beam is normally exposed to a flammable atmosphere, such a device must activate before ignition can occur under overpower fault conditions. Knowledge of ignition delay times would therefore be helpful to properly use the fiber optic power limiters as ignition prevention devices in these situations. The NIOSH Research to Practice (r2p) initiative emphasizes translation of research findings to effective products, and the need to evaluate and demonstrate the effectiveness of these products.⁸ A commercial fiber optic fuse was identified with activation powers and delays sufficient to prevent ignitions based on the experimental findings.

¹Electronic mail: tcd5@cdc.gov
of this study.9 Samples of the fiber optic fuses were tested to evaluate their potential for ignition prevention purposes, in accordance with the NIOSH r2p initiative.

**II. LITERATURE REVIEW**

Table I lists threshold igniting powers as a function of beam diameter for propane-air and butane-air observed by Hawksworth,11 Hills et al.,10 and Welzel et al.12 Propane threshold igniting powers generally increase with fiber core diameter for diameters >0.1 mm (Table I). Dubaniewicz et al.13 observed an approximately linear relationship between igniting power and beam diameter for methane-air mixtures using beam diameters from 200 to 800 μm. In the current study, fiber optic core diameters ranging from 9 μm to 2.0 mm were used to measure threshold igniting powers for butane-air and propane-air mixtures as a function of beam diameter. These diameters and gases were selected to see if the linear relationship between igniting power and beam diameter applied over a larger range of beam diameters for several straight chain hydrocarbons. The resulting ignition curves could potentially be used as a guide for using relatively powerful beams guided by large core fibers in Class I Group D or Group IIA hazardous (classified) locations.5 As suggested by Montgomery,2 large core fibers may have practical application for hazardous (classified) locations for several other reasons as well.

Optical equipment may be installed in locations where potential beam targets are not well known or controlled. For these situations, researchers have taken a worst-case approach in selecting targets for experimental research. Using cw lasers with small beam diameters, strongly absorbing and thermally stable targets appear to ignite gases most easily. Moore and Weinberg14 were unable to ignite methane-air mixtures using laser-heated cotton wool particles, which turned to ash and disintegrated. They were able to ignite methane-air mixtures using thermally stable refractory insulating wool as the laser target. The insulating wool absorbed the selected laser wavelength well. Welzel et al.12,15 found black iron manganese oxide (FeMn)2O3 targets produced the lowest gas igniting powers of a number of targets tested under most experimental conditions using cw lasers. Dubaniewicz et al.13 found Fe3O4 targets produced slightly lower igniting powers than coal targets in methane-air mixtures, using a nonflammable grease to attach the targets to large core optical fibers. Also, larger coal particles required higher laser powers to ignite the methane-air, suggesting the heat of combustion from the coal was not a significant contributor to ignition compared to the heat generated by the laser. Hawksworth10 observed combustible targets burn away without igniting selected gases at power levels that produced ignitions with (FeMn)2O3. Also, the (FeMn)2O3 produced lower igniting powers for selected atmospheres when it was mixed with a ceramic adhesive and applied to large core fiber tips as a paste. One exception was Hills et al.,11 who reported that Appin coal particles ignited selected atmospheres at the lowest powers. Dubaniewicz16 suggests some aspects of Hills results are more indicative of pulsed ignition, possibly due to laser overshoot. Dubaniewicz16 found iron oxide-ceramic adhesive targets on single mode fiber tips ignited selected mixtures more readily than other selected targets. Iron oxide-ceramic adhesive mixtures were used as targets in the current study as a conservative worst-case approach to targets that may obstruct optical fibers, for situations where potential targets are unknown or not controlled.

Knowledge of ignition delay times would be helpful for selecting power limiters that activate quickly enough to prevent ignition under overpower fault conditions. Although Moore and Weinberg14 did not use optical fibers with their laser beam, they found ignition delays generally decreased hyperbolically as radiant power flux increased for several hydrocarbons including propane, methane, pentane, and ethylene. Methane produced the longest ignition delays while ethylene, a Class I Group C or Group IIB material,4 produced the shortest ignition delays. Moore and Weinberg14 also found ignition delays near the minimum radiant power flux were on the order of seconds. Schenk et al.17 observed high volatile coal targets produced longer ignition delays than low volatile coal targets for selected flammable atmospheres. Also, the ignition delays near the minimum igniting power of selected gases were on the order of seconds. Dubaniewicz16 found ignition delays for methane were approximately proportional to the inverse square of laser powers using iron oxide targets on single mode fibers. Ignition delays were about 90 ms or longer for laser powers up to 800 mW. In the current study, ignition delays were measured as a function of beam power using targets attached to
SMF-28 and 62.5 μm diameter fibers. The resulting ignition curves were used to select power limiters for the ignition prevention tests.

III. EQUIPMENT AND MATERIALS

An IPG Photonics PYL-10M ytterbium fiber laser system was used for ignition experiments. The fiber laser wavelength was centered at 1064 nm and the output power was adjustable up to 10 W cw. IPG indicated the overshoot was less than twice the set power, settling to the set power within 10 μs. The laser controller provided a laser-on electrical output signal used for ignition delay measurements. The system combines a red aiming laser with the high power beam within a single mode fiber optic pigtails. The pigtail was fusion spliced to a Corning single mode 1 by 2 coupler to protect the laser from fiber fuses. Optical fibers used for ignition experiments were fusion spliced or connectorized to one of the coupler's output ports. The unused port was terminated with a "black hole" connector to minimize back reflections. Power levels were also kept below 1 W for tests involving single mode fiber to avoid possible fiber fuses.

Optical fibers used for experiments included 9/125 (core/clad) μm Corning SMF-28 silica, 62.5/125 μm silica, 100/140 μm silica, 200/220 μm FiberGuide AFS silica, 400/430 μm Spectran HCS silica, 800/880 μm FiberGuide AFS silica, and 2000/2150 FiberGuide APC plastic clad silica fibers. The SMF-28 single mode fiber core diameter is the mode field diameter at the 1300 nm wavelength. More than one mode propagates through the SMF-28 optical fiber at the 1064 nm wavelength. Fibers with core diameters up to 100 μm were fusion spliced to the couplers output port. SMA connectors were used to couple the laser beam to fibers with core diameters from 200 to 2000 μm. A fiber optic cleaver (York model FBK 11C) provided a flat, perpendicular, optical surface on the 9–400 μm core fiber tips. A manual cleaving tool was used for 800 and 2000 μm core fibers.

Two KiloLambda optical fuses were used for ignition prevention tests. The two samples were preproduction versions with specified activation threshold powers of 20.0±1.0 dB m (100±1.3 mW). The fuses were constructed with Corning SMF-28 fiber pigtails on both ends. The samples were directional, i.e., there was a specified input end and output end.

A Scientec power meter (model D200PC) with attached calorimeter (model AC2500) measured the laser powers. Scientec checked the meter accuracy annually, traceable to National Institute of Standards and Technology standards. Power measurements are reported to be accurate to within ±5%.

Ignition experiments were conducted in a 20 L test chamber (Fig. 1) designed for explosion testing of dusts, gases, and hybrid mixtures. The chamber can be used at partial pressures. The chamber pressure was set to 1 bar at room temperature. The mixture was allowed to settle for about 1 min after fan mixing. Non ignitions were generally repeated ten times before ending a test series.

IV. METHODS

An adequate length of fiber was pulled through a feed-through in the 20 L chamber (Fig. 1) to allow preparation of the fiber tip. The power emanating from the cleaved end of the fiber was measured before and after the test. A thin layer of the Fe₃O₄-Resbond 904 target paste sufficient to block the red aiming laser was applied to the fiber tip and air dried with the aid of the mixing fan. Except for the 2 mm core fiber, the fiber was placed in the chamber, pointing upward. The 2 mm fiber had to be inserted straight into the chamber horizontally because of its stiffness. The chamber was evacuated, and flammable gas-air concentrations were set using partial pressures. The chamber pressure was set to 1 bar at room temperature. The mixture was allowed to settle for about 1 min after fan mixing. Non ignitions were generally repeated ten times before ending a test series.
The ignition delays were measured from the PC data plots of the laser-on signals, pressure traces, and rate of pressure rise \((dP/dt)\) traces versus time. High speed video recordings of selected experiments showed the flame front emanating from the fiber tip before an appreciable rate of pressure rise in this chamber. Ignition delay times reported here based on the pressure transducer measurements were reduced accordingly to account for the difference.

For an ignition prevention test, the fiber pigtail to the input end of the optical fuse was fusion spliced to the output port of the coupler. A low power beam was directed through the fuse during the fusion procedure to help align the fibers. The power through the fuse was monitored during and after the fusion procedure to ensure the device was not activated before the ignition prevention test. The red aiming laser was also visible at the output end of the fuse after the fusion splice procedure, indicating the devices were not activated prior to the ignition prevention tests. The fiber pigtail to the output end of the fuse was pulled into the 20 L chamber (Fig. 1), and \(\text{Fe}_3\text{O}_4\)-Resbond 904 target paste was applied to this end sufficient to block the red aiming laser. The laser power was set to 800 mW for both tests. After the tests, the gas-air mixtures were ignited with another ignition source to verify flammability.

V. RESULTS

Figures 2 and 3 show results of tests to determine the most easily ignited gas-air mixtures. Data points were adjusted to avoid overlap. Propane-air mixtures ranging from 4% to 6% and butane-air mixtures ranging from 3% to 5% produced the lowest igniting powers. 5% propane-air and 4.5% butane-air mixtures were selected for subsequent tests to measure threshold igniting power as a function of beam diameter. These concentrations were also selected for testing by other researchers.

Figures 4–7 show results of tests to measure igniting powers vs. beam diameters for 5% propane-air or 4.5% butane-air mixtures. Data points were adjusted to avoid overlap. Threshold values are listed in Table II. Threshold igniting irradiances were calculated by dividing the threshold igniting power by the surface area of the fiber-optic core.

Additional tests were conducted at power levels above the threshold values to provide the ignition delay data shown in Figs. 8–11. Ignition delays became more variable at the lower igniting powers. In Fig. 8 for example, delays ranged...
from about 0.3 to 1.2 s @ 350 mW, compared to delays ranging from about 45 to 75 ms @ 800 mW. The shortest delay measured at a particular power was taken as a threshold value. Threshold values are listed in Table III. Figures 8–11 include curve fits to threshold delays \( t \) versus igniting power \( p \). In Figs. 8 and 9, the threshold delays at the minimum igniting powers were unusually long and were not included for the curve fit. The unusually long delays near the threshold power are attributed to convection or variable target thickness (see Sec. VI).

The SMF-28 constructed optical fuses prevented ignitions in two tests using a set power of 800 mW, Fe\(_3\)O\(_4\)-Resbond 904 targets, and 5% propane-air. No target incandescence was apparent from the high speed video recordings of the two tests. This was in contrast to significant target incandescence leading to ignition for all observed ignitions in prior tests. The fiber tips were cleaved after the tests and the red aiming laser was not visible, indicating activation. The power throughput of one activated fuse was about 10 mW, monitored for 15 min following the test. The power throughput of the second activated fuse was about 10 mW after the test, but rose to 180 mW after 10 min of continuous irradiation. The input side of the fuse was cleaved after each test and input powers to the fuses were measured at 780 and 790 mW. The difference between these values and the 800 mW set power is attributed to the fusion splice loss.

### VI. DISCUSSION

Rich propane and butane-air mixtures ignited most easily. (Stoichiometric concentrations for propane-air and

<table>
<thead>
<tr>
<th>Beam diameter (µm)</th>
<th>Igniting power (W)</th>
<th>Igniting irradiance (W/mm(^2))</th>
<th>Nonigniting power, ten tests (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>0.304</td>
<td>4780</td>
<td>0.25</td>
</tr>
<tr>
<td>62.5</td>
<td>0.253</td>
<td>82.5</td>
<td>0.20</td>
</tr>
<tr>
<td>100</td>
<td>0.258</td>
<td>32.8</td>
<td>0.25</td>
</tr>
<tr>
<td>200</td>
<td>0.452</td>
<td>14.4</td>
<td>0.40</td>
</tr>
<tr>
<td>400</td>
<td>0.805</td>
<td>6.41</td>
<td>0.75</td>
</tr>
<tr>
<td>800</td>
<td>1.80</td>
<td>3.58</td>
<td>1.7</td>
</tr>
<tr>
<td>2000</td>
<td>4.62</td>
<td>1.47</td>
<td>4.4</td>
</tr>
<tr>
<td>5% propane-air</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.5% butane-air</td>
<td></td>
<td></td>
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butane-air are 4.02% and 3.12%, respectively.) This is in contrast to methane-air mixtures that ignite most easily with lean mixtures. Hertzberg\textsuperscript{19} explains lean methane-air mixtures ignite most easily because of selective diffusion. The lighter methane molecules enter the combustion zone faster than oxygen molecules, creating a fuel rich mixture in the ignition volume close to the ignition source. Lean methane-air mixtures should therefore create most easily ignited stoichiometric mixtures (9.48% by vol) in the ignition volume. Similar arguments were used to explain why rich mixtures ignite more easily for the heavier-than-oxygen propane and butane. The lighter oxygen molecules enter the combustion zone faster than the heavier hydrocarbons, creating an oxygen rich mixture in the ignition volume close to the ignition source. Rich propane or butane-air mixtures should therefore create most easily ignited stoichiometric mixtures in the ignition volume.

Figures 4 and 7 show threshold igniting powers leveled off for beam diameters <100 μm and increased with beam diameters for beam diameters >100 μm. Figures 12 and 13 shows threshold powers found here combined with those listed in Table II. The curve fits in Figs. 12 and 13 indicate the threshold igniting power was approximately proportional to beam diameter for beam diameters ≥100 μm. Figure 13 shows threshold irradiances calculated from the butane-air threshold power data. There is an inverse relationship between threshold powers and irradiances as a function of

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>5% propane-air ignition delay (s)</th>
<th>4.5% butane-air ignition delay (s)</th>
<th>5% propane-air ignition delay (s)</th>
<th>4.5% butane-air ignition delay (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>7</td>
<td>0.288</td>
<td>0.309</td>
<td>0.299</td>
</tr>
<tr>
<td>0.30</td>
<td>0.654</td>
<td>0.298</td>
<td>0.407</td>
<td>0.171</td>
</tr>
<tr>
<td>0.35</td>
<td>0.199</td>
<td>0.210</td>
<td>0.224</td>
<td>0.192</td>
</tr>
<tr>
<td>0.4</td>
<td>0.107</td>
<td>0.112</td>
<td>0.224</td>
<td>0.113</td>
</tr>
<tr>
<td>0.6</td>
<td>0.085</td>
<td>0.112</td>
<td>0.087</td>
<td>0.09</td>
</tr>
<tr>
<td>0.8</td>
<td>0.045</td>
<td>0.050</td>
<td>0.052</td>
<td>0.053</td>
</tr>
</tbody>
</table>

FIG. 12. Propane-air threshold igniting power (p) vs beam diameter (d) using laser heated targets on optical fiber tips. Fit to power for diameters ≥0.1 mm and coefficient of determination (R²) shown.

FIG. 11. Ignition delays vs laser powers (p) for butane-air mixtures using Fe₂O₃-Resbond 904 targets on 62.5 μm fiber tips. Fit to threshold delays (t) shown.

FIG. 10. Ignition delays vs laser powers (p) for butane-air mixtures using Fe₂O₃-Resbond 904 targets on SMF-28 fiber tips. Fit to threshold delays (t) shown.

FIG. 9. Ignition delays vs laser powers (p) for 5% propane-air mixtures using Fe₂O₃-Resbond 904 targets on 62.5/125 μm fiber tips. Fit to threshold delays (t) for powers ≥300 mW shown.
beam diameters. These trends are in agreement with observations of Adler and Carleton\cite{21} and Carleton and Weinberg,\cite{21} who concluded that a minimum power is the limiting ignition criteria for small cw beam diameters, and a minimum irradiance is the limiting ignition criteria for large cw beam diameters. Figure 13 shows that beams of intermediate dimensions that exceeded both the minimum igniting power for small diameters and minimum igniting irradiance for large diameters were needed to cause ignition. These results suggest that relatively powerful beams can be used in these gas-air mixtures without causing ignition, provided the beam power and irradiance remain conservatively below an appropriate ignition curve such as shown in Fig. 13. Figure 14 shows similar threshold powers for straight chain hydrocarbons butane-air and propane-air, and somewhat higher threshold powers for methane-air. The data for methane-air in Fig. 14 was obtained from Dubanieicz et al.,\cite{13,16} Hills et al.,\cite{11} Hawksworth,\cite{10} and Welzel et al.\cite{12}

Other potential ignition mechanisms should be considered as appropriate. For example, Hawksworth\cite{22} reported 300 mW caused smoldering in a 15 mm deep coal dust layer, which could possibly lead to large scale burning. Power thresholds derived from tests of targets obscuring fiber optic tips suspended in flammable gas atmospheres such as studied here may not be conservative for all conceivable ignition mechanisms.

Ignition delays became more variable at the lower laser powers (Figs. 8–11). The variability may have been caused in part by air currents generated from the target heating. The longer heating times required for ignition using the lower powers would allow more time for stronger air currents to develop past the fiber tip, dissipating thermal energy at the fiber tip. Another possible reason for the variability is a variable thickness of target material applied to the fiber tip. Thicker targets would take longer to heat to attain the needed ignition temperature. These possible effects may explain why ignition delays at the lowest igniting powers tended to occur significantly above the threshold curve fits.

Figures 15 and 16 show ignition delays vs laser power for several hydrocarbons grouped by optical fiber diameter. The curve fit exponents averaged 2.4 and 1.87 in Figs. 15 and 16, respectively. The curve fits suggest the ignition delays were approximately proportional to the inverse square
of the laser powers using the SMF 28 and 62.5 μm fibers. The curve fits are similar in shape to the hyperbolic relationships observed by Moore and Weinberg.\(^\text{14}\)

Figures 15 and 16 were used to select fiber optic power limiters that should activate quickly enough for the ignition prevention tests. The preproduction versions of the Kilo-lambda optical fuses prevented ignitions using about 800 mW under selected test conditions. Effects of the IPG laser overshoot on fuse activation were not measured. Target heating was not significant based on the video recordings showing no apparent incandescence. The activation time for the optical fuses was reported to be about 5 μs for input powers near the activation threshold power. Activation time varies with power. The 5 μs activation time is significantly less than the ignition delays found in this study (Figs. 15 and 16) and reported by Hills et al.\(^\text{11}\) One of the activated fuses showed a self-healing effect, allowing a throughput power above the specified threshold power several minutes after activation under continuous irradiation.

**VII. CONCLUSIONS**

Rich mixtures of propane-air and butane-air ignited most easily. Most easily ignited mixtures for propane-air ranged from 4% to 6%, and for butane-air ranged from 3% to 5%.

Threshold igniting powers for these straight chain hydrocarbons were approximately proportional to beam diameter for beam diameters ranging from 0.1 to 2 mm. Threshold igniting irradiances decreased as beam diameters increased. Relatively powerful beams of intermediate dimensions were typically needed to ignite these hydrocarbon-air mixtures under selected test conditions. Other potential ignition mechanisms should be considered as appropriate.

Igniting powers tended to level off for beam diameters <100 μm, in agreement with observations of several other researchers. Minimum igniting powers for the propane-air and butane-air were about 250 and 300 mW, respectively.

Threshold ignition delays for these hydrocarbons were approximately proportional to the inverse square of the igniting power using targets attached to SMF-28 and 62.5 μm diameter fibers. Ignition delays became more variable at the lower laser powers, possibly due to thermally induced air currents or variable target thickness. Ignition delays were about 45 ms or longer using laser powers up to 800 mW under selected test conditions.

The ignition curves were used to select fiber optic power limiters that activated quickly enough to prevent ignitions under selected test conditions. A self-healing effect was observed for one sample.

**ACKNOWLEDGMENT**

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\(^4\) National Fire Protection Association, NFPA 497 Recommended Practice for the Classification of Flammable Liquids, Gases, or Vapours and of Hazardous (Classified) Locations for Electrical Installations in Chemical Process Areas (National Fire Protection Association, Quincy, MA, 1997).


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\(^22\) S. J. Hawksworth, Ignition of Coal Dust Layers by Optical Radiation, EC/01/009 (Health and Safety Laboratory, Agency of the Health and Safety Executive, Buxton, 2001).