THE EFFECT OF INERT GAS TEMPERATURE
EXTINGUISHING CLASS A AND B FIRES

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ABSTRACT
Dry ice is currently being sold as a fire extinguishing agent for firefighters to use; however, neither the method of extinguishment nor the effectiveness of dry ice at putting out fires has been described sufficiently in the scientific literature. One paper by Hatakeyama [1] studied extinguishing small confined hydrocarbon fires but only from 50-100mm in diameter. Dry ice has also been used to extinguish experimental fires in silos [2]. Even though the scientific literature is scarce, a number of patents have been filed for the use of dry ice in extinguishing fires [3-6].

To determine whether dry ice is a reasonable extinguishing agent for different kinds of fires the mechanism of primary extinguishment needs to be determined. Dry ice has four main effects on a liquid pool fire: the solid CO₂ cools the liquid fuel, the gaseous CO₂ cools the gaseous fuel vapor, the CO₂ acts as an inerting agent to the fuel air mixture, and the CO₂ is efficient at absorbing infrared radiation which reduces re-radiation back to the fuel. It is hypothesized that the first and last effects are minimal in rapid extinguishment of the flame. For class B fires, it is hypothesized that the gas phase cooling is the dominant method of extinguishment. The cold gaseous CO₂ gas re-condenses the vaporized fuel gas into a mist which must be re-vaporized by the flame before the fuel can burn. Eventually, the energy required to re-vaporize the fuel and the reduced amount of fuel vapor being created causes the flame to be extinguished, but this can take a significant amount of time. The delay in extinguishing the flame indicates that it is not the CO₂ gas acting as an inerting agent that extinguishes the flame, but the cooling effect of the gas on the fuel vapor itself which is extinguishing the fire. For class A fires, it is hypothesized that there is not enough gas phase CO₂ sublimating off of the solid dry ice pellets to significantly affect the fire. Experiments are conducted to determine the following: the effect of super cooling gaseous CO₂, the mass flux of dry ice required to extinguish a lab scale fire, the mass of dry ice required to put out confined kerosene fires over a range of diameters, and the effectiveness of dry ice on extinguishing class A and smoldering fires. The results show that the cooling effect is the major parameter in extinguishing confined class B fires. These tests also show that the dry ice needs to be submerged in a liquid to be effective and that pelletized dry ice is ineffective on smoldering and class A fires.

NOMENCLATURE

\( c_p \) specific heat
\( D \) diameter
\( FEC \) flame extinguishment concentration
\( L_v \) latent heat of vaporization
\( L_{\text{sublimation}} \) latent heat of sublimation
\( m \) mass loss rate
\( m' \) mass flux
\( m'_{\text{ent}} \) entrainment mass flux
\( m'_{\text{CO}_2} \) mass flux of CO₂
\( \dot{Q} \) heat release rate
\( \dot{Q}_c \) convective heat release rate
\( T \) temperature
\( \Delta H_c \) heat of combustion
\( \rho_{\text{CO}_2} \) density of CO₂
\( \rho_{\text{air}} \) density of air
\( \eta \) efficiency
INTRODUCTION
Dry ice has a history of being used in a variety of firefighting efforts. Using dry ice to extinguish small fires 50mm-100mm in diameter was studied by Hatakeyama et al. [1]. Dry ice was used to extinguish silo fires by Eckhoff [9]. Several patents have been filed for the use of dry ice to extinguish different types of fires. Using an apparatus to launch dry ice into fires was patented by De Mange et al. [3]. Using planes, helicopters, or mortars to introduce dry ice into fires was patented by Primlani [6]. A patent application for a hand held system of launching pellets which could contain dry ice or other extinguishing agents similar to a paint ball gun was published by Silverstein [5].

Confined class B fires are a significant problem throughout the world. Current extinguishment methods mainly focus on using foams to put out the fires. While these techniques work well, they have several drawbacks/risks including the potential for the fire to spread if the confinement is overcome due to the added water, the toxicity of runoff, and in the case of heavy hydrocarbons, boilover. The risk of these drawbacks occurring could be potentially reduced by using solid state CO₂ which is effective at reducing the heat release rate and extinguishing certain fires. Potentially, suppression personnel could combine the use of dry ice with traditional firefighting methods to increase efficiency and safety. There are four main effects of adding dry ice to a fire:

- Cooling the fuel
- Cooling combustible vapors
- Adding an inert gas into the fuel/air mixture
- Absorbing infrared radiation (IR) back to the fuel surface

The cooling of the fuel and the absorbing of IR radiation are believed to have minimal effects on extinguishing the flame and are discussed briefly. To determine if it is the cooling of combustible vapors, the inert gas, or a combination of the two effects which extinguish the fire, a series of experiments are completed and compared to the results of theoretical mathematical models.

Using dry ice to cool the liquid fuel to put out a fire is not effective because of the time required to cool the liquid fuel. While the dry ice does slowly cool the liquid fuel, this cooling does not have a large effect on immediate extinguishment of the flame. One of the selling points of using dry ice is that it can freeze hydrocarbon fuels which responders do not want to spread. As the sublimation temperature for dry ice at normal temperature and pressures is -80°C and the freezing point for kerosene is -40°C, it is possible to freeze hydrocarbon fuels. Tests were done to show that this works and an example is shown in Fig 1. The problem becomes the amount of dry ice required to freeze the liquid fuel, and the time required for the CO₂ to absorb the energy from the liquid fuel. Testing was conducted using a beaker filled with 250ml of 25°C liquid kerosene. For this condition, over 250ml of dry ice is required to freeze the majority of the kerosene in the beaker. After 6.5 minutes of cooling, there was still some liquid kerosene in the beaker. This test indicates that a volume of dry ice nearly equal to the volume of liquid to be frozen is required. This is not feasible on an industrial scale. A generic equation could be derived to determine the time required to freeze a given volume of fuel but the heat transfer parameters are fuel and geometry dependent and require an iterative solution method so it is not done here. It can be stated that dry ice will require a significant amount of time to freeze a large amount of hydrocarbon fuel; therefore, it is not a good option for spills that need to be contained/frozen rapidly as some finite amount of time. During this time, rapidly spreading liquid fuel could move away from the dry ice preventing it from being frozen.
CO₂ is known as a “greenhouse” gas because it absorbs IR. For this reason, the transmittance of CO₂ over the IR spectrum [7] was compared to the infrared radiance of a fire [8] to see if there was a significant overlap, this comparison is shown in Fig. 2. While the CO₂ does absorb significant portions of the IR spectrum at wave numbers around 600 cm⁻¹, 2400 cm⁻¹, and 3650 cm⁻¹ the fire radiates over the whole wavelength band. Due to the wave number mismatch and the short distance between the flame and the fuel surface, CO₂ would typically not block a significant amount of IR to the fuel surface.

Assuming that it is the inerting effects of the CO₂ coming from the dry ice which extinguishes a fire, the amount of CO₂ produced by the dry ice can be compared with the amount required to typically extinguish a flame based on values reported in the literature. The flame extinguishing concentration (FEC) of CO₂ has been published in literature [10-15] and ranges from 4 – 26.2% by volume in air depending on measurement technique, type of fuel, and equivalence ratio of the reactants. The entrained mass flux at the average flame height can be calculated using \[ \dot{m}_{\text{env}} = 0.0058 \dot{Q}_c \] [16]. Assuming that the ΔT=500K and the convective heat release rate is 70% of the total heat release rate \( \dot{Q}_c = (0.7) \dot{m} \Delta H_c \), the mass flux of CO₂ off of the surface of the pool required to cause extinguishment at the average flame height can be calculated using:

\[
\dot{m}_{CO_2}^* = (0.0058)(0.7)FEC\left(\frac{\rho_{CO_2}}{\rho_{\text{air}}(798K)}\right) \tag{1}
\]
Using a small scale experiment, the mass flux of CO$_2$ can be calculated using the inputs shown in Table 1. Using Eq. 1 and the shown input parameters, 0.49 g/s of CO$_2$ is required to inert the atmosphere above the fire. This calculated value is nearly identical to the measurement of the mass of CO$_2$ measured to extinguish the small kerosene fire of the same size as discussed in the next section.

### Table 1: Input values to calculate mass flux requirements for small scale kerosene fire

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
<th>Source</th>
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<tbody>
<tr>
<td>$\rho_{air}$,798K</td>
<td>0.4565 kg/m$^3$</td>
<td>[17]</td>
</tr>
<tr>
<td>$\rho_{CO_2}$,798K</td>
<td>0.6614 kg/m$^3$</td>
<td>[18]</td>
</tr>
<tr>
<td>FEC</td>
<td>15%</td>
<td></td>
</tr>
<tr>
<td>$\dot{Q}$</td>
<td>19.57 kW</td>
<td></td>
</tr>
<tr>
<td>$\lambda$</td>
<td>85%</td>
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</table>

To look at the effect of the temperature of the CO$_2$, an experiment was built to flow room temperature CO$_2$ and super cooled CO$_2$ into a fire and measure the amount required to extinguish the fire. Dry ice was used to cool the heat exchanger and a flow meter was used to measure the flow of the CO$_2$ before the gas was cooled in the heat exchanger. For the experiment using a 11 cm diameter pool fire containing 50ml of kerosene. The fuel is allowed to burn for 60 seconds to reach steady state before gaseous CO$_2$ is applied. When CO$_2$ is at room temperature (25°C), it takes a flow rate of 34.6 lpm to extinguish the fire. When the CO$_2$ is cooled to -30°C, it takes a flow rate of 9.6 lpm to extinguish the fire. The difference in the room temperature vs super cooled flow rates shows the dramatic effect of introducing cold CO$_2$ as the extinguishing agent.

Assuming that the cold CO$_2$ gas is extinguishing the flame, the effect could be from the gas re-condensing the fuel vapor. Based on the mass flux from the pool fire, the amount of energy required to condense the gas phase fuel vapor can be calculated and compared with the amount of cold CO$_2$ being produced by the applied dry ice.

To confirm it is the energy absorption of the cold CO$_2$, another experiment was done to measure the specific amount of CO$_2$ being released at the time of extinguishment by having the steady-state fire burning on a load cell when the CO$_2$ was introduced. For the small scale experiment, the mass flux of the burning kerosene was found to be 0.000533 kg/s. The mass flux of super-cooled CO$_2$ to condense the
fuel vapor coming off the liquid fuel can be calculated using an energy balance equation

\[ \dot{m}_{\text{CO}_2} c_{p,\text{CO}_2} \Delta T_{\text{CO}_2} = \dot{m}_{\text{kerosene}} L_{v,\text{kerosene}} \]

Rearranging this equation for the mass flux of \( \text{CO}_2 \) allows the theoretical mass flux of \( \text{CO}_2 \) to be compared to the measured value of \( \text{CO}_2 \) released by the dry ice when the flame is extinguished.

\[ \dot{m}_{\text{CO}_2} = \frac{\dot{m}_{\text{kerosene}} L_{v,\text{kerosene}}}{c_{p,\text{CO}_2} (T_{\text{boiling, kerosene}} - T_{\text{CO}_2})} \]  

(2)

Evaluating Eq. 2, the \( \text{CO}_2 \) required to extinguish a small scale 11 cm diameter kerosene fire is 0.49 g/s. Measuring the mass loss rate of the \( \text{CO}_2 \) on a small scale 11 cm diameter kerosene fire, minimum amount of \( \text{CO}_2 \) which will extinguish this small scale fire is found to be nearly identical at 0.48 g/s.

<table>
<thead>
<tr>
<th>Table 2: Input values for ( \text{CO}_2 ) requirements calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \dot{m}_{\text{kerosene}} )</td>
</tr>
<tr>
<td>( L_{v,\text{kerosene}} )</td>
</tr>
<tr>
<td>( c_{p,\text{CO}_2} ) (average from 175K-500K)</td>
</tr>
<tr>
<td>( T_{\text{boiling, kerosene}} )</td>
</tr>
<tr>
<td>( T_{\text{CO}_2} ) (sublimation temperature)</td>
</tr>
</tbody>
</table>

Since the two mathematical theories produce the same results at the size of the small scale experiment, the mathematics were extrapolated to larger scales as shown in Fig. 4. These results elucidate how the inert theory grows as a squared function of fire diameter while the cooling theory grows in a much slower fashion. At small diameters, the two theories predict nearly identical results, but when the fires grow in diameter the results diverge significantly.

![Figure 4: Comparison of theoretical rates of \( \text{CO}_2 \) required to extinguish flame for inerting theory vs cooling theory](image-url)
Larger scale tests were done which help clarify the results of the above theoretical analysis. In the larger scale tests, dry ice pellets were introduced into burning pool fires of various diameters in order to determine the minimum total mass of dry ice required to extinguish the fire. This work extends the work of Hatakeyama et al. [1] to more realistic fire sizes ranging from 0.22m to 2.44m in diameter. Figure 5 shows a pair of firefighters using a radiation shield to approach the fire and throw dry ice onto a 2.44m diameter kerosene fire.

Figure 5: Dry ice being thrown onto 2.44m diameter kerosene fire

Figure 6 shows the total amount of dry ice as a function of pool fire diameter on the left axis and the cooling theory extrapolated out to the diameter of the large scale experiment on the right axis. The cooling theory follows the same general trend as the experimental data. This matching trend leads to the conclusion that it is the cooling effect and not the inerting effect (which increases much faster as a function of diameter) that is causing the extinguishment of the flame.

Figure 6: Left axis - Mass of dry ice required verses pool fire diameter. Right axis – Cooling theory CO₂ requirements versus pool fire diameter

Experiments are conducted to see if dry ice affects class B fires when not submerged in the liquid fuel. Results show that the gas phase CO₂ sublimating off of the dry ice ineffective at extinguishing confined class B fires when the dry ice is not applied directly into the liquid fuel. It was found that when dry ice
was not submerged in liquid fuel, the amount required for extinguishment was increased significantly. Tests are completed using the same liquid pool fires, but the dry ice is placed around the fire instead of in the liquid. There was no discernable effect on the fire from either the dry ice alone or when water was sprayed on the dry ice to try and induce an increase in sublimation rate as shown in Fig 7.

![Figure 7: Dry ice spread around pool fire with and without water being applied onto the dry ice](image)

For class A fires and smoldering fires, dry ice is relatively ineffective when the pellets are not in direct contact with the fuel itself. Experiments were done in a fume hood on 11 cm cube wood cribs with open tops. Placing dry ice into a burning crib did not readily extinguish the fire once the crib was burning. A worst case test was done, filling the crib up completely with dry ice. In this configuration, the front and sides of the crib were still able to burn. This is believed to be because the influx of air into the fume hood pulled the cold gaseous CO₂ to the rear which protected the back of the crib and prevented it from burning. Experiments were also done on smoldering steel wool. In these tests, the dry ice was only able to extinguish the smoldering front when in direct contact with the burning material. This is to be expected after the results of placing the dry ice around a pool fire discussed above. Figure 8a shows a wood crib filled with dry ice where the wood is able to burn in a fume hood. Figure 8b shows steel wool with dry ice pellets placed on the surface maintaining a smoldering reaction which burns around the dry ice pellets but consumes the rest of the steel not in direct contact with the dry ice. Figure 8c shows a fire of assorted sticks which continues to burn where dry ice is not in direct contact with the sticks or coals.

Based on the tests described in this work, the use of solid state CO₂ on open class A fires is not particularly effective. This follows the results of the class B tests where the dry ice was not submerged in a liquid fuel. The problem stems from the reduction in heat transfer to the dry ice surface which leads to a reduction in gaseous CO₂ production. Without direct contact to the fuel or the rapid sublimation of a significant amount of gas phase CO₂, dry ice makes an ineffective extinguishing agent.
CONCLUSION
The ability of dry ice to put out class A and B fires has been examined. While dry ice pellets are very effective at putting out relatively small class B fires, the ability of dry ice pellets to put out full scale fires in a cost effective manner cannot be extrapolated from this work. The physical method of extinguishment was determined to be the re-condensing of vaporized fuel into the liquid state. This change in phase requires the flame to re-evaporate the fuel vapor. The energy required to do this eventually quenches the thermal runaway reaction. This work shows that solid state CO$_2$ is much less effective at putting out class A and smoldering fires than class B fires due to the minimal heat transfer to the dry ice pellets when the pellets are not submerged in a hot liquid. To be effective against class A fires, the solid state CO$_2$ tends to need to be in direct contact with the fuel material. As many forest fires travel through the canopy, this is not feasible as an extinguishment method. The ability of solid state to freeze a hydrocarbon fuel is shown, but both the amount of dry ice and time required make this of minimal benefit in a rapidly changing fire scene.

In future experiments, dry ice will be introduced into a set of full-scale compartment fires to evaluate the effectiveness of the material in this format. It is possible that the upper layer will radiate enough energy to rapidly sublimate a significant amount of the CO$_2$, which could theoretically influence the fire in the closed compartment. Since the compartment has minimal openings and the CO$_2$ is in the lower layer, it is possible that this geometry will have a positive effect on the extinguishing properties of the dry ice.

ABOUT THE AUTHORS
Scott R. Rockwell is an assistant professor at Eastern Kentucky University where he teaches classes on fire behavior & combustion and fire dynamics. His degrees include a BS in Aerospace Engineering along with a MS and Ph.D. in Fire Protection Engineering. His current research includes active learning teaching techniques that minimize the student’s cognitive load during learning, alternative flame extinguishing techniques, radiation from dust flash fires compared to gas flash fires. He also manages a website to provide fire related teaching tools to educators and students called firesciencetools.com.

Jason Reigelsperger is a senior student in the Fire Protection and Safety Engineering Technology department at Eastern Kentucky University. He worked as a research assistant during the experimental phase of the small scale dry ice testing and has been interested in the fire protection industry since going to Fairdale High School Magnet Career Academy. Jason is pursuing his degree after serving in the United States Navy as an Aviation Boatswains mate where he earned the Rank of Petty Officer Third Class. After serving honorably during Operation Enduring Freedom/Operation Iraqi Freedom, Jason returned to Eastern Kentucky University to continue his education.
REFERENCES