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Laboratory Evaluation of Bicarbonate Powders as Fire Suppressants

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The Combustion Dynamics Section of the Navy Technology Center for Safety and Survivability is actively involved in addressing US Navy needs for fire protection, concentrating on the effectiveness of current and future fire extinguishing agents, with the responsibility to recommend and help design Navy shipboard total flooding fire suppression systems. We are currently examining several replacement agents and alternative suppression technologies including the use of aerosols and powders.

This paper describes recent collaborative work with Kidde International on the flame extinction properties of various bicarbonate powders. We have examined the concentration of bicarbonate powders required to extinguish both laboratory counterflow propane-air diffusion flames and small obscured n-heptane pan fires. Extinction information as a function of powder composition and size has been obtained. Within experimental uncertainty, smaller particles were more effective than larger ones. Potassium bicarbonate was more effective than sodium bicarbonate for each particle size studied. Similar dependence on size and powder composition was observed in both the counterflow diffusion flame and small chamber pan fire tests. Powder extinction data are given as well as implications of the findings.

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INTRODUCTION

The phaseout of halon production, as required by the Montreal Protocol, continues to challenge researchers to find an effective alternative to the superior fire fighting agents of the halon family. Halon 1301 has been used quite effectively in many applications where a clean agent is not absolutely required. With the phaseout of halons and the lack of a suitable backfit replacement it is now more critical to design fire protection systems appropriate for the application.

There are certainly many applications where fire extinguishment by a gaseous suppression agent is highly desired and there are halon replacement clean agents commercially available. Gaseous hydrofluorocarbon (HFC) agents and inert gases are the front runners in the race for a halon replacement, but none reach the level of overall effectiveness and safety as Halon 1301. Although HFC's cause no significant damage to the ozone layer, they do produce hydrogen fluoride, an extremely corrosive byproduct of the fire suppression process. There is still a need for an efficient and economical replacement/alternative for many spaces currently protected by Halon 1301.

Flame extinguishment by dry chemicals, most notably alkali metal salts, is not a new technology. Agents such as sodium bicarbonate have been used in hand extinguishers since the 1940's. Small particle size alkali metal salts are known to have excellent extinguishing capabilities [1], more effective on a mass basis than even gaseous agents such as Halon 1301 [2-4]. Highly efficient dry chemical agents can provide excellent fire protection while consuming minimal space.

The most common alkali metal salt agents in use are sodium bicarbonate ($NaHCO_3$) and potassium bicarbonate ($KHCO_3$). $NaHCO_3$ is widely used in fire extinguishers because of its low cost. Both agents also have markets in such applications as paint spray booths, fuel filling stations, restaurant cooking areas, and in explosion protection. In addition to high efficiency, the powders have many other advantages including low toxicity and corrosivity. The impact on the environment from $NaHCO_3$ or $KHCO_3$ is minimal. They have zero ozone depletion potential (ODP) and global warming potential (GWP). The powder left by the dry chemicals following suppression remains a drawback, limiting their application to areas that can tolerate the residue. Decreased visibility during application is also a concern. Particle suspension is another limitation, especially for applications requiring a total flooding agent. In these applications the particles must remain suspended in the fire threat area sufficiently long to eliminate the chances of a reignition. The agent must also flow around objects to extinguish obstructed fires in a similar manner to gaseous agents. For conventional sized extinguishing powders (i.e. 20-100 μm) the majority of the particles are too massive and are not capable of suspension for extended periods of time. Pyrotechnic generation [1] can yield micron sized aerosol. Also, very small, aerosol sized particles of non-pyrotechnic potassium bicarbonate powder have been developed [3] to address the questions of flow and suspension, and are currently being tested in Europe for use in scenario specific applications [5].

EXPERIMENTAL

The flame extinguishing performance of powdered agents was evaluated in a propane-air counterflow diffusion flame at NRL and in an obscured n-heptane pan fire within a fire test chamber at Kidde. Extinction testing was conducted with both sodium bicarbonate ($NaHCO_3$) and potassium bicarbonate ($KHCO_3$). Preparation of the tested samples was performed by Kidde in separate runs for both laboratories using the same method and base stock powders. Prior to particle size fractionation the $KHCO_3$ sample was ground using a ball mill (Fritsch Pulverisette type 06.102) to reduce the large chunks of powder into small enough sizes to permit sieving. Due to the lower mean particle size of the $NaHCO_3$ (Dessikarb) powder as received, it was fractionated without any prior grinding. Both powders were then mechanically sieved (Fritsch Analysette type 03.502) in a shaker to size ranges of <38 μm, 38-45 μm, 45-53 μm, 53-63 μm, and 63-75 μm. Silica (2% by mass) was

added to the powder samples as a drying/anti-caking additive. All powder samples flowed very freely with no agglomeration noticed. A scanning electron microscope (Cambridge S200) was used to examine the powdered test samples following sieving. Photomicrographs of the $NaHCO_3$ showed a very even distribution of particle sizes throughout each size range. Conversely, photomicrographs of the $KHCO_3$ showed that there was a significant percentage of very small particles (i.e. <<38 μm) in each size bin.

Experiments were conducted in a counterflow diffusion burner [6]. The counterflow diffusion flame is laminar and one-dimensional and allows for variation of the strain rate (see below). Extinction testing enables a fundamental study of the extinction mechanism and the influence of such factors as size, chemical composition, and strain rate. The burner consists of two axisymmetric, 1 cm ID burner tubes separated by 1 cm as shown in Figure 1. A flame is established in the region between the two tubes where the opposed fuel and oxidizer flows meet and diffuse. Air and propane were used for the oxidizer and fuel, respectively, with the air flow through the top and the propane through the bottom tube. The flame can be described in terms of the strain rate. The strain rate is defined as the maximum velocity gradient on the oxidizer side of the flame and has units of s^{-1}. Laser- Doppler velocimetry (LDV) is used to measure the velocity profile along the tube centerline. In an uninhibited flame, extinction is achieved when the air and fuel flow rates are increased such that the velocity gradient exceeds the critical value referred to as the *extinction strain rate*. For an uninhibited propane-air flame this has a value of 560 s^{-1}. For these flames, extinction was typically only achieved along the centerline, leaving an annular flame.

Powder concentrations for flame extinction were measured at three different flame conditions characterized by the respective flows of air and fuel. Strain rates determined for the flames using an LDV system were 180, 310, and 480 s^{-1} for what are referred to as low, medium, and high strain, respectively. For the powder extinction concentration tests, the flame was established approximately midway between the two tubes at one of the predetermined strain rates. The powder was injected and mixed into the air stream from above the flame to best simulate an actual fire suppression situation. The agent delivery system consisted of a vibrating, variable orifice device. The orifice was changed for gross adjustment and the vibration frequency for fine adjustment. The powder flow was quantified by light scattering using a modulated He-Ne laser beam just below the air exit tube. The powder scattered the laser light, which was collected by optics at 90° and processed in a lock-in analyzer synchronized to the frequency of the modulated beam. The powder flow was correlated to the light scattering by collecting and weighing powder in the absence of the flame. For flame extinction, the powder flow was introduced into the air side of the flame and gradually increased until the flame extinguished. Extinction occurred only along the centerline as in the uninhibited flame. The addition of powder to the flame dramatically increased the excited C_2 emission from the flame. A suitable optical filter was used to block this emission.

Data were collected by a computer using an analog to digital board (Scientific Solutions Lab Tender). The board was 8 bit, bipolar, with an input range of -5 to +5 volts. The data collection rate of the computer was set at 2 Hz. In addition to the He-Ne scattering signal collected by the system, a second channel recorded the intensity of the central, luminous zone of the flame as imaged into a photomultiplier tube. Extinction of the flame was marked by a dramatic decrease in the light intensity signal. The scattering signal was evaluated at the time corresponding to the flame emission decrease to determine the powder scattering signal at extinction. Calibration of the He-Ne scattering was performed following extinction measurements at each strain and for each particle size bin.

The powders were also tested in a 287 liter fire test chamber [3] modified as shown in Figure 2. The fire is obscured from above and on the sides by metal plates as shown. This test design was chosen to evaluate the total flooding ability of the powders. The suppressant tested was weighed to

0.01 g and loaded into the reservoir. It was then pressurized to 140 psig with nitrogen and dispersed through a simple nozzle (shown in insert) in the roof of the chamber. Water and n-heptane were added to the fire pan and the baffles put in place. The fire was then ignited and the chamber sealed. At 45 s after ignition the fan was switched off and the fan door closed; at t=55 s, the test chamber side vents were closed; at t=60 s, the suppressant was discharged. If the fire remained lit at t=75 s, the test was classified as a failed suppression.

For each test, fresh water and fuel were used. Between tests, the chamber was cleaned of residual suppressant. The dispersion apparatus was cleaned with a compressed air line when different particle size fractions were being evaluated to prevent cross-contamination. By changing the amount of suppressant used in the subsequent tests according to the results of those previous, it was possible to find an increasingly smaller range around the "critical" mass measured for extinction of the flame.

RESULTS

Counterflow Diffusion Flame

Extinction mass concentration measurements for $NaHCO_3$ and $KHCO_3$ powders in the air flow of a propane-air counterflow diffusion flame as a function of the measured strain for each size bin are tabulated in Table 1 and plotted in Figure 3. In general, they show that the extinction mass concentration varies inversely with the strain rate of the flame and directly with the particle size of the agent. Figure 4 is a plot of the extinction mass concentration ratio of $NaHCO_3$ to $KHCO_3$ versus strain for each particle bin size tested. The figure shows that $KHCO_3$ is approximately 2.5 times more effective than $NaHCO_3$ on a mass basis in extinguishing the flame (3 times more effective on a molar basis).

A number of factors have been postulated to contribute to the inhibition of fires by powders. The powder adds a great deal of heat capacity to the flame, and solid particles are often effective infrared radiators, leading to radiational cooling of the flame zone. In addition, some chemicals (including the alkali metal bicarbonates) [7] will undergo endothermic decomposition at elevated temperatures, releasing carbon dioxide. The residual metal hydroxide may itself vaporize and decompose at a much higher temperature. Furthermore, there exists the possibility of free radical scavenging processes involving either the solid surface of the particle (heterogeneous) or gaseous by-products of the solid's decomposition (homogeneous) [8-10].

The exact mode of the alkali metal bicarbonates' effectiveness is still not completely understood. The difference in effectiveness between sodium and potassium could be due either to differences in the decomposition temperature and enthalpy, or to differences in catalytic scavenging cycles between the two elements.

One point worth noting is that for nearly all of the possible modes of operation, the particles' effectiveness should scale with surface area. This includes heat transfer, radiation, decomposition/vaporization, and surface catalysis. Therefore small particles are expected to be more effective at fire suppression, in accord with our experimental observations. This dependence does not, however, allow us to determine the primary means by which these particles extinguish fires.

The size of the particles in the flame is an important characteristic in the effectiveness of an agent. The sooner a particle begins the decomposition phase, the sooner it can act out its role in suppressing the flame, whether it be physical or chemical. As shown in Figure 1, in a stagnation point flow field the streamlines turn radially upon impingement by the opposing flow. Particles will either follow these streamlines if small enough, or will deviate from the streamlines and begin to fall

downward for the case of particles large enough that the gravitational force overcomes the drag force imposed by the carrier gas. Thus, the residence time of each particle in the flame is a function of the trajectory that it follows and the resulting velocity. Also, the rate of heat absorption by a solid particle is proportional to its surface area and a smaller particle presents more surface area per unit mass to the flame than a large one. Within the experimental uncertainty there was an increase in extinction mass concentration (i.e. decrease in effectiveness) with increasing particle size, which has also been seen previously at NRL [1,11]. This is seen in Figure 3 for both agents.

Plots of the extinction mass concentration as a function of average particle diameter and surface area can be found in Figures 5a and 5b, respectively. The figure contains data for the medium strain case for both powders tested. The average particle diameter was calculated as the arithmetic mean of each particle size bin, assuming an even distribution. This average particle diameter was then used in the calculation of the average particle surface area. In Ref. [11], the authors concluded that the fire extinguishing effectiveness of dry chemicals can be fully explained on the basis of particle size and distribution. They found that the effectiveness of the agent increased gradually as the particle diameter decreased until reaching a critical diameter. At this diameter there was a dramatic increase in the flame suppression efficiency and the effectiveness remained constant for all particles below the limit size. The limit sizes were reported as 16 μm and 22 μm for $NaHCO_3$ and $KHCO_3$, respectively. We noticed a dramatic increase in the efficiency at about 45 μm for the $NaHCO_3$ sample at medium strain. A sizable increase was also noted for $KHCO_3$, but at a much larger particle size of about 65 μm. The higher value found for $KHCO_3$ may be influenced by the large percentage of very small particles in all size bins of this agent. The data show that the required extinction concentration increases with the diameter and surface area. A linear correlation between extinction mass concentration and diameter was not found at the medium strain tested as seen in Figure 5a. There does appear to be a linear correlation at the medium strain case for the extinction mass concentration versus average particle surface area as seen in Figure 5b. For this strain, the particle surface area available to interact with the flame more closely correlates with suppression effectiveness than does the particle diameter.

For the high and low strain cases the correlation between surface area and effectiveness was complicated by other factors. For the low strain flame, the largest particles were not suspended near the stagnation plane by the opposing fuel flow, but fell directly through the flame and into the bottom tube. A dramatic drop off in effectiveness was observed for the two largest particle bins, which may have resulted from the reduced residence time. For the high strain case, the amount of powder required to extinguish the flame was so small that the particle delivery was difficult to accurately measure and control with our seeding apparatus, leading to uncertain and poorly reproducible values. It was thus difficult to quantify a relationship between particle size and effectiveness for these two strains, but smaller particles were once again more effective. Effectiveness did correlate more closely with surface area than with diameter. Note that the determination of surface area in this study was based on the assumption of a spherical particle of the average diameter for the sieve fraction. A more accurate determination of the effect of surface area on suppression will require direct measurement of surface area (i.e. by gas adsorption). These observations are, however, consistent with "real world" experience that smaller particles are preferable due to both increased surface area and more favorable suspension properties [3].

Pan Fire Chamber Test

Extinction mass concentration measurements for $NaHCO_3$ and $KHCO_3$ powders on an obscured n-heptane pan fire in a 287 liter chamber are tabulated in Table 2 and plotted in Figure 6. The results show $KHCO_3$ to be more efficient in suppressing these fire than $NaHCO_3$. Smaller

particles are also more efficient in suppressing fires than are large particles. It is difficult to determine the dependence of surface area on the effectiveness because of the many interrelated variables affecting the chamber test results.

The extinction mass ratio (Na/K) for the two powders tested was determined to be 2.1, 2.8, and 1.9 for the size ranges of < 38 μm, 45-53 μm and 63-75 μm, respectively. The values are not monotonic with particle diameter. This may be due to the poor sieving of the $KHCO_3$ into the particular size ranges. This may also be due to the greater hygroscopicity of $KHCO_3$ compared with $NaHCO_3$. There is a great number of small particles visible in the photomicrographs of the 45-53 μm sieve fraction of $KHCO_3$, perhaps explaining the apparently much higher efficiency associated with this sample (i.e. 2.8) compared with the other two size ranges (i.e. 2.1 and 1.9). The 63-75 μm sieve fraction for $KHCO_3$ was seen to comprise some very large particles, with one axis much greater than 75 μm, and some very small particles. Though these effects will, to some extent, cancel one another, this cannot be a basis for scientific comparison.

SUMMARY

We have examined the fire suppression properties of bicarbonate powders in two different environments. Similar dependence on size and powder composition was found in both studies. $KHCO_3$ was shown to be more effective on a mass basis than $NaHCO_3$ for all particle sizes tested. It was also shown that the effectiveness of an agent varies inversely with the particle size for the ranges tested; smaller particles are more effective in suppressing the flame than the larger ones. However, the results are not readily transferable to full scale fire applications. Factors such as the throw (i.e. fire penetration), suspension, and flow as a function of particle size are all important considerations in determining the optimum particle size for each application. Additional testing is recommended to help evaluate these characteristics. Better understanding of these characteristics will help to determine the applicability of dry chemical agents as an alternative to Halon 1301.

The testing reported here is preliminary work of an ongoing collaborative effort between the Naval Research Laboratory and Kidde International. Additional testing by both is planned to better evaluate the effectiveness of powdered extinguishing agents. Experiments are underway at NRL to determine the size distribution of the samples used. Kidde is also currently involved in the assessment of particle sizes using a commercial particle analyzer. Extinction testing with better characterized particle size distributions is planned. These results will be used to gain a better understanding of flame extinguishment by dry chemicals and to help determine the characteristics of the optimum agent.

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Chemical	Measured Strain (s^{-1})	Extinction Mass Concentration for Specified Size Bin (g/m^3)				
		<38 μm	38-45 μm	45-53 μm	53-63 μm	63-75 μm
$NaHCO_3$	180	70	52	150	270	730
	310	8	15	53	56	80
	480	4	1	7	7	4
$KHCO_3$	180	12	18	70	100	370
	310	3	12	20	18	51
	480	1	6	3	1	2
Halon 1301	180	110				
	310	56				
	480	15				

Table 1: Propane-air counterflow diffusion flame extinction mass concentration for the indicated agent. Halon 1301 data derived from Ref. [12].

Chemical	Extinction Mass Concentration for Specified Size Bin (g/m^3)		
	<38 μm	45-53 μm	63-75 μm
$NaHCO_3$	52	82	130
$KHCO_3$	25	29	69

Table 2: Obscured pan fire mass extinction concentration for the indicated agent.

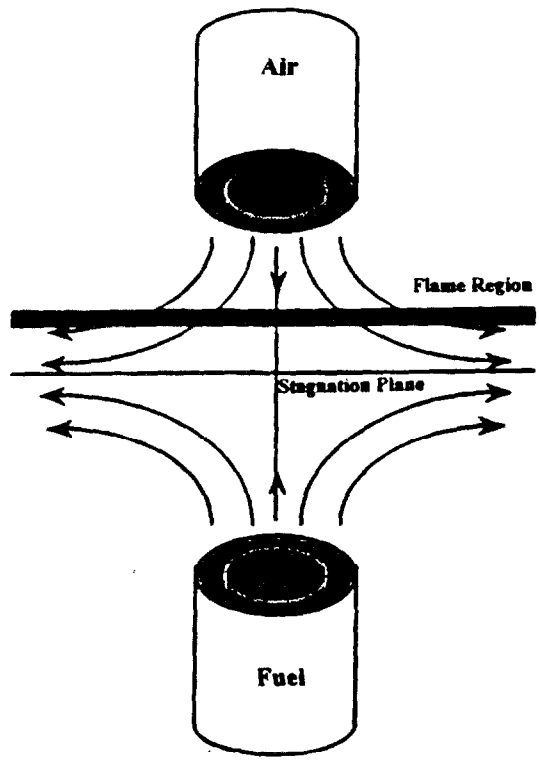

Figure 1: Schematic of the counterflow diffusion flame apparatus from Ref. [6].

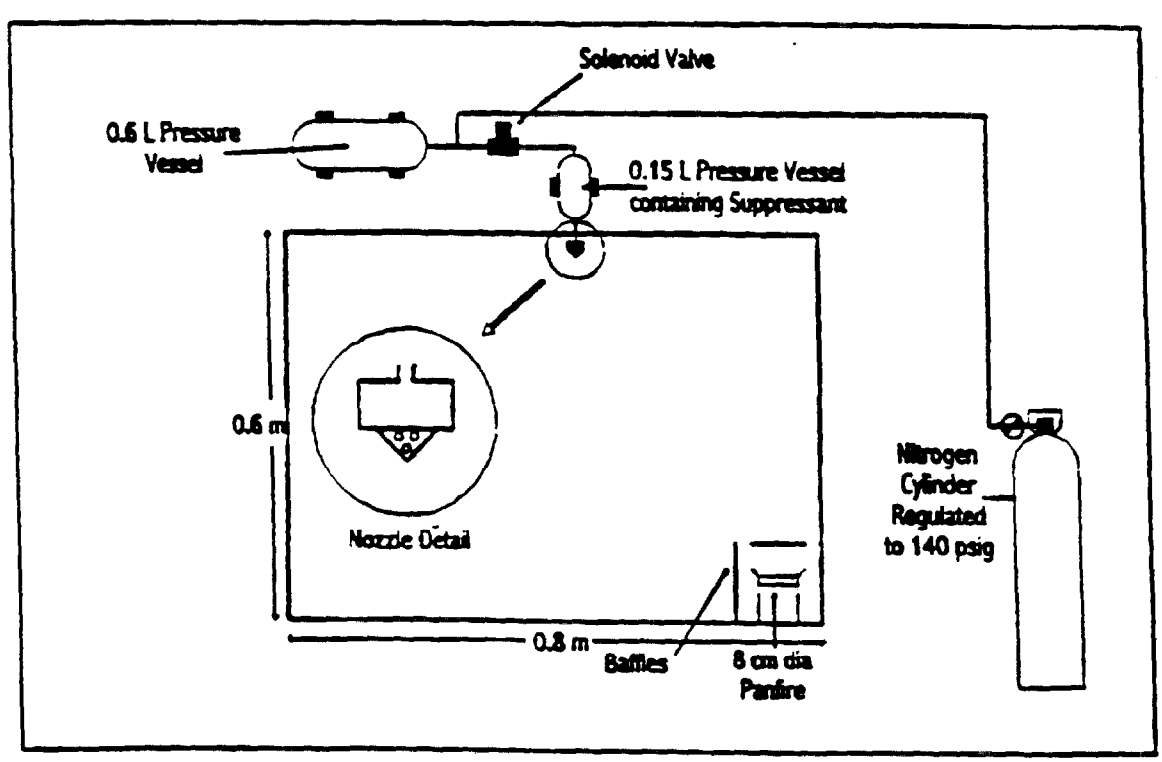

Figure 2: Schematic of 287 liter obscured fire test chamber.

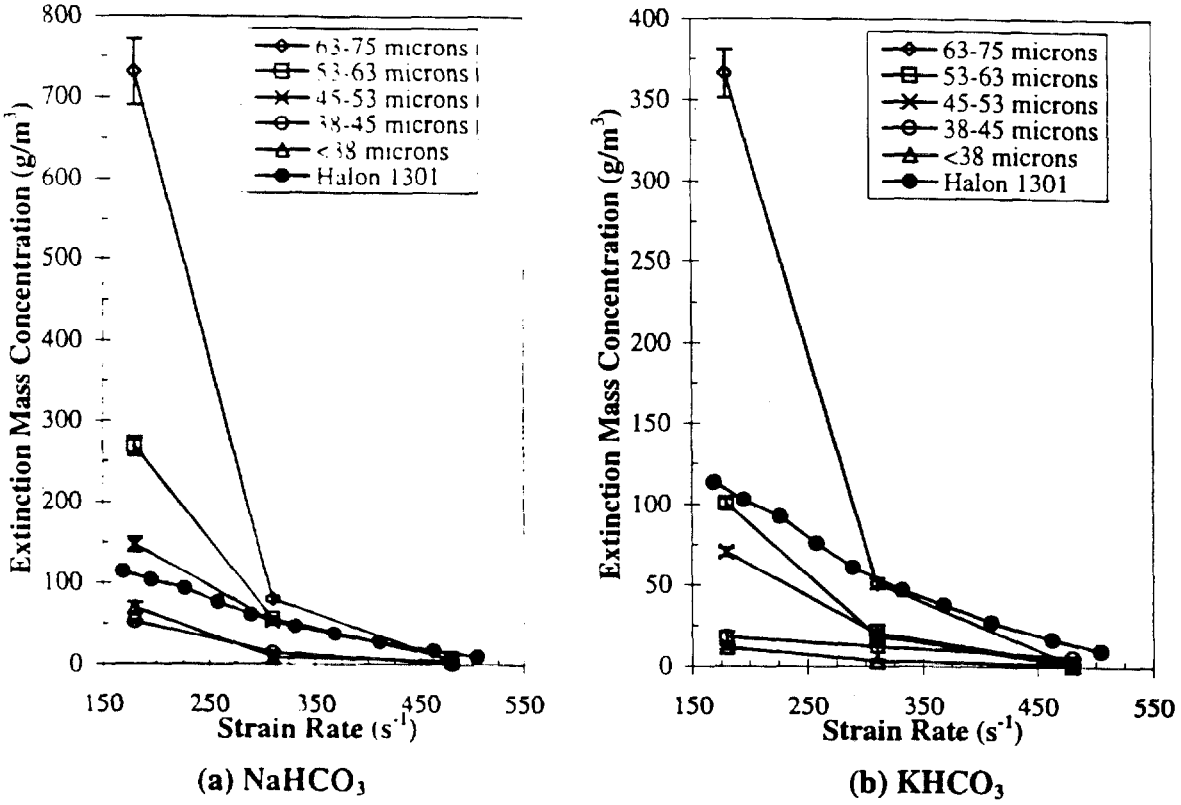

Figure 3: Extinction mass concentration as a function of strain rate for each particle size range of (a) $NaHCO_3$ and (b) $KHCO_3$ powders in a propane-air counterflow diffusion flame. Halon data from Ref. [12].

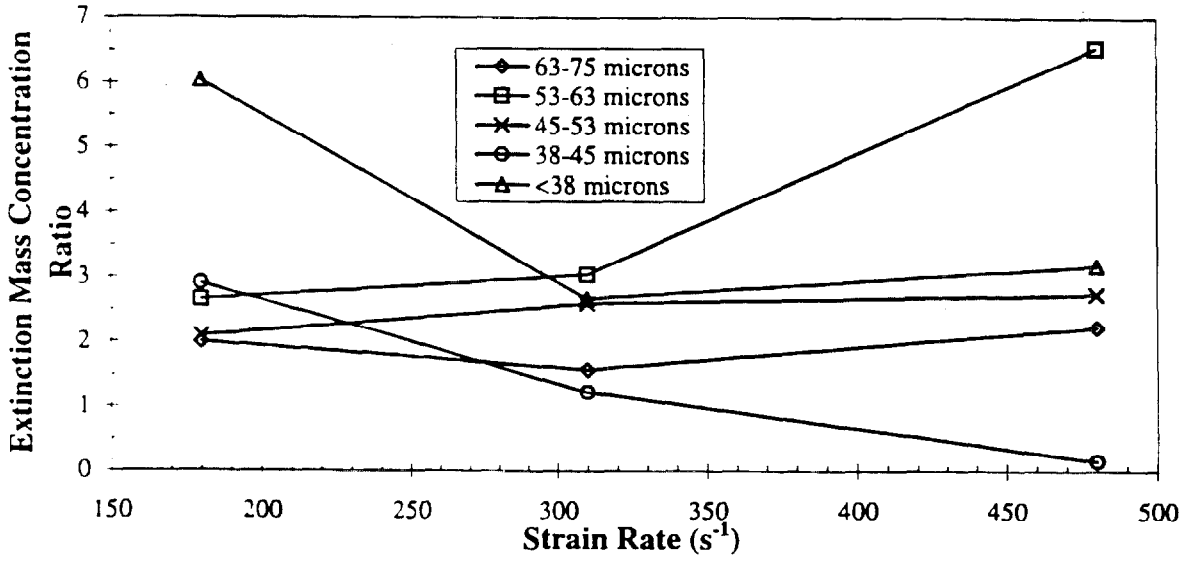

Figure 4: Extinction mass concentration ratio (Na/K) as a function of strain rate for each particle size range in a propane-air counterflow diffusion flame.

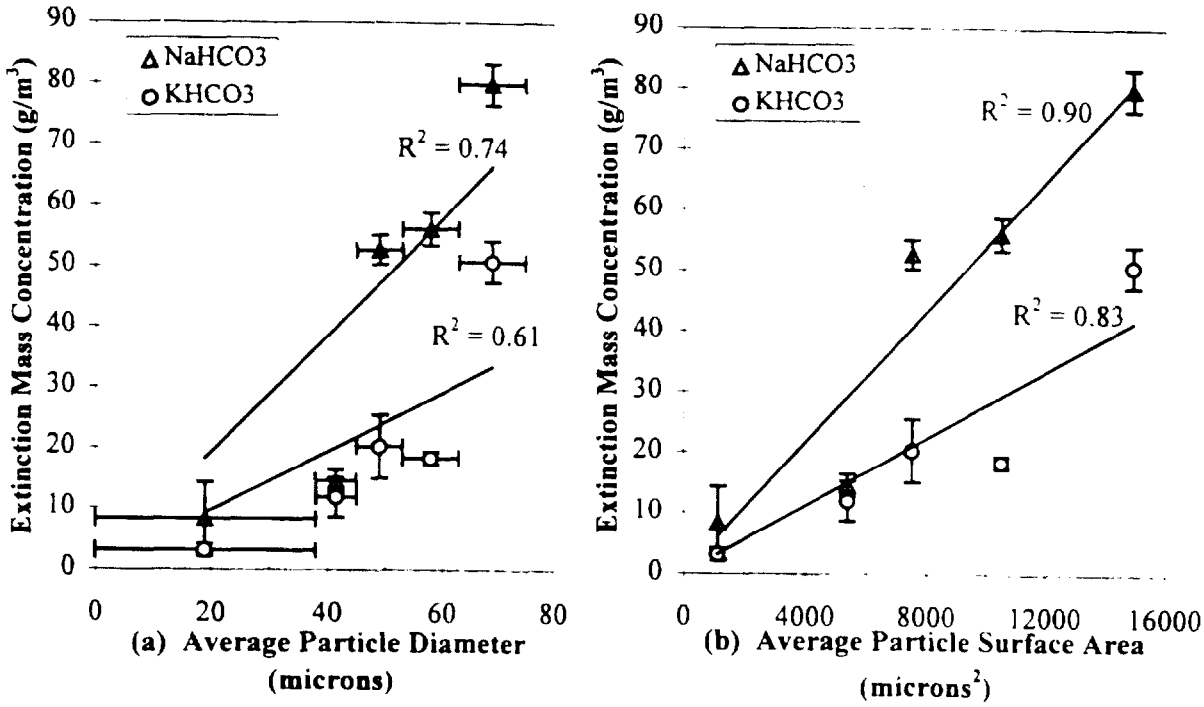

Figure 5: Extinction mass concentration as a function of (a) average particle diameter of the indicated size range and (b) average particle surface area, for a medium strain (310 s^{-1}) propane-air counterflow diffusion flame.

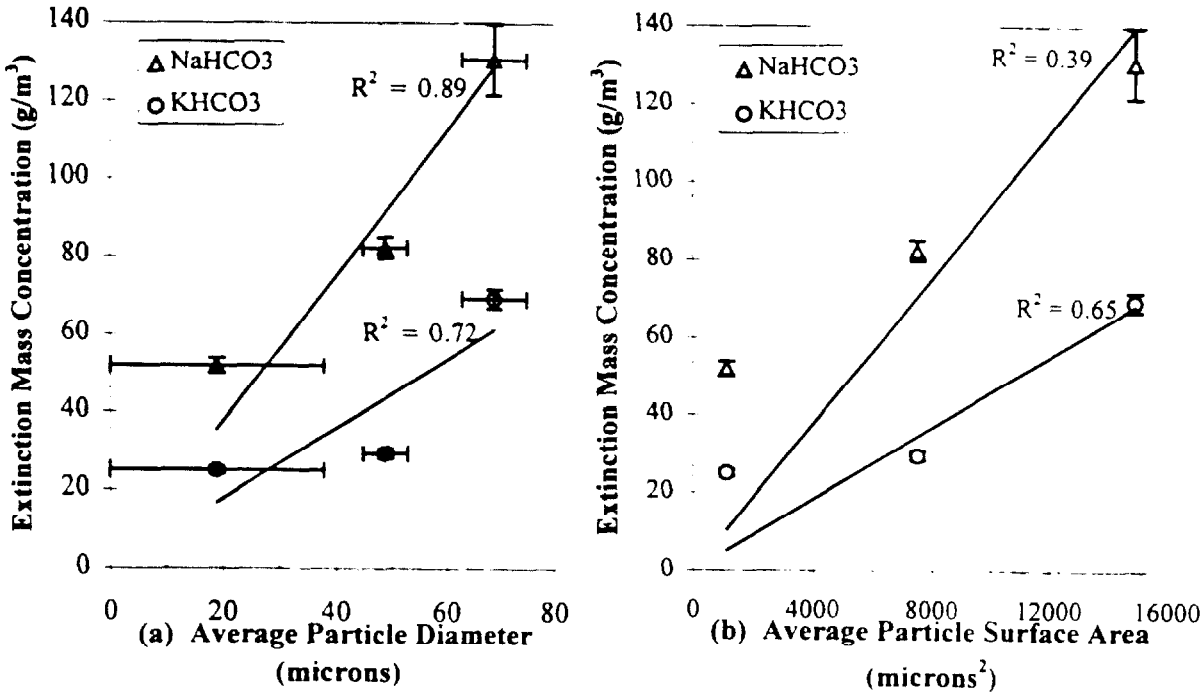

Figure 6: Extinction mass concentration as a function of (a) average particle diameter for the indicated size range and (b) average particle surface area, for an obscured n-heptane pan fire.