

UNMIXED COMBUSTION: A NEW TECHNOLOGY FOR PREVENTION
OF PUFFING BY ROTARY KILN INCINERATORS AND OTHER APPLICATIONS

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INTRODUCTION

The Problem of Puffing in Civilian Incinerators The United States currently produces 265 million tons per year of hazardous waste. In most instances the toxicity of this waste come from toxic organic materials which, in principle, can be completely destroyed by incineration. Since all other disposal technologies involve the risk that some of the toxic materials will return to the environment incineration is, in principle, the ideal solution to the problem. Presently available incinerator technology is subject to a number of limitations, one of the most important of these limitations being the puffing problem of rotary kiln incinerators, i.e. these incinerators are observed to occasionally emit puffs of toxic organic materials. This is a serious failure since as discussed by Oppel (1) rotary kiln incinerators are a substantial fraction of total U. S. incineration capacity. Detailed mathematical models of this puffing phenomenon has been presented in references 2, 3, and 4. As these references discuss rotary kiln incinerators handle both solid and liquid wastes. For combustible liquid wastes the practice is to mix the liquid waste with a sorbent, which is then placed in a container (typically a cardboard, plastic, or steel drum), and feed to the rotary kiln incinerator. These large closed containers are heated until the vapor pressure of the liquid is sufficient to cause them to rupture. This results in a sudden discharge of a large amount of combustible vapors into the incinerator. The supply of combustion air can be much less than sufficient for complete oxidation of these suddenly released vapors and this can cause substantial amounts of these toxic organic vapors to be discharged from the incinerator into the environment.

Disposal of Chemical Weapons A problem very similar to puffing is likely to occur during the U.S. Army's planned incineration of its stockpile of chemical weapons. If during the unpacking of these weapons a live munition were inadvertently included in the packing material sent to the dunnage incinerator most of the nerve agent it contains would be discharged to the environment. A risk analysis by GA Technologies (5) estimates a probability of 0.01 per year per site for such a mishap. Since there are nine sites and the destruction of the munitions will require a number of years, the probability of such an accident happening at least once is significant.

Puffing Control via CuO In both civilian and military incinerators the fundamental problem is that organic matter can go into the combustion chamber in slugs while combustion air is supplied continuously. It occurred to the author that this problem of mismatch between the supplies of fuel and air could be solved by using a bed of copper oxide. Organic matter passing through copper oxide at elevated temperatures is rapidly oxidized and air readily reoxidizes the copper to copper oxide. Thus a bed of copper oxide can, in effect, provide a means of storing an inventory of combustion air.

The Concept of Unmixed Combustion The research reported herein was initiated to test on a laboratory scale the feasibility of this method of controlling puffing. During the course of this work, however, it was recognized

that the use of copper oxide to maintain an inventory of combustion air make s possible a novel type of combustion system, one in which the fuel and air do not mix. Such an unmixed combustion system would be unique in that in all other combustion systems the stoichiometric ratio (i.e. the fuel/air ratio) is a critical parameter but in unmixed there are two stoichiometric ratios each of which is important, the ratio of the amount of fuel passed through the bed during a cycle to the maximum capacity of the bed to oxidize fuel and the ratio of the amount of air passed through the bed during a cycle to the maximum capacity of the bed to reduce O_2 .

Preliminary experiments were done to examine the properties of such an unmixed combustor and are reported below.

APPARATUS AND EXPERIMENTAL PROCEDURES

Three sets of experiments were done, two to demonstrate puffing control with a fixed bed and fluid bed CuO on high surface area alumina and one to explore unmixed combustion.

Fixed Bed Experiments for Puffing Control In the former experimental setup rotameters were used to prepare a flowing gas mixture containing oxygen and nitrogen in known proportions. For experiments involving volatile organic compounds a third rotameter was used to send a measured flow of nitrogen through a bubbler partially filled with the volatile organic compound and this stream of nitrogen saturated with the volatile organic was added to the flow of the oxygen/nitrogen mixture. A fourth rotameter was then used to take a measure portion of this flowing mixture and the rest was sent to vent via a back pressure regulator. For experiments with materials which are not readily volatile, i.e. phosphonoacetic acid, a precision metering pump send a flow of an aqueous solution of the material to the top of the fixed bed where the temperature was high enough to cause it to vaporize.

From the fourth rotatmeter the flowing gas mixture was sent to a three way valve and thence either went downward through the fixed bed and then to the analytical instruments or went directly to the analytical instruments. In these experiments the fixed bed was housed in a 1" OD stainless steel tube inside an electrically heated furnace. Two type K thermocouples were used to monitor and control its temperature.

The analytical instruments used were a Beckmann 400 Hydrocarbon analyzer (i.e. a flame ionization detector) and a Teledyne O_2 analyzer.

The fixed bed consisted of 25.5 wt% CuO supported on 5/16" alumina rings and was prepared by the incipient wetness method. In this method a solution of copper nitrate was added to the alumina with constant stirring until the bed could not absorb more without becoming macroscopically wet. The alumina rings were then heated to $800^\circ C$ to drive off water and decomposed copper nitrate to copper oxide. Manufacturer's specifications on these alumina rings list them to have a surface area of $2B4 M^2/gm$, total pore volume, H_2O , of $1.10 cc/gm$, total pore volume, Hg , of $1.038 cc/gm$, and a median pore diameter of 0.009 microns.

In doing these experiments the following procedure was used: an oxygen/nitrogen mixture without organic matter was passed through the bed and the oxygen level measured for the gas exiting the bed. Initially the concentration of oxygen in the gas going out of the bed could be extremely low because all the input oxygen was reacting will copper metal formed in the previous experiment. The oxygen level in the output gas would remain very low until virtually all of the metallic copper was consumed then would rise rapidly to equal the input level. Once the level of oxygen in the output gas was stable organic matter could

be added via either the bubbler or the metering pump and the change in the oxygen level of the exit gas noted. Since flame ionization detector was limited to concentrations less than 1000 ppmC, the change in the oxygen content which occurred when organic matter was added was used to calculate the input concentration of the organic matter. After making these observations the oxygen content of the gas going into the bed was reduced to zero and the flame ionization detector was used to measure the amount of organic matter which survived passage through the copper oxide bed as a function of time.

Fluid Bed Experiments for Puffing Control For fluid bed experiments the experimental apparatus and procedures were the same the following exceptions. The fluid bed was housed in a 26mm ID, 91 cm long, quartz tube which was placed inside an electric furnace with a 30 cm. heated length. The bed had a settled height of 13 cm. It operated in a slugging mode with a height of 30cm. Gases flowing out of the quartz tube went directly into a laboratory hood. Sample gas for the analytical instruments was obtained by a probe. The material in the fluid bed was 16.8 wt% CuO supported on Alcoa type F-1 activated alumina, 28-48 mesh. A single batch of this material was prepared, loaded into the fluid bed reactor, and used for all fluid bed experiments.

Examination of Unmixed Combustion For these experiments a setup was used in which flows of methane and air were measured by two rotameters and then each went to the common inlet of an electrically activated three way valve. (The use of three way valves allowed the flow through the rotameters to be continuous and hence more accurately measurable.) One of the flows was passed through the three way valve to vent while the other was passed through a 0.902 ID steel tube in an electric furnace, the heated length of this tube having a volume of 160cc and containing 87grams of 25.5% copper oxide on alumina rings. An electrical cycle timer was used to switch the three way valve at predetermined intervals.

RESULTS

Demonstration of Puff Suppression Figure 1 shows raw data from a packed bed experiment, i.e. in this experiments a mixture of 2520ppm C_5H_5N , 3.6% O_2 , balance N_2 , the O_2 was shut off, and the flame ionization detector is used to measure the amount of C_5H_5N surviving passage through the bed as a function of time. From the known initial and observed final concentrations of the C_5H_5N one can calculate as a function of time both the DRE and the extent to which the bed's oxidation capacity have been used. Figure 2 shows the data from Figure 1 recalculated in this manner. Using this procedure the experimental results from the fixed bed and fluid bed experiments were reduced to determine the initial DRE and the extent to which the oxidation capacity of copper oxide can be used before the DRE falls below some predetermined value. Capacity of the copper oxide bed is conveniently expressed in terms of the volume of combustion air a volume of the bed is equivalent to. The results of these calculations are shown in Table 1.

The following observation is also to be reported: when oxygen was present in the gas going into the hot copper oxide bed the amount of organic matter surviving passage through the bed was zero within the noise level of the FID. This was found in all experiments with one exception: during the experiments with CCl_3F 76% of the input CCl_3F survived passage through the bed both in the presence and absence of oxygen.

Using the unmixed combustion setup the bed of CuO was subjected to approximately 5400 puffs of pure CH_4 and showed no signs of mechanical deterioration or of its losing chemical activity. On completion of this test a

series of experiments was done to examine the operational characteristics of the unmixed combustor. Figure 3 shows the variations in the oxygen level of the postcombustion gases when the bed was operated at a fuel to capacity ratio less than one but an air to capacity ratio much greater than one. Figure 4 also shows oxygen level but with the combustor operating at fuel to capacity and air to capacity ratios which are both less than one. Figure 4 also shows the amount of NOx being produced by unmixed combustion.

A series of experiments was done in which the variations of levels of NOx and oxygen in the postcombustion gases was measured over a range of overall fuel to air stoichiometric ratios with the results shown in Figures 5 and 6

In another experiment the electrical furnace was shut off and the combustor was allowed to operate autothermally with a CH_4 input of 3212 cc/min for 2 seconds, off for 15 seconds, and an air input of 3000cc/min for 15 seconds, off for 2 seconds. Initially the bed temperature in this experiment was 775°C. After dropping to 635°C the bed temperature wandered, slowly rising to 681°C. At 2.8 hours after shutting off the electric furnace the run was voluntarily terminated.

DISCUSSION

Laboratory Scale Demonstration of Puffing Control The results in Table 1 show that for a considerable variety of compounds (i.e. hydrocarbons and organic compounds containing nitrogen, phosphorous, chlorine and sulfur) copper oxide can provide both the DRE and the capacity needed in a practical method of puffing control. While the results for $\text{C}_2\text{H}_5\text{F}$ were not as good, they still indicate that this technique may be useful for fluorine containing hydrocarbons. Similarly the results for CCl_3F were arguably positive. Freons are extremely refractory materials and even in the absence of puffing would normally be expected to pass unchanged through an incinerator. Thus in addition to providing a solution to the occasional problem of puffing, the use of a copper oxide bed also provides a means of substantially reducing the continuous emission of freons from incinerators.

Controlling NOx production by Unmixed Combustion The data reported above show that it is in principal possible to use supported CuO as the basis for a novel combustion system, one in which the fuel and air are largely unmixed. During unmixed combustion the production of NOx was found to be extremely low. Given the generally accepted mechanisms for NOx production this result is not surprising. For fuels which do not contain chemically bound nitrogen it is generally agreed that NOx is chiefly thermal NOx, i.e. most of the NOx is produced by the "extended" Zeldovitch mechanism, $\text{O} + \text{N}_2 = \text{NO} + \text{N}$, $\text{N} + \text{O}_2 = \text{NO} + \text{O}$, $\text{OH} + \text{N} = \text{NO} + \text{H}$. The other source of NOx is the prompt NOx mechanism, i.e. the attack of hydrocarbon radicals such as CH on N_2 to produce HCN which is then oxidized to NO. Both these mechanisms are strongly disfavored at lower temperatures and both depend on the superequilibrium concentrations of free radicals which conventional combustion produces. By eliminating direct contact between the fuel and air both the extremely high temperatures normally associated with combustion and the high free radical concentrations are avoided and thus NOx production is suppressed.

Controlling CO₂ emissions by Unmixed combustion The problem of global warming due to the emissions of CO₂ during combustion has recently begun to receive a great deal of serious attention. In many locations pure CO₂ could economically be used in tertiary oil recovery or put to other use but the possibility of recovering dilute CO₂ from combustion gases have been given little consideration because the expense and large energy consumption involved. In an unmixed combustion system, however, the fuel is converted to CO₂ and water without being diluted with nitrogen. Thus unmixed combustion may, in favorable situations, be the basis of burning fuel without CO₂ emissions.

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TABLE 1 SUMMARY OF FIXED BED EXPERIMENTS

Puff being Oxidized	Reaction Conditions	Initial DRE	DRE as a function of Bed Oxidation Capacity, Equivalent cc of air per cc of bed
1974 ppmC of C ₆ H ₅ Cl	802°C for 0.53sec.	99.9985%	99.99% at 37.3cc/cc
3683 ppmC of C ₆ H ₅ Cl	812°C for 0.53sec.	>99.999%	99.9% at 136cc/cc 99% at 207cc/cc
10,000 ppmC of C ₆ H ₆	811°C for 0.53sec.	99.997%	99.9% at 118cc/cc 99% at 197cc/cc
19,000 ppmC of C ₅ H ₄ S	814°C for 0.53sec.	99.9999%	99.9% at 186cc/cc 99% at 373cc/cc
7,800 ppmC of C ₆ H ₅ F	815°C for 0.53sec.	99.3%	
7,800 ppmC of C ₆ H ₅ F	991°C for 0.45sec.	99.94%	99.9% at 2.8cc/cc 99.3% at 59cc/cc
2,520 ppmC of C ₅ H ₅ N	817°C for 0.53sec.	99.9968%	99.99% at 99cc/cc
6000 ppmC of CCl ₃ F	821°C for 0.53sec.	76%	
3110 ppmC of (HO) ₂ POCH ₂ COOH	818°C for 0.53sec.	99.993%	99.9% at 29cc/cc 99% at 54 cc/cc

SUMMARY OF FLUID BED EXPERIMENTS

8000 ppmC of C ₆ H ₆	806°C for 0.75sec.	>99.994%	99.9% at 43cc/cc 99% at 73cc/cc
3900 ppmC of C ₆ H ₅ Cl	805°C for 0.75sec.	>99.95%	99.9% at 169cc/cc 99% at 215 cc/cc

Oxidation of C₅H₅N by CuO

Run 7

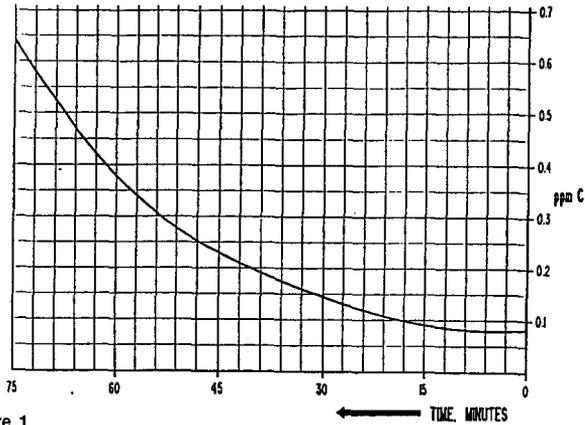
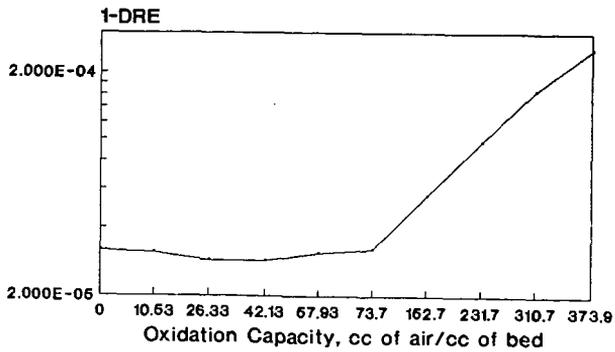


Figure 1

Destruction and Removal Efficiency for Oxidation of C₅H₅N by CuO



Run 7
Figure 2

Unmixed Combustion

CH₄ and Air feed alternately to a bed of CuO on alumina, long pulses of air

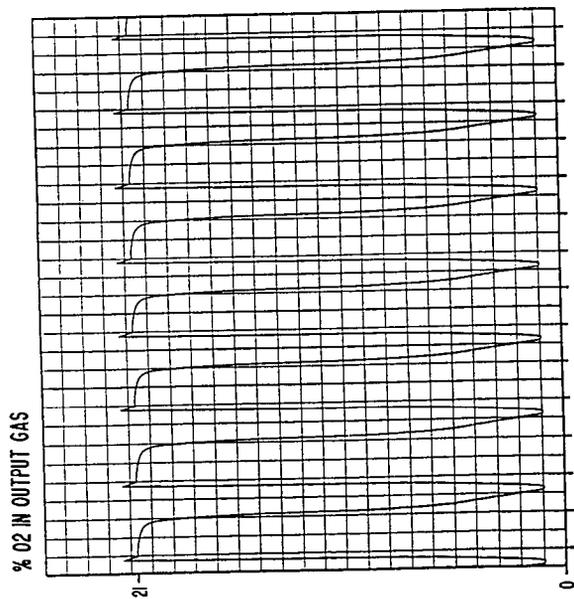


FIG. 3

STOICHIOMETRIC RATIO = 0.315
 B5C, 87% OF 25.5 WT% CuO IN A 160 cc BED
 AIR = 3470 cc/MIN FOR 1/5 SEC. OFF FOR 5 SEC.
 CH₄ = 2513 cc/MIN FOR 5 SEC. OFF FOR 1/5 SEC.

Unmixed Combustion

CH₄ and Air feed alternately to a bed of CuO on alumina, short pulses of air

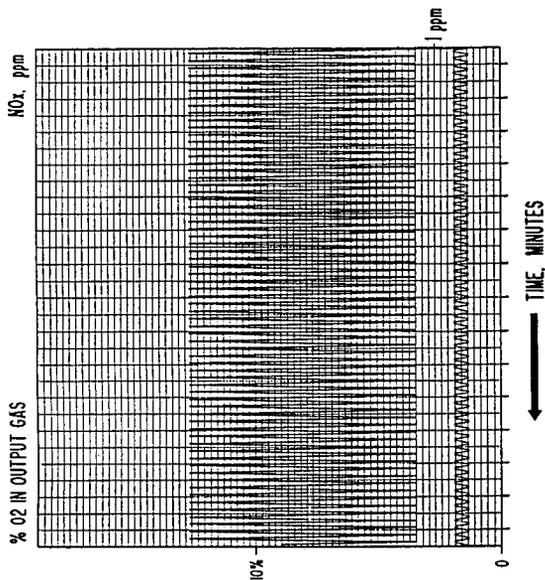
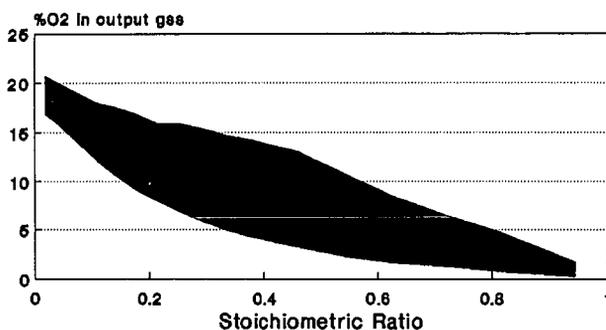


FIG. 4

STOICHIOMETRIC RATIO = 0.458
 AIR = 3660 cc/MIN FOR 1/5 SEC. OFF FOR 1 SEC.
 CH₄ = 1 SEC ON, 1/5 SEC OFF

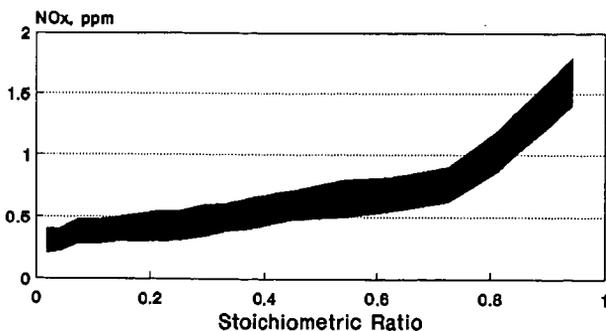
Effect of Stoichiometric Ratio on the variance of O₂ in the output gas from unmixed combustion



816C, 87g of 25.5wt% CuO in a 180 cc bed
Air - 3660cc/min for 16 sec, 1 sec off
CH₄ - 1 sec on, 15 sec off,

Figure 5

Effect of Stoichiometric Ratio on the variance of NO_x in the output gas from unmixed combustion



816C, 87g of 25.5wt% CuO in a 180 cc bed
Air - 3660cc/min for 16 sec, 1 sec off
CH₄ - 1 sec on, 15 sec off,

Figure 6