HAZARDOUS AIR POLLUTANT EMISSIONS FROM THE EXTERNAL COMBUSTION OF HYDROCARBON GASEOUS FUELS CAN BE PREDICTED!

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INTRODUCTION

Passage of the 1990 Amendments to the Clean Air Act made it clear that maximum available control technology ("MACT") regulations on the emission of hazardous air pollutants ("HAPs") from process heaters and industrial boilers, used extensively in the petroleum and petrochemical industries, would be promulgated under congressional mandate by the U. S. Environmental Protection Agency in the year 2000. Unfortunately, it had also become clear that *understanding*, the "good science" upon which we aspire to base sensible regulations, was simply non-existent and, further, that the little field data then extant was severely flawed. To amend those deficiencies, a 4-year $7-million fundamental attack on the origin and fate of trace toxic emissions in the external combustion of gaseous hydrocarbon fuels has been conducted by a government-university-industry collaboration[1] that has been, by all accounts, one of the most successful ever.

A number of challenges were encountered during the course of the project. Perhaps foremost among them and exemplary of the remarkable strength of this collaboration, was the need not only to expand the capabilities of the Sandia National Laboratories, Livermore, Combustion Research Facility Burner Engineering Research Laboratory (BERL) by the addition of 4-component fuel mixing capability (formerly natural gas only); and bunkering and delivery capability for the various gases to be employed in the full-scale burner trials (hydrogen, propane, propylene, ethylene); but also, at the cost of over a quarter of a million dollars that was quickly raised by the CRADA-signatories, to convert the former BERL flame laboratory into a process heater laboratory by the addition of a convection section simulator.

This allowed the project successfully to reproduce at full-scale the generally very low normal-operation gaseous-combustion emissions that are observed in the field, as well as higher hypothetical extreme failure-mode emission levels of aldehydes, volatile organic compounds, polycyclic aromatic hydrocarbons and total organics fully comparable to the highest levels reported in field tests, however sparse and unreliable they might be, observed under extreme combustion conditions that would neither be tolerated nor observed in actual field operations but that, nevertheless, proved to be required to generate toxic emissions of any significance.

Through the rigorous and highly reliable measurements of regulatory development quality, as guaranteed by the project's exemplary Quality Assurance Project Plan that was produced in cooperation with U. S. Environmental Protection Agency experts, carried out during the full-scale burner trials conducted at the Sandia National Laboratories, Livermore, Combustion Research Facility Burner Engineering Research Laboratory, a great deal has been learned, in far more detail and under many more conditions, about the normal and hypothetical extreme limiting emissions from full-scale burners than was heretofore known. However, this paper discusses only the findings that most pertinently address the question, "Can we predict HAP emissions based on fuel composition?"

HAP EMISSIONS UNIFORMLY LOW

In this program we saw over and over again that the nature of the gaseous hydrocarbon fuel mixture doesn't make much difference, neither in the total toxic emissions nor in the individual species levels. This observation includes natural gas which is itself, after all, merely just another hydrocarbon mixture; *i.e.*, there is no reason to distinguish "refinery fuel gas" from "natural gas." Figures 1 and 2 illustrate this equivalency on a speciated basis, there being only small and statistically insignificant differences in the individual species emissions.

Almost stochastic in nature, the individual species levels are uniformly exceedingly low, seemingly less dependent upon physics and chemistry and more dependent upon the vagaries of the sophisticated sampling methods and precise analytical techniques that are required to detect them at all in the minute concentrations in which they appear in the combustion products. In Figures 3-6, these facts are illustrated by the mass emission of total hydrocarbons. Except for an operationally unrealistic super-aerated (450% stoichiometric air) case, we see that there is no significant effect of heating value, combustion zone stoichiometry, propylene or ethylene spikes, nor hydrogen content in the gaseous hydrocarbon fuel mixtures.

The heating value variation was achieved at the constant base case 16% hydrogen content simply by increasing the proportion of propane in the hydrogen, natural gas, propane mixture. The field-operational typical ±15% theoretical air variation around the base case 125% was extended substoichiometrically in the combustion zone to 50% or one-half of the air theoretically required for complete combustion with overfire air added to simulate a leaky furnace while still maintaining the base case 125% theoretical air in the stack. The theoretical air variation was extended super-stoichiometrically in the combustion zone to 450% or four-and-one-half times the air theoretically required for complete combustion simply by increasing the air delivery to the

[1] Petroleum Environmental Research Forum Project Number 92-19 sanctioned under a Stevenson-Wydler (15 USC 3710) Cooperative Research and Development Agreement

burner. The effect of spikes of ethylene and propylene on the emissions of the base case 16% hydrogen, 1050 Btu/scf fuel mixture was tested by utilizing the four component mixing capability that was added by this program to the Sandia National Laboratories, Livermore, California, Combustion Research Facility's Burner Engineering Research Laboratory, while the effect of hydrogen variation on emissions from the 1050 Btu/scf base case was tested simply by compensating adjustments to the natural gas and propane fractions in the fuel mixture.

The absence of systematic variability in the trace emission of toxic byproducts in gaseous external combustion is strikingly illustrated in Figures 7 and 8. We see that the reproducibility of the reference regulatory base cases ("A1" was a 1050 Btu/scf mixture of 16% hydrogen, natural gas, and propane while "A4" was 1050 Btu/scf natural gas) remained good throughout all of the conventional diffusion flame burner ("CDFB") trials in test sequences A, B and C. While test sequence A spanned a broad range of fuel compositions and operating conditions around the normal-operation base cases A1 and A4, we saw no systematic variation in emissions; all emissions remained exceedingly low and the small differences were well within the typical bounds of experimental variability.

Worried that, even in the sequence B "failure mode" tests, we were not able to reproduce polycyclic organic hydrocarbon ("PAH") emissions as high as those reported in some field tests, however unreliable those field tests may have been, we redoubled our efforts to fail combustion and, in the sequence C "super-failure mode" trials, we were rewarded with stack emissions up to 5E-6 lb-PAH/mmBtu (*e.g.*, B13' in Figures 7 and 8), fully as high as any in the "real world" field data base. These high emissions are often attributed, but without much definition and no detailed understanding, to "gross mixing failures." We saw in this program, as illustrated in Figures 7 and 8, that to generate high stack emissions from gaseous hydrocarbon mixtures in external combustion, fuel-air mixing failures of the grossest kind are indeed required, egregious hypothetical extreme combustion conditions that would hardly be tolerated nor permitted to persist in any well-run plant.

HIGH VELOCITY JET MIXING ACCOUNTS FOR LOW TOXICS

The strong mixing potential of sonic jets is well known. In the case of the multiple, small reacting jets of the conventional diffusion flame burner, surrounded as they are under normal conditions with an excess supply of air, why would we not expect very low toxic emissions?

Early in the program, we hypothesized that the hot, rich combustion regions that are necessarily present in a diffusion flame ought to be prolific generators of toxics. The early stirred-reactor, plug-flow computations carried out by Lawrence Livermore National Laboratory supported the hypothesis, while later the laboratory flame measurements carried out at the UCLA Chemical Engineering Laboratory, as well as the research furnace experiments carried out at the Sandia National Laboratories, Livermore, Combustion Research Facility, confirmed it. The Lawrence Livermore calculations also suggested that, in the presence of excess air, the toxics that are necessarily profusely-generated in the rich zone would subsequently quickly be consumed to near-extinction, a prediction that we have now seen borne out time and time again in the full-scale burner trials carried out at the Sandia Combustion Research Facility's Burner Engineering Research Laboratory.

Most significant are the results of Sandia's application of a two-stage Lagrangian jet model to a typical conventional diffusion flame burner jet. Based upon the observed flame structure of the conventional burner, the jet model was applied twice: first to the individual jet flames that emerge from the burner tips inside the quarl and again for the merged jet exiting the quarl; thereafter, when mixing is completed, a plug-flow reactor model is utilized to represent the remaining flow to the furnace exit. To give confidence in the results, it may be observed that the model predicted a final CO level of 2 ppm, consistent with the actually measured level below the detection limit of 5 ppm, and a final NOx concentration of 106 ppm, compared with the measured value of 118 ppm. The jet model predicts that the air toxic species should be produced to significant levels within the in-quarl flames but should be consumed well within the substoichiometric regime, both just as we have seen in the full-scale trials.

The Lagrangian jet model confirms and illustrates the expected behavior. Initially, where the reactions are just beginning, there is nothing but the original fuel reactants and oxidant in abundance. As the reactants and oxidant begin to mix, the reacting part of the "reacting jet" begins, too, and the reaction products begin to appear. Then as more and more air is mixed into the jet, with theoretical air % increasing but still well within the substoichiometric regime, the reaction products peak but then are rapidly consumed even before the mixture reaches stoichiometric.

The prediction confirmed that toxic species, manufactured in abundance in the hot, rich diffusive regime, are subsequently consumed in the high-mixing-potential jet well before it reaches even stoichiometric conditions, is, of course, extremely significant, not only with regard to its implication upon the robustness of practical combustion systems in the field but also with respect to the predictability of HAP emissions based on fuel composition.

Moreover, it is perhaps remarkable to note that, in the super-failure mode full-scale trials carried out at the Sandia National Laboratories, Livermore, Combustion Research Facility's Burner Engineering Research Laboratory, it was not until severely substoichiometric conditions (stoichiometric ratio below 0.80) were achieved in the combustion zone and maintained right through and out the stack to the atmosphere, and just as predicted by the Lagrangian jet model, that high levels of toxics emerged.

This goes a long way toward explaining why the conventional diffusion flame burner, composed as it is of burner tips out of which emerge high-mixing-potential jets surrounded by an abundant supply of oxidant, simply has to be a low toxics burner.

CONCLUSION

Jet-mixed gaseous hydrocarbon diffusion flames, such as those produced by the burners that are typically used in petroleum industry process heaters and industrial boilers, result in a combustion process that is extremely robust, producing predictable, exceedingly low emissions of hazardous air pollutants even when subjected to extreme mixing failures. Readers who are interested in learning more about this interesting subject are referred to the papers published in learned journals that emerged from this program, many of which are listed in the references.

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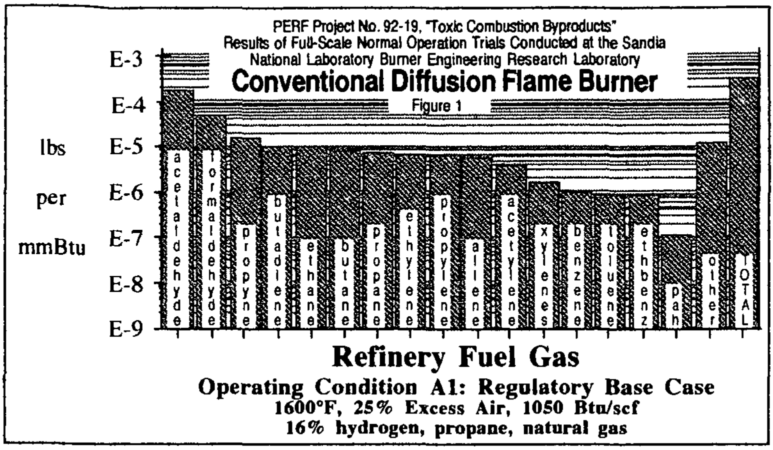
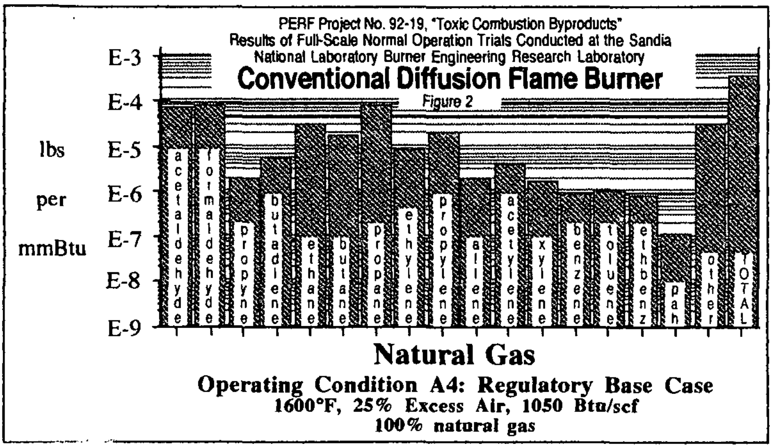
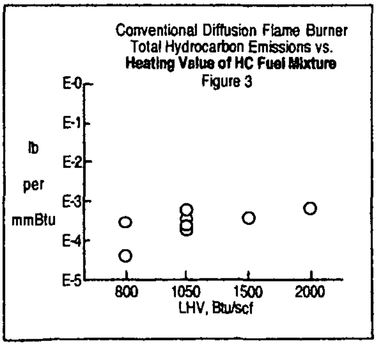
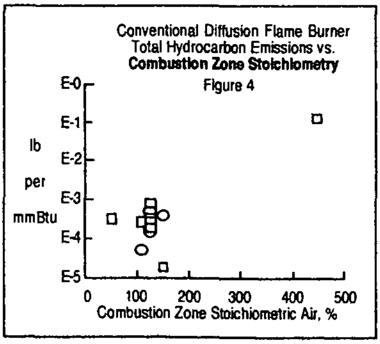
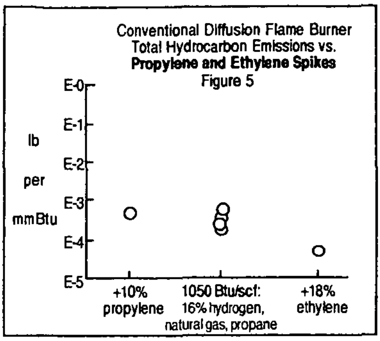

PERF Project No. 92-19, "Toxic Combustion Byproducts"
Results of Full-Scale Normal Operation Trials Conducted at the Sandia
National Laboratory Burner Engineering Research Laboratory
Conventional Diffusion Flame Burner
Figure 1
lbs per mmBtu
E-3
E-4
E-5
E-6
E-7
E-8
E-9
acetaldehyde
formaldehyde
propyne
butadiene
ethane
butane
propane
ethylene
propylene
allene
acetylene
xylenes
benzene
toluene
ethbenz
pah
other
TOTAL
Refinery Fuel Gas
Operating Condition A1: Regulatory Base Case
1600°F, 25% Excess Air, 1050 Btu/scf
16% hydrogen, propane, natural gas

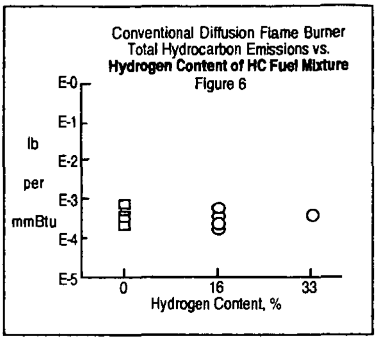

PERF Project No. 92-19, "Toxic Combustion Byproducts"
Results of Full-Scale Normal Operation Trials Conducted at the Sandia
National Laboratory Burner Engineering Research Laboratory
Conventional Diffusion Flame Burner
Figure 2
lbs per mmBtu
E-3
E-4
E-5
E-6
E-7
E-8
E-9
acetaldehyde
formaldehyde
propyne
butadiene
ethane
butane
propane
ethylene
propylene
allene
acetylene
xylene
benzene
toluene
ethbenz
pah
other
TOTAL
Natural Gas
Operating Condition A4: Regulatory Base Case
1600°F, 25% Excess Air, 1050 Btu/scf
100% natural gas


Conventional Diffusion Flame Burner
Total Hydrocarbon Emissions vs.
Heating Value of HC Fuel Mixture
Figure 3
lb per mmBtu
E-0
E-1
E-2
E-3
E-4
E-5
800
1050
1500
2000
LHV, Btu/scf

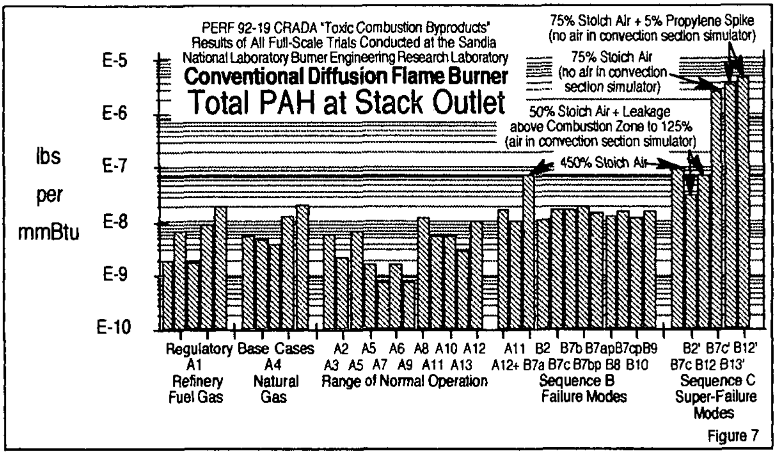

Conventional Diffusion Flame Burner
Total Hydrocarbon Emissions vs.
Combustion Zone Stoichiometry
Figure 4
lb per mmBtu
E-0
E-1
E-2
E-3
E-4
E-5
0
100
200
300
400
500
Combustion Zone Stoichiometric Air, %



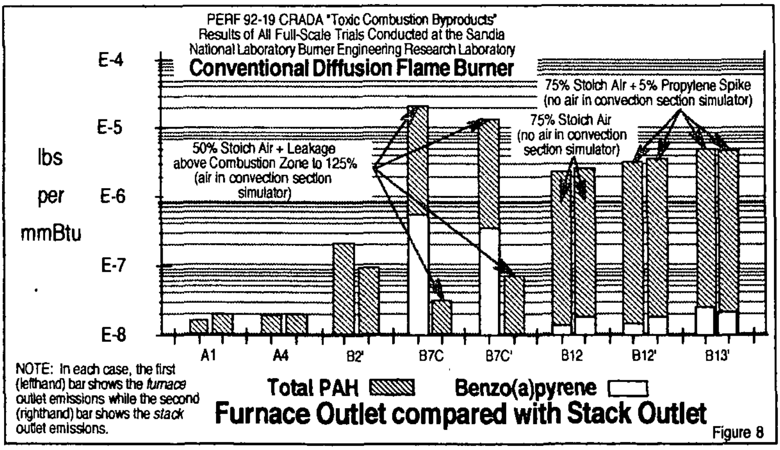
Conventional Diffusion Flame Burner
Total Hydrocarbon Emissions vs.
Propylene and Ethylene Spikes
Figure 5
lb per mmBtu
E-0
E-1
E-2
E-3
E-4
E-5
+10% propylene
1050 Btu/scf: 16% hydrogen, natural gas, propane
+18% ethylene



Conventional Diffusion Flame Burner
Total Hydrocarbon Emissions vs.
Hydrogen Content of HC Fuel Mixture
Figure 6
lb per mmBtu
E-0
E-1
E-2
E-3
E-4
E-5
0
16
33
Hydrogen Content, %



PERF 92-19 CRADA "Toxic Combustion Byproducts"
Results of All Full-Scale Trials Conducted at the Sandia
National Laboratory Burner Engineering Research Laboratory
Conventional Diffusion Flame Burner
Total PAH at Stack Outlet
lbs per mmBtu
E-5
E-6
E-7
E-8
E-9
E-10
75% Stoich Air + 5% Propylene Spike (no air in convection section simulator)
75% Stoich Air (no air in convection section simulator)
50% Stoich Air + Leakage above Combustion Zone to 125% (air in convection section simulator)
450% Stoich Air
Regulatory Base Cases
A1 Refinery Fuel Gas
A4 Natural Gas
A2 A5 A6 A8 A10 A12
A3 A5 A7 A9 A11 A13
Range of Normal Operation
A11 B2 B7b B7apB7cpB9
A12+ B7a B7c B7bp B8 B10
Sequence B Failure Modes
B2' B7c' B12'
B7c B12 B13'
Sequence C Super-Failure Modes
Figure 7



PERF 92-19 CRADA "Toxic Combustion Byproducts"
Results of All Full-Scale Trials Conducted at the Sandia
National Laboratory Burner Engineering Research Laboratory
Conventional Diffusion Flame Burner
lbs per mmBtu
E-4
E-5
E-6
E-7
E-8
75% Stoich Air + 5% Propylene Spike (no air in convection section simulator)
75% Stoich Air (no air in convection section simulator)
50% Stoich Air + Leakage above Combustion Zone to 125% (air in convection section simulator)
A1
A4
B2'
B7C
B7C'
B12
B12'
B13'
NOTE: In each case, the first (lefthand) bar shows the furnace outlet emissions while the second (righthand) bar shows the stack outlet emissions.
Total PAH
Benzo(a)pyrene
Furnace Outlet compared with Stack Outlet
Figure 8