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SOME CHEMICAL AND PHYSICAL ASPECTS OF COMBUSTION

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SOME CHEMICAL AND PHYSICAL ASPECTS OF COMBUSTION

by

T.D. Brown*

ABSTRACT

This report represents the basic text of a verbal presentation in which the differing roles of chemical and physical processes in combustion are discussed. Chemical processes are described as dominating the formation in flames of such atmospheric pollutants as nitric oxide and sulphur trioxide and physical process are shown to dominate the combustion rates in heterogeneous combustion systems. The role of combustion aerodynamics, in particular swirling air flows, is seen to be important in defining flame characteristics such as shape and combustion efficiency.

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CONTENTS

	<u>Page</u>
Abstract	i
Contents	ii
Introduction	1
Chemical Processes	1
Adiabatic Flame Temperature	2
Is Chemical Equilibrium Achieved?	3
The Formation of Nitric Oxide in Flames	5
The Formation of Sulphur Trioxide in Flames	6
Soot Formation in Flames	7
Physical Processes	8
Heterogeneous Combustion	8
Atomization of Liquid Fuels	9
Pressure Jet Atomization	9
Twin Fluid Atomizers	10
Rotary Cup Atomizers	10
The Role of the Combustion Air Flow	11
Axial Airflows	11
Swirling Airflows.....	11
System Efficiencies	12
Combustion Additives and System Efficiency	13
Retrospect	14
References	15
Appendix	A1

FIGURES

<u>No.</u>		
1	Heats of Combustion of some simple Hydrocarbons	17
2	Gross Calorific Values of Fossil Fuels	18
3	The Calculation of Adiabatic Flame Temperature	19

<u>No.</u>		<u>Page</u>
4	The Adiabatic Flame Temperatures of selected Hydrocarbons	20
5	The Effect of Excess-Air on Adiabatic Flame Temperature	21
6	Factors affecting SO ₃ in Flames (after Hedley)	22
7	Possible Sequences of Soot Formation (after Foster)	23
8	Burning Constants for Typical Hydrocarbon Fuels	24
9	Typical Configurations of Pressure Jet Atomizers	25
10	The Effect of Axial-Air Momentum on Flame Shape	26
11	Flow Patterns in a High Swirl Flame	27
12	The Effect of Increasing Swirl on the Size of the Recirculation Core	28
13	The Effect of Swirl on the Burn-out of Coal in a Pulverized Coal Flame	29
14	The Effect of Swirl on Soot Formation in a Residual-Fuel-Oil- Fired Boiler	30
15	The Calculation of System Efficiency for a Liquid Fuel	31
16	Losses Due to Hydrogen in the Fuel	32
17	Dry Flue-Gas Losses	33
18	The Effect of a Fuel Additive on Burner Performance	34
19	A Comparison of Methods of Reducing Particulate and Nitric Oxide Emissions from a Residual Fuel-oil Flame	35
20	The Effect of a Commercial Soot Remover on the Performance of a Warm-Air Furnace	36

INTRODUCTION

Combustion is a complex mixture of chemical and physical processes which, acting simultaneously, lead to the production of heat. This heat can be used in a variety of ways across a wide spectrum of sizes. The term "combustion process" is generally applied only to hydrocarbon fuels although in the strictest sense any heat-generating reaction involving a fuel and an oxidant could be included in the generic terminology. The discussion in this report is restricted to conventional hydrocarbon fuels in the gaseous, liquid and solid state. The most widespread application of combustion at the low end of the size range is in domestic heating where the thermal input lies in the range 50,000 to 200,000 Btu/hr and the design objective is to heat a working fluid such as air or water which in turn is used to maintain the internal temperatures of a home in a satisfactory environmental range.

At the large end of the spectrum comes the utility boiler where the thermal input can be as high as 7×10^9 Btu/hr. In this case the design objective is to heat the working fluid (steam) to a temperature and pressure such that it can be used to drive a steam turbine where energy is recovered as work and converted into electricity. In process applications the heat is transferred directly to a charge to induce a reaction which can only occur at high temperatures. Examples of this occur in the majority of metal refining processes and in lime and cement manufacturing processes.

CHEMICAL PROCESSES

In combustion, chemistry can provide us with some insight into what happens in flames.

Let us have a look at one of the most familiar properties of a fuel - the heat of combustion. Some values are listed in Figure 1 where two important factors emerge. As the hydrocarbon chain length increases so the heat of combustion increases; in fact the addition of one CH_2 group consistently increases the heat of combustion by approximately 160 kilocalories/mole.

It should also be noted that this heat of reaction is not affected by the chemical mechanism by which the conversion to CO_2 and H_2O occurs - it depends only on the initial and final composition and temperature.

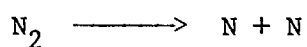
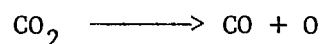
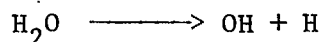
When these chemical units of the heat of reaction are converted we get the calorific values in the more familiar engineering units as shown in Figure 2.

Adiabatic Flame Temperature

This kind of information lets us do a simple calculation to estimate the maximum flame temperature that can be achieved under the idealised condition when no heat is lost from the flame. To do this, we go back to the chemical expression for the heat released in the combustion reaction. The outline of the method is shown in Figure 3. Most adiabatic flame temperatures are at the levels shown in Figure 4. When you do the same calculation for a hydrocarbon ($\text{C}_n \text{H}_{2n}$) and look at the effect of excess-air, then you get the result shown in Figure 5. The calculation was actually done using a base fuel and air input temperatures of 200°C . The maximum temperature occurs just above the precise stoichiometric level at a small excess-air level. As the excess-air level increases so the flame temperatures decreases.

The lower, solid, curve represents the result when a more sophisticated calculation is performed; this recognizes that all the heat of

combustion does not go into raising temperature but rather some goes into dissociating gases, i.e., breaking chemical bonds.



Is Chemical Equilibrium Achieved?

An important chemical question is - do these idealised end products described by the simple equation used in Figure 3 really happen? Are the chemical reactions complete in a combustion system?

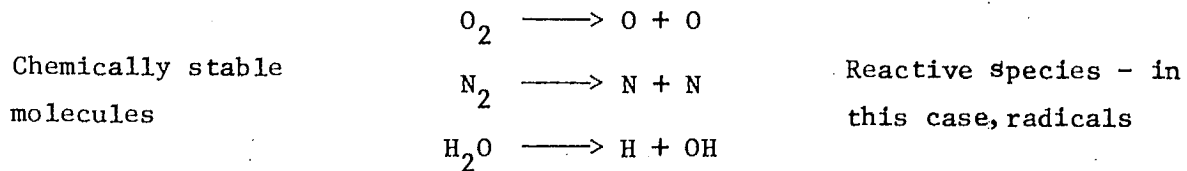
A consideration of the equilibrium products of combustion of a hydrocarbon burning in air leads to the following conclusions:

1. All the carbon in the fuel will be converted to CO_2 unless the oxygen content is below 0.25%; i.e., no free carbon should exist.
2. All the hydrogen in the fuel will be converted to water.
3. A small proportion (0.01%) of the nitrogen in the combustion air will be converted to nitric oxide (NO); of this a further quantity may convert to nitrogen peroxide (NO_2). At 300°F and $\text{O}_2 = 5\%$ all the NO should convert to NO_2 .
4. At equilibrium at 300°F , all the sulphur in the fuel should convert to sulphur trioxide (SO_3).

Of these conclusions above only one occurs in practice. This is conclusion No. 2: all the hydrogen in the fuel is converted to water. The

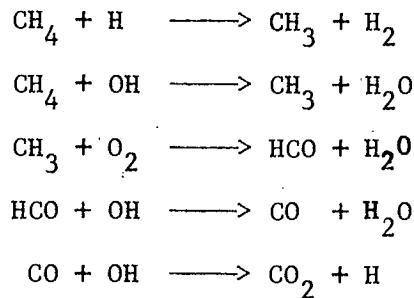
other four conclusions are offended to varying degrees because equilibrium is not achieved. The rates of the chemical and physical processes involved do not allow the achievement of equilibrium in the residence time available in the combustion system. In some instances this is an advantage; in other instances it is a disadvantage.

We must look at the individual chemical reactions and consider the nature of the process to understand this. Some elementary chemical reactions of air at high temperatures (2000°C) are:



These reactions can go in both directions.

If methane is present, then:



At flame temperature these reactions are all extremely rapid; at lower temperatures they slow down and eventually become extinct.

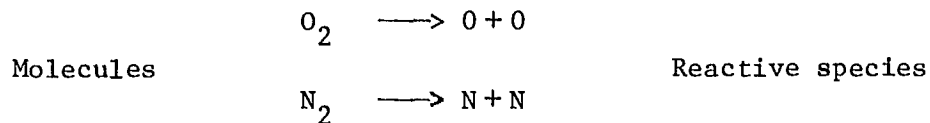
If chilling or "quenching" occurs, then the radicals O or OH recombine and are no longer available to continue the combustion process.

Flame chilling could therefore lead to carry-over of unburnt CH_4 or of the partial combustion product CO.

The reaction $\text{CO} + \text{O}_2$ was not listed above since it is relatively slow; in the majority of hydrocarbon flames there are substantial quantities of O and OH radicals to continue the "fast" reactions.

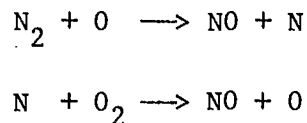
The Formation of Nitric Oxide in Flames

If we look at another series of chemical reactions, we get an insight into the formation of the pollutant nitric oxide. Since we always use air as the oxidant in hydrocarbon flames we can always have the following two reactions occurring at high temperatures.



These are typical thermal dissociation reactions; small amounts of the reactive species are produced.

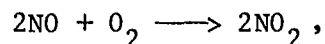
Subsequent reactions could be:



If this happens we regenerate the reactive species during the formation of the nitric oxide.

It is fortunate that nitrogen is an extremely stable gas, even at high temperatures, and does not produce high concentrations of N; otherwise the emission levels of NO would be very much higher than the observed concentration of less than 1000 parts per million.

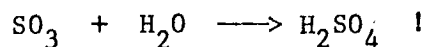
The reaction,



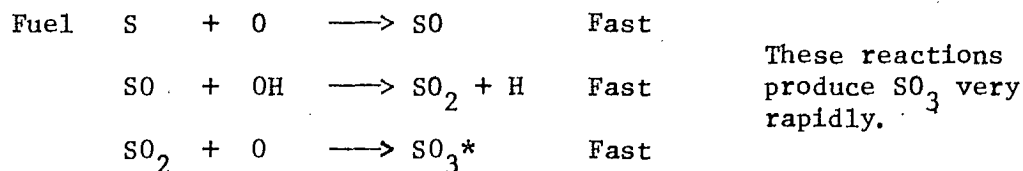
can occur at low temperatures but it is extremely slow and most flames and combustion systems do not produce significant concentrations of N₂.

The Formation of Sulphur Trioxide in Flames

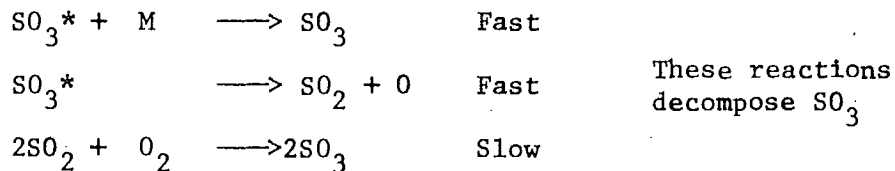
If we look at the formation of the atmospheric pollutants sulphur dioxide and trioxide in combustion systems we encounter one of the major instances where fuel suppliers and equipment operators should be very happy that predictions of chemical equilibrium are not achieved. Equilibrium calculations show that, at 300°F, all the sulphur in a fuel will be converted to sulphur trioxide. We could then get the following reaction:



This would be an extremely dangerous product both internally to the combustion system and externally to the environment. In fact the sequence of reactions and their rates tells us what really happens.



SO₃* is an unstable species,



Only the final reaction is important beyond the flame. It is slow and gets slower as the gas temperature decreases. The net result of this is shown in Figure 6. You can see that the reaction is slow and equilibrium is not achieved.

In this context it is interesting to consider the effect of a platinum catalyst on the reaction, $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$.

It accelerates both the forward and backward reactions to such an extent that equilibrium is achieved. If we look at Figure 6, at a temperature of 1000°K the equilibrium condition suggests that 20% of the fuel sulphur can exist as SO_3 (potentially H_2SO_4); the typical actual figures indicate a conversion below 10%. Introduction of a catalyst will drive the conversion upwards, more SO_3 will be formed and potentially more sulphuric acid will be produced. This type of behaviour is currently a concern of the supporters and detractors of the catalytic exhaust system for automobiles.

Soot Formation in Flames

This is probably the least well-understood area in the chemistry of combustion, in some cases because of the lack of knowledge of the nature of soot.

Soot is generally composed of small (30 - 1000 Angstrom) carbon particles which aggregate into chains. At high temperatures this soot emits a visible radiation; this is what you see in a typical yellow flame. The concentration is very high ($10^{10} - 10^{18}$ particles/cm³) and the particle size distribution is normal for oil and gas. In the case of coal a bi-modal distribution is sometimes found and has been attributed to different formation mechanisms from the two different sources:

- 1) tarry and heavy residues;
- 2) methane, ethane and volatile components.

The alternative postulations for the mechanism of soot formation are illustrated in Foster's diagram (Figure 7). The alternatives can be titled:

- a) the C_2 condensation theory;
- b) the acetylene theory;
- c) the polymerisation - dehydrogenation theory.

It seems probable, as is often the case, that the alternative mechanisms are not mutually exclusive. It is certainly the author's opinion that, in flames from liquid hydrocarbons, polymerisation during heating is the most likely first step.

Once formed, how does soot burn out? The facetious answer "slowly" has a great deal of merit when the rates of soot burnout are compared to the chemical reactions that have already been discussed.

However, it is important to remember that the equilibrium calculations discussed earlier in this presentation showed that free carbon (soot) should not exist in flames when the excess-oxygen content is above 0.25%. To get soot we must have had a non-homogeneous system with some fuel-rich regions. The target in soot control must therefore be to minimize the volume and lifetime of these fuel-rich regions.

This leads directly into a consideration of some of the physical processes involved in combustion. In the case of homogeneous combustion it might be argued that chemistry plays a dominant role in combustion; in the case of heterogeneous combustion, where liquid droplets (oil) or solid particles (coal) are involved, the emphasis must always be on the physical processes which bring the fuel and oxidant together.

PHYSICAL PROCESSES

Heterogeneous Combustion

Here we have the condition where a droplet or particle is immersed in air and volatile fuel components are diffusing away from the particle

surface. Reaction (combustion) occurs at some distance away from the particle. If the fuel is not volatile, e.g., anthracite or a petroleum coke, then the combustion reaction can occur at the surface.

Under these circumstances the rate of combustion depends only on physical parameters such as rates of evaporation and diffusion and on the rate of heat transfer to the particle. The chemical reactions, of course, still must occur but they are extremely fast and the combustion rate is controlled by the slower physical process.

For a single droplet or particle in still air the rate of combustion can generally be expressed by a simple equation:

$$\frac{dm}{dt} = Kd$$

For a droplet burning from an initial diameter d_o to completion the burning time is given by

$$t_B = K d_o^2$$

A comparison of the burning constant (K) for a series of common liquid and solid fuels is shown in Figure 8.

Atomization of Liquid Fuels

An oil spray contains a distribution of particle sizes. To compare sprays the "Sauter Mean Diameter" (SMD) is used. The SMD of a spray is the monosize spray with the same surface to volume ratio as the actual size distribution of the spray.

Pressure Jet Atomization

In this, the commonest form of oil atomization, the oil is forced through a small orifice at an elevated pressure. The oil may, in some

instances, be given a rotational velocity immediately prior to its entry into the orifice. The oil leaves the atomizer in a conical sheet, friction between the oil sheet and the atmosphere breaking the sheet up into small droplets.

For this kind of burner the Sauter Mean Diameter is generally in the range 50 - 100 microns and has been found to be responsive to both orifice diameter and pressure:

$$\text{SMD} \propto \frac{d^{.55}}{p^{.39}}$$

Twin Fluid Atomizers

In these systems the oil spray is generated by impinging a high pressure steam or air flow onto the oil supply thus breaking the liquid into droplets. The advantage is that a lower oil pressure can be used than in direct pressure jet atomizers. General equations to describe droplet size are not available but generally this type of system gives smaller droplets than pressure atomization alone, the Sauter Mean Diameter being in the range 40 - 80 microns.

Rotary Cup Atomizers

In these systems the initial oil sheet is generated at the edge of a rotating disc or cup where oil is centrifugally thrown from the rim of the cup. Again friction breaks the sheet up to droplets. The droplet size is close to uniform and the SMD is given by:

$$\text{SMD} = \frac{360,000}{(\text{rpm})} \cdot \frac{n}{D\rho}$$

n surface tension of fuel.

D diameter of cup.

ρ density of fuel.

THE ROLE OF THE COMBUSTION AIR FLOW

Axial Airflows

If we consider a simple pressure jet-oil atomizer and supply the air in different ways then we can significantly alter the characteristics of the flame.

When the air is introduced with a low momentum then the flame shape and temperatures are determined almost entirely by the oil spray angle (Figures 10a and 10b). When we go to a higher air momentum then the oil spray angle becomes less dominant and the flame narrows and becomes less sooty (Figure 10c).

If a further modification is introduced, a stabilizer disc, the flame can anchor back to the disc and both air momentum and oil spray angle have little or no effect on the characteristics of the flame (Figure 10c).

Swirling Airflows

Swirl or rotation in the airflow is introduced by one of three general mechanisms:

- 1) tangential entry of air;
- 2) guide vanes;
- 3) rotating components in the burner.

In practice the third alternative is of academic interest only.

The highly desirable feature inherent in the use of a swirling air flow is the central core recirculation which is generated downstream of the air injection point; this is illustrated in Figure 11. This constitutes a well mixed core of combustion products which acts as a source of heat and active species in the centre of the fuel jet and produces a stable flame.

In contrast to bluff bodies (stabilizer discs) there is no solid surface that is exposed to high temperatures or carbon deposition. The effect of increasing the degree of rotation is to increase the length of the recirculation core without increasing its width as shown in Figure 12.

The effect of this swirl on the burnout of the carbon in a pulverized coal flame is shown in Figure 13. It can be seen that as the swirl number increases from 0.25 to 2.25 so the degree of burnout at any given downstream location improves; at the highest swirl number, 3.9, the burnout had marginally deteriorated. It appears therefore that an optimum swirl existed for this system.

The effect of swirl on the soot formation in a residual-fuel-oil-fired system is shown in Figure 14.

In this case again it appears that an optimum swirl condition exists at which the solids burden expressed as a per cent of the input fuel is at a minimum. It was also observed that, at this condition, the effect of oil spray angle on the solids emission was negligible.

SYSTEM EFFICIENCIES

Discussion of system efficiencies is of current national interest. If we consider a simple heat transfer system, such as an oil-fired residential heating system, a simple knowledge of the elemental composition of the fuel can give a valuable indication of what efficiencies are possible and how the efficiency is affected by combustion parameters.

Figure 15 shows the mechanics of the calculation of efficiency. It should be noted that the flue losses from a combustion are composed of two

parts, the loss due to the hydrogen in the fuel and the losses due to the excess-air used in combustion.

Figure 16 shows the "hydrogen" loss. This is only slightly affected by the flue-gas temperatures.

Figure 17 shows the "dry-flue-gas losses" or the losses due to nitrogen, excess oxygen and excess nitrogen. These losses are significantly increased by increased excess-air level, i.e., decreased CO_2 concentration, and increased flue-gas temperature.

Combustion Additives and System Efficiency

Many additives are on the market which claim to improve system efficiency. There are only two mechanisms by which this can be achieved in any given system. The first is by allowing the system to operate at a lower excess-air level. It is worth noting that a survey of combustion additives carried out in the United States covering over 100 additives found only three to be effective in allowing operation at a reduced excess-air level. The results for one of the effective additives are presented as a typical burner performance curve in Figure 18.

Results from another source are presented in Figure 19.

It is worth commenting that the authors of both of these fuel additive studies concluded that burner optimization was a more attractive route to improved efficiency and reduced emissions than was the use of a fuel additive.

The second method whereby an additive could improve system efficiency is by reducing the ignition temperature of deposited soot to a level at which it can ignite, and burn and thus remove the insulating effect of the deposits. A series of tests carried out at CCRL with a soot remover of

this type showed the results presented in Figure 20. The beneficial effects of this particular soot remover were not only short-lived but its active ingredient corroded the metal heat exchange surfaces.

RETROSPECT

The chemical reactions involved in the overall combustion process can, in the case of sulphur trioxide and nitric oxide emissions, lead to a first-order understanding of the parameters affecting the formation of these pollutants. In the case of incomplete combustion and/or soot emissions from heterogeneous combustion systems the physical processes are the dominant factors. Control of these physical processes can frequently be achieved by control of the swirl (rotation) of the input air.

Investigations of the use of fuel oil additives as combustion improvers have not been conclusive.

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Heat of Combustion in Kilocalories per Mole (at 25°C)

H_2	Hydrogen	68.4
CH_4	Methane	212.8
C_2H_6	Ethane	372.8
C_3H_8	Propane	530.6
CH_3OH	Methyl Alcohol	173.6

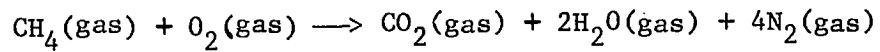
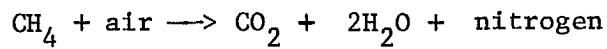
These are the heats of reaction that are generated when these compounds react with oxygen to produce carbon dioxide and water. They depend only on the initial and final compositions and temperatures and do not have anything to do with the mechanism by which the reactions occur.

FIGURE 1 Heats of Combustion of some simple Hydrocarbons

Gross Calorific Values of Fossil Fuels

<u>Gases:</u>				
	H ₂	343	Btu/ft ³	
	CH ₄	1067	"	
	C ₂ H ₆	1856	"	
	C ₃ H ₈	2660	"	
<u>Liquids</u>				
	CH ₃ OH	9,550 Btu/lb	-	76,000 Btu/gallon
	C ₂ H ₅ OH	12,780	"	101,000 "
n Octane	C ₈ H ₁₈	20,600	"	
Ethylbenzene	C ₈ H ₁₀	18,500	"	
	No. 1 Fuel Oil	20,000 Btu/lb		156,000 Btu/gallon
	No. 2 Fuel Oil	19,500	"	164,000 "
	No. 6 Fuel Oil	18,500	"	165,000 "
<u>Solids</u>				
	Anthracite	15,500		Btu/lb
	Bituminous Coal	15,000 - 16,000		"
	Lignites	10,000 - 14,000		"

FIGURE 2 Gross Calorific Values of Fossil Fuels



Heat of Combustion = 191.76 kilocalories

If T_2 is the maximum flame temperature achieved, then the heat of combustion goes into raising the temperature of the gases from the original temperature T_0

$$\begin{aligned} \text{Heat of Combustion} &= [T_2 - T_0] C_p (\text{CO}_2) \\ &+ 2[T_2 - T_0] C_p (\text{H}_2\text{O}) \\ &+ 4[T_2 - T_0] C_p (\text{N}_2) \end{aligned}$$

Knowing the specific heat values:- $C_p (\text{CO}_2)$
 $C_p (\text{N}_2\text{O})$
and $C_p (\text{N}_2)$

$$\text{We get } \underline{\underline{T_2 = 1980^\circ \text{C}}}$$

FIGURE 3 The Calculation of Adiabatic Flame Temperature

Hydrogen	—————>	2100°K
Methane	—————>	1980°K
Acetylene	—————>	2250°K
NO.2 Oil	—————>	2260°K

FIGURE 4 The Adiabatic Flame Temperatures of selected Hydrocarbons

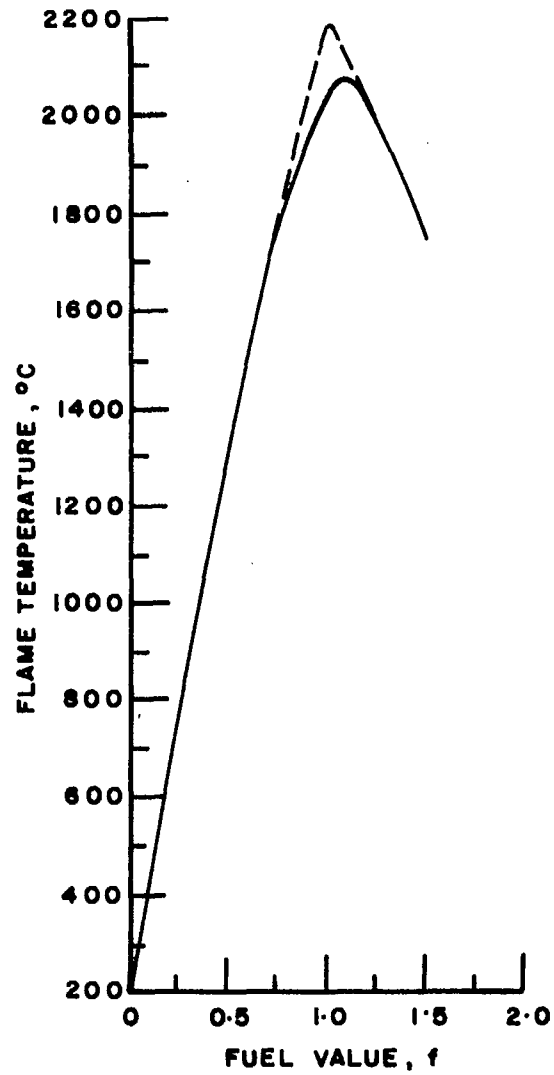


FIGURE 5 The effect of fuel value on adiabatic flame temperature.
($f=1$ represents stoichiometric combustion.)

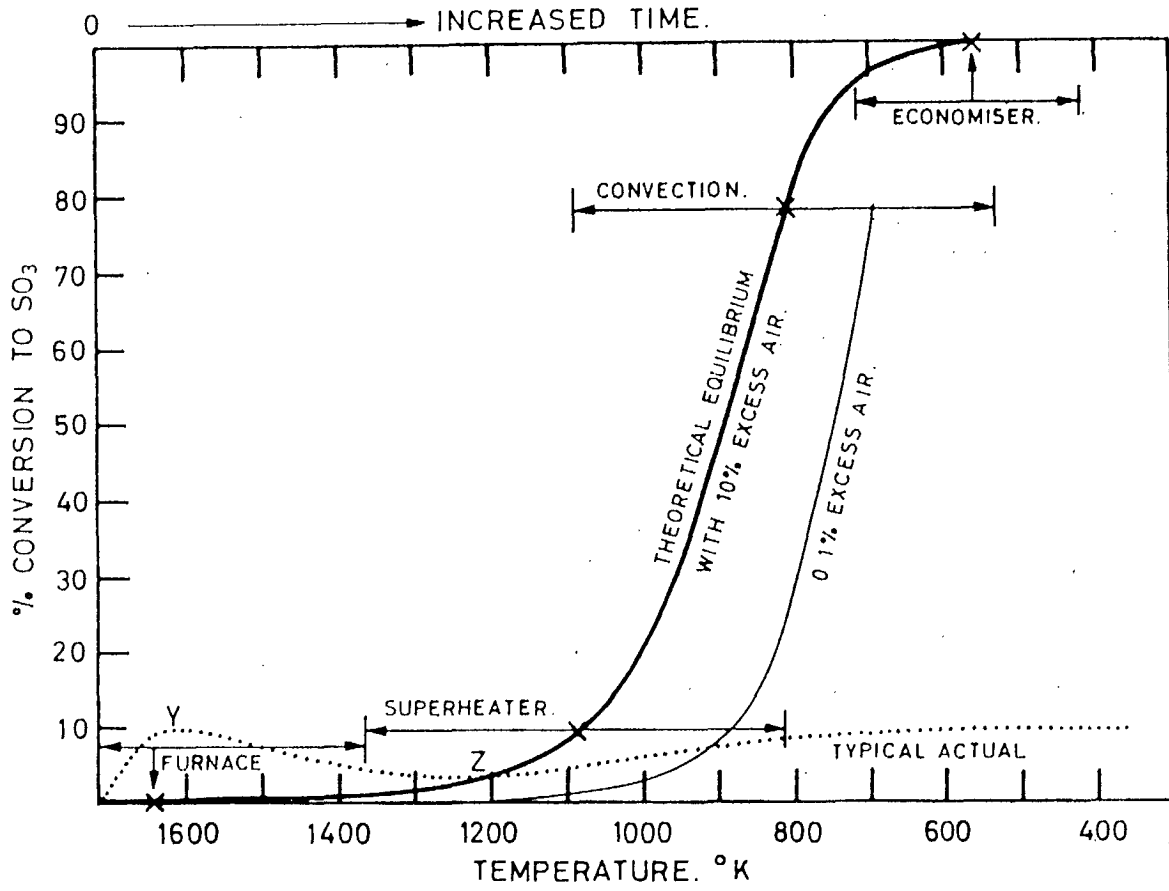


FIGURE 6 Factors affecting SO₃ in Flames (after Hedley)

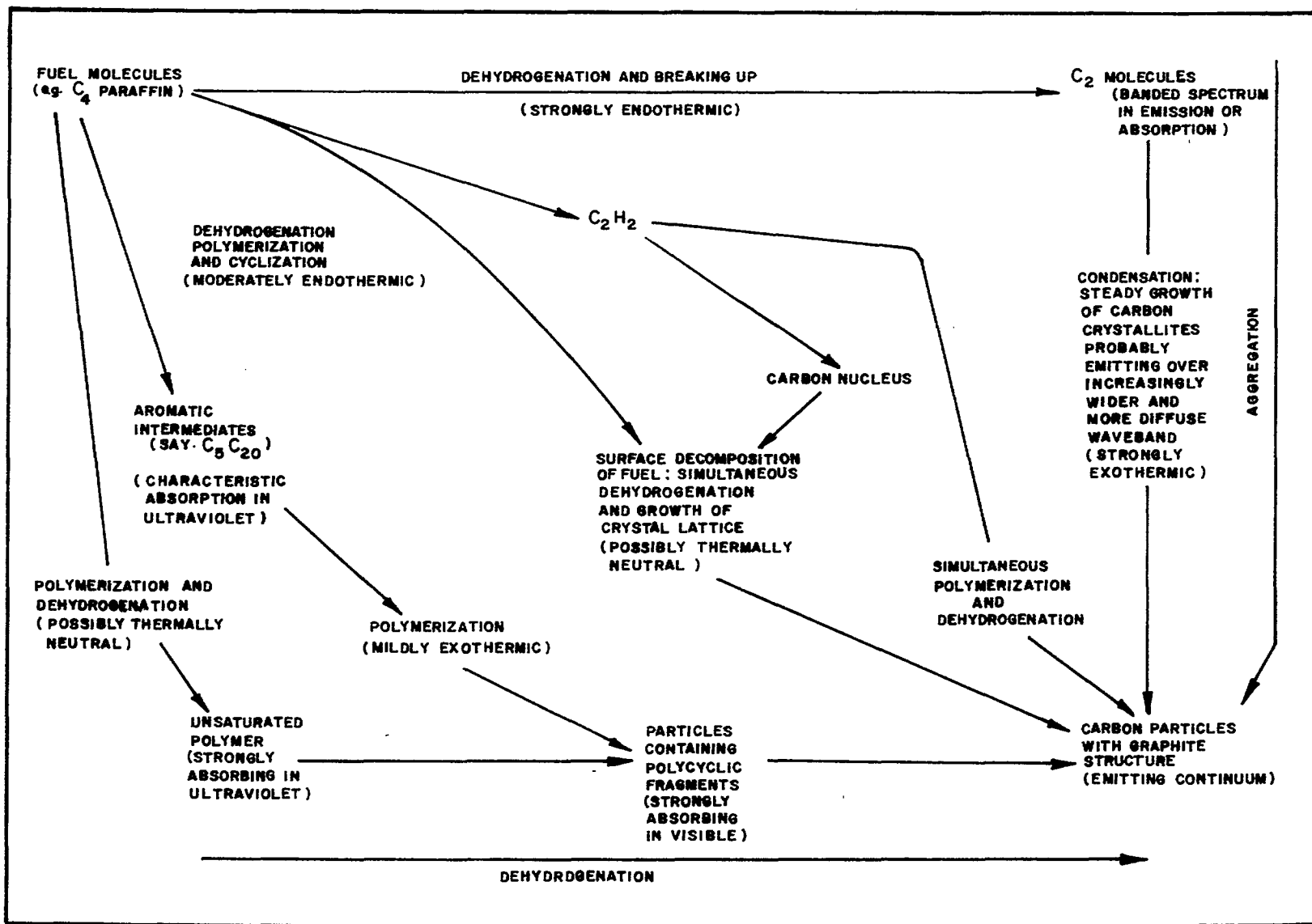


FIGURE 7 Possible Sequences of Soot Formation (after Foster)

For a single droplet or particle in still air the rate of combustion:

$$\frac{dm}{dt} = Kd$$

For a droplet burning from an initial diameter d_0 to $d = 0$, the

burning time is given by:

$$\underline{t_B = K \cdot d_0^2}$$

K is the burning constant

	K
Volatiles in coal	100
Volatile liquid fuels (gasoline, kerosine)	100 - 150
Non-volatile liquid fuels (No.6 oil)	200 - 300
Coke residues from No. 6 oil	350 - 400
Coal residues	1000
Carbon (soot)	2000

FIGURE 8 Burning Constants for Typical Hydrocarbon Fuels

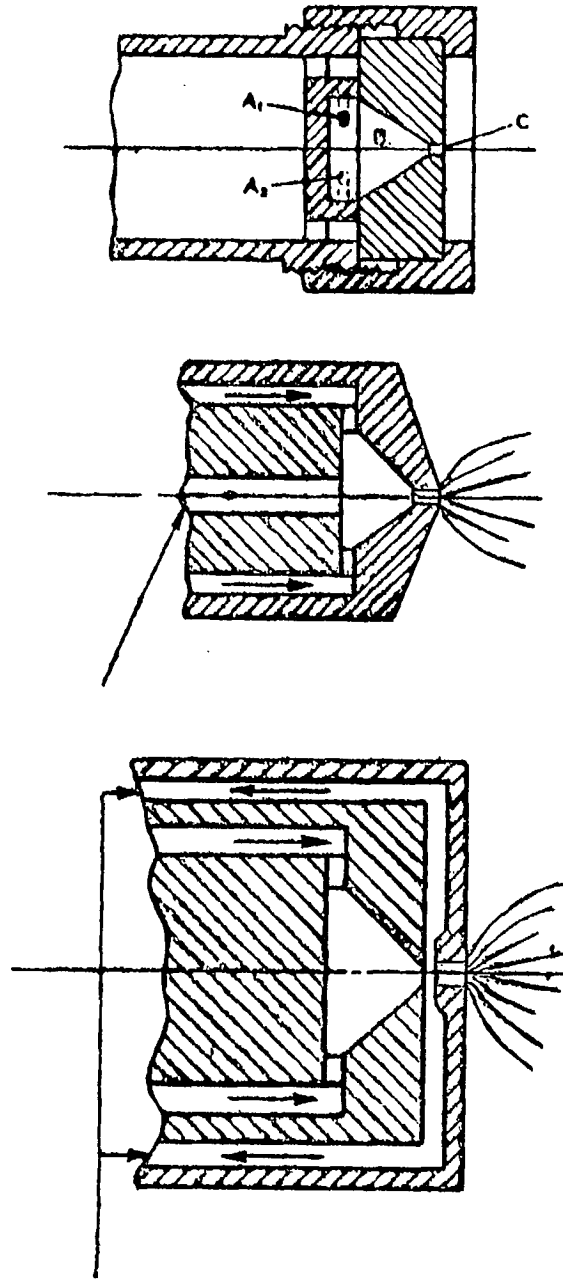


FIGURE 9 Typical Configurations of Pressure Jet Atomizers

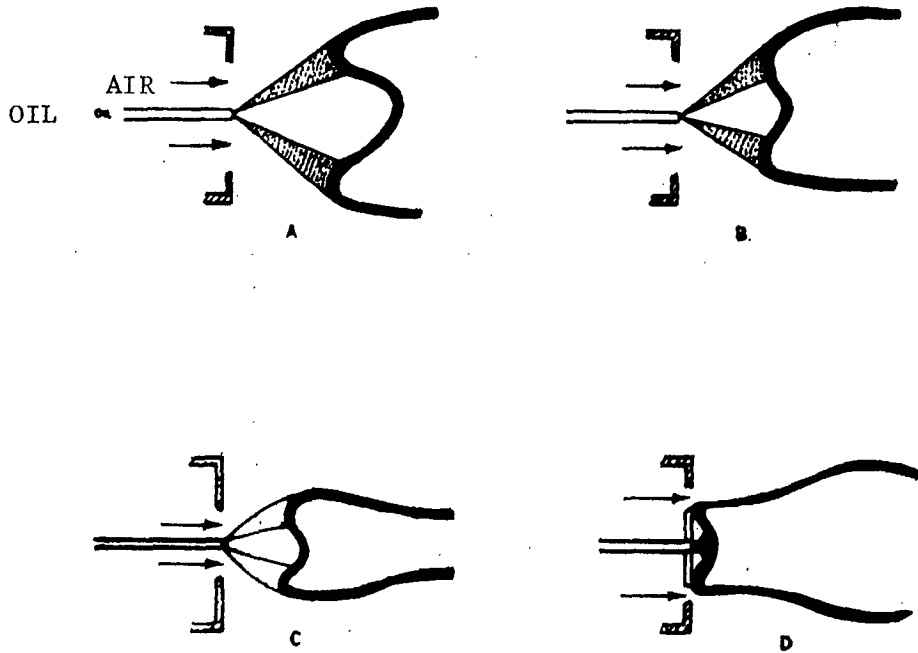


FIGURE 10 The Effect of Axial-Air Momentum on Flame Shape

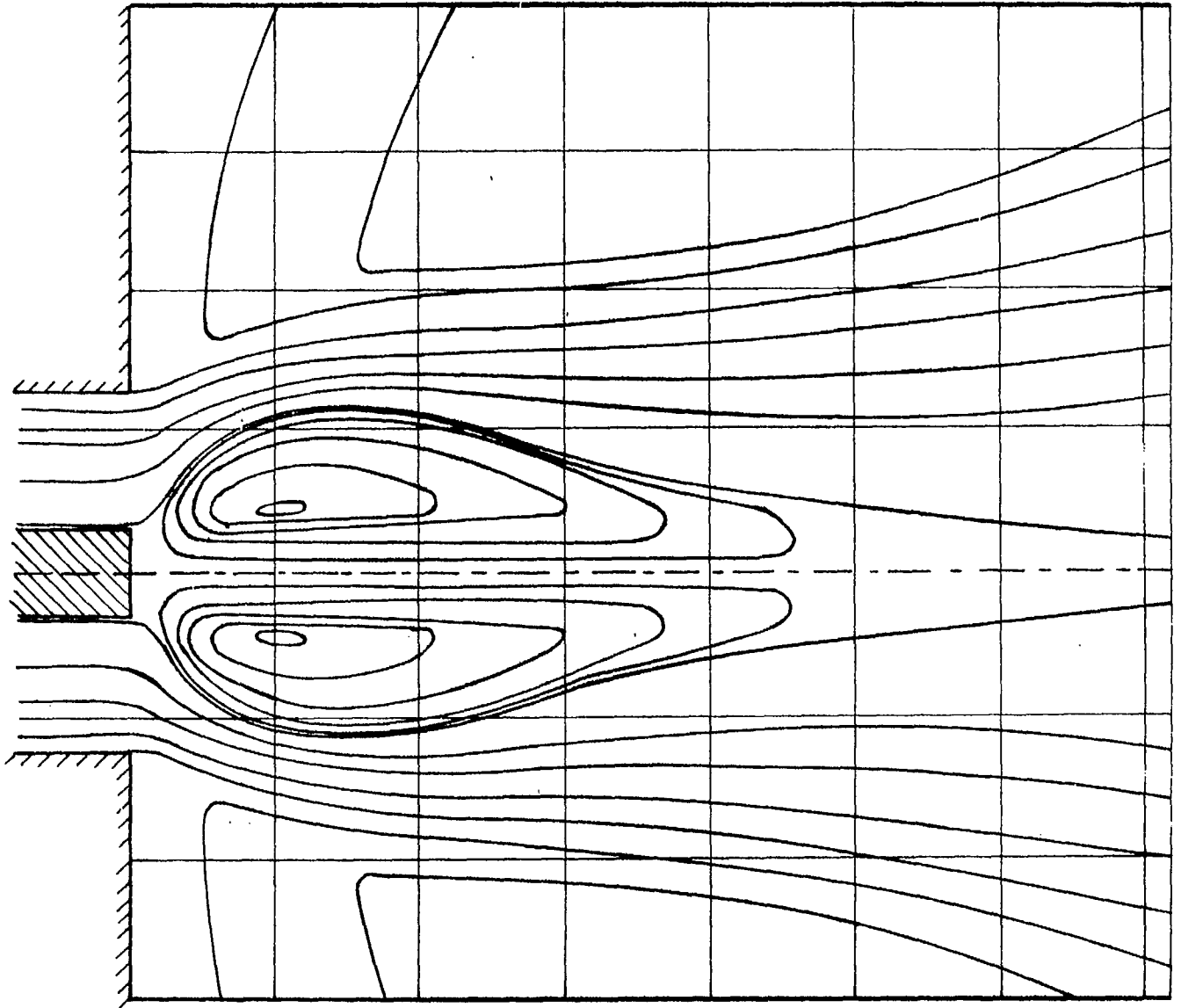


FIGURE 11 Flow Patterns in a High Swirl Flame
Typical Streamline Pattern for a Burner having
a Swirl no. $S = 1.60$. (Ref. 7,10)

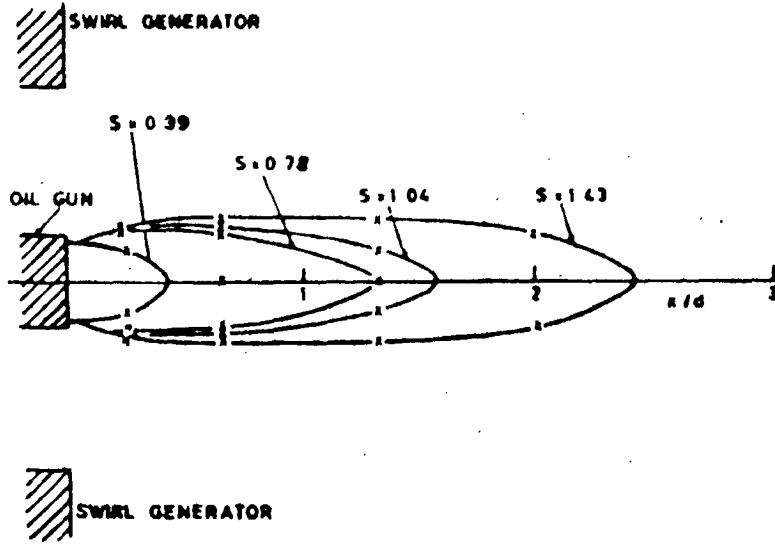


FIGURE 12 The Effect of Increasing Swirl on the Size of the Recirculation Core

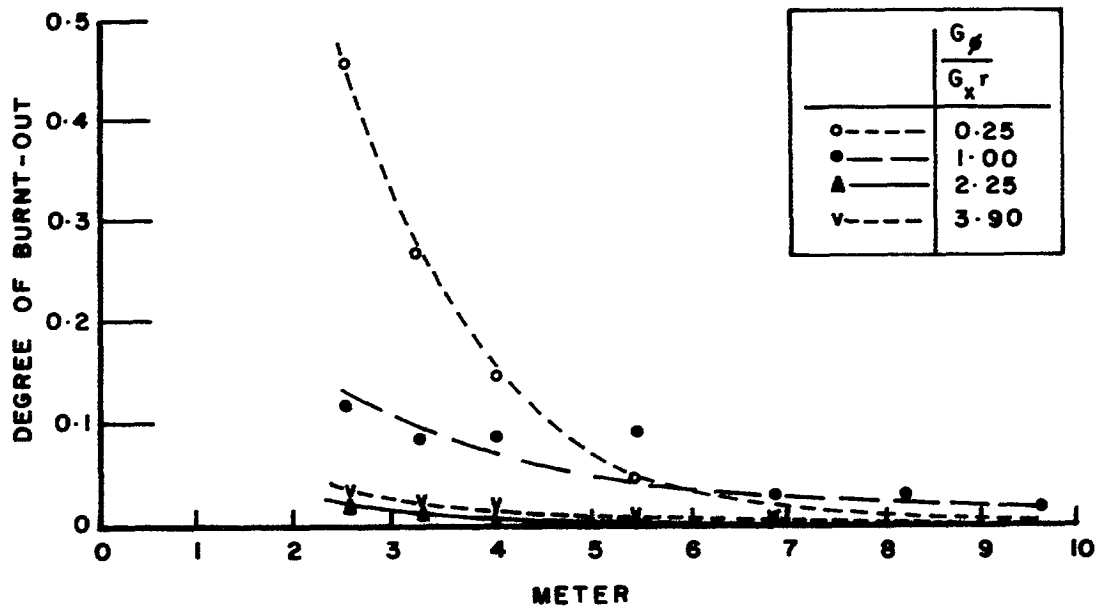


FIGURE 13 The Effect of Swirl on the Burn-out of Coal in a Pulverized Coal Flame

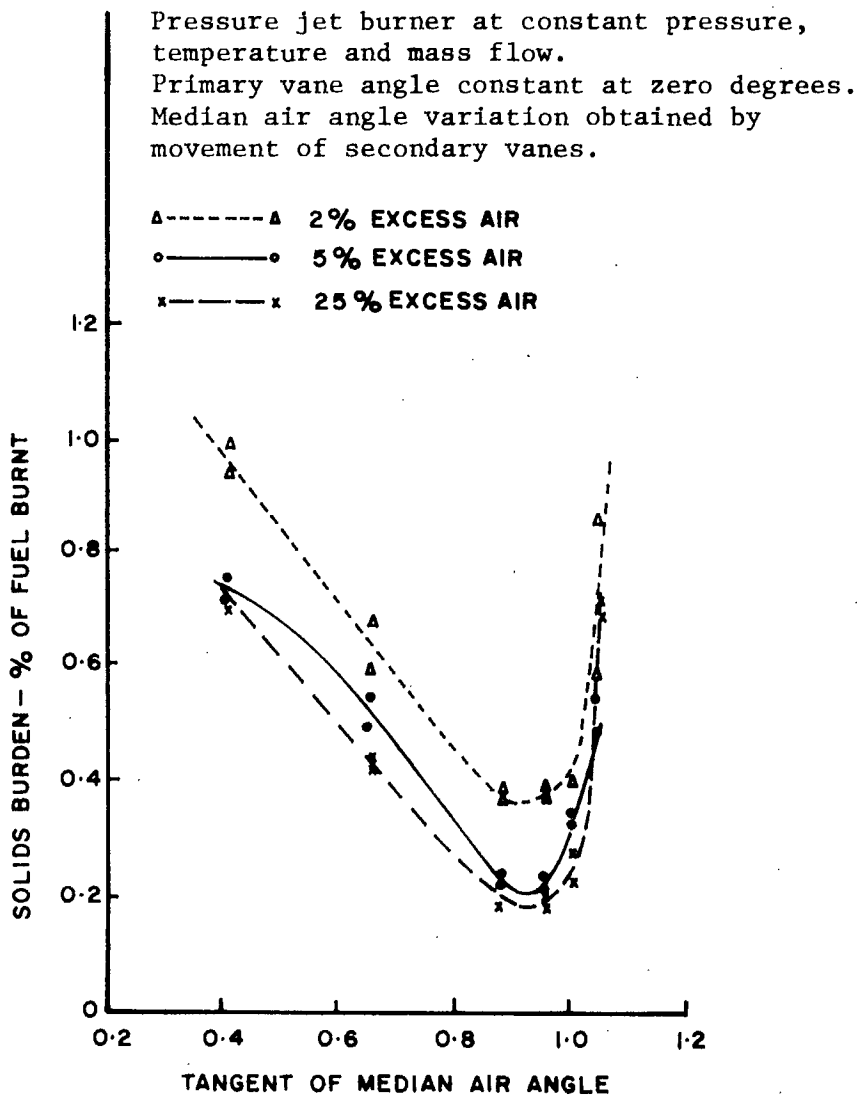


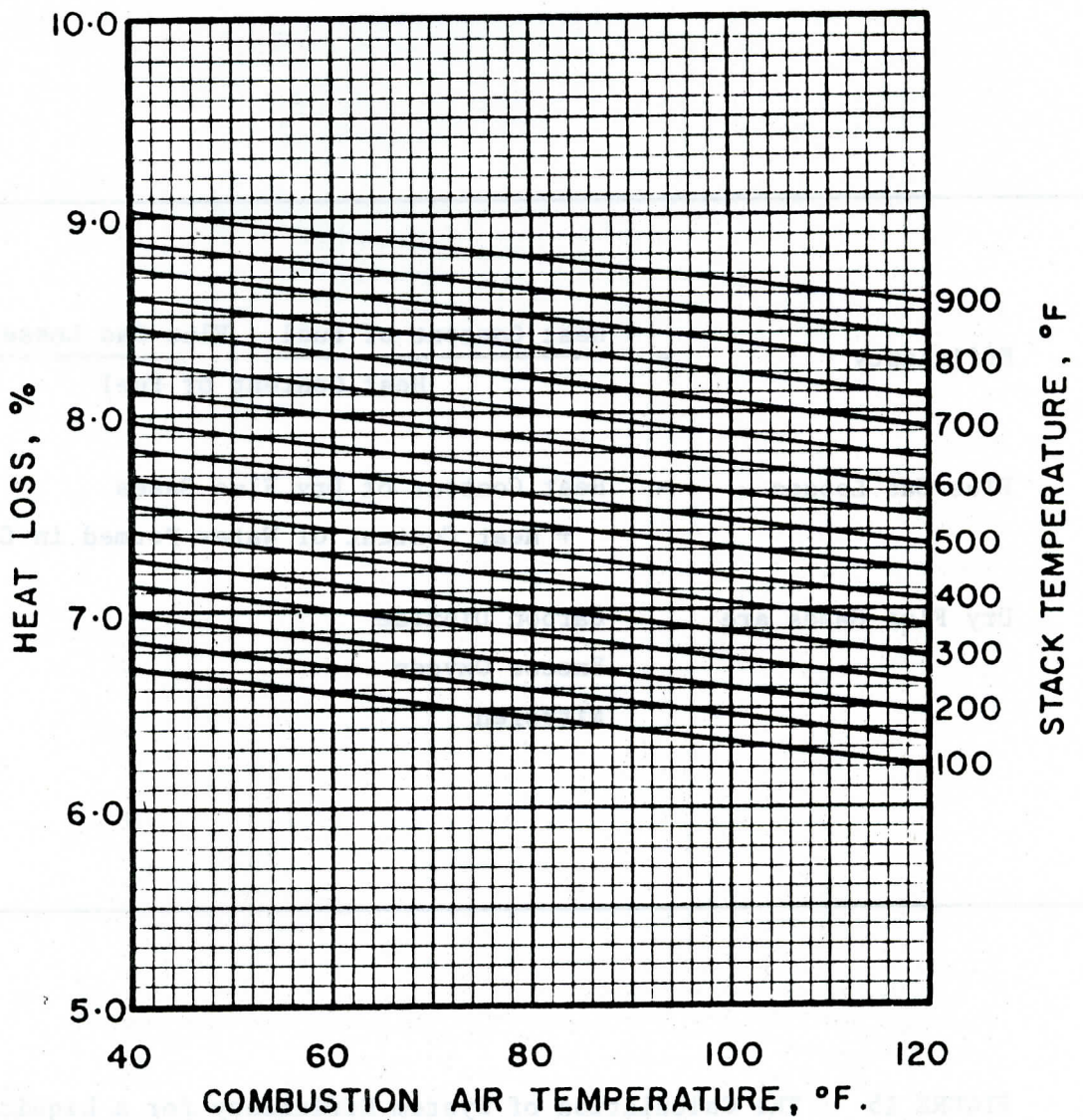
FIGURE 14 The Effect of Swirl on Soot Formation in a Residual-Fuel-Oil-Fired Boiler

$$\text{Efficiency} = \frac{\text{Heat Content of Fuel} - \text{Flue Gas Losses}}{\text{Heat Content of Fuel}} \times 100$$

$$\text{Flue Gas Losses} = \text{Heat Content of Dry Flue Gases} \\ + \text{Heat Content of Water Formed in Combustion}$$

Dry Flue Gases are Carbon Dioxide
 Excess Oxygen
 Nitrogen

FIGURE 15 The Calculation of System Efficiency for a Liquid Fuel



DOMESTIC FUEL OIL
(No. 2)

FIGURE 16 Losses Due to Hydrogen in the Fuel

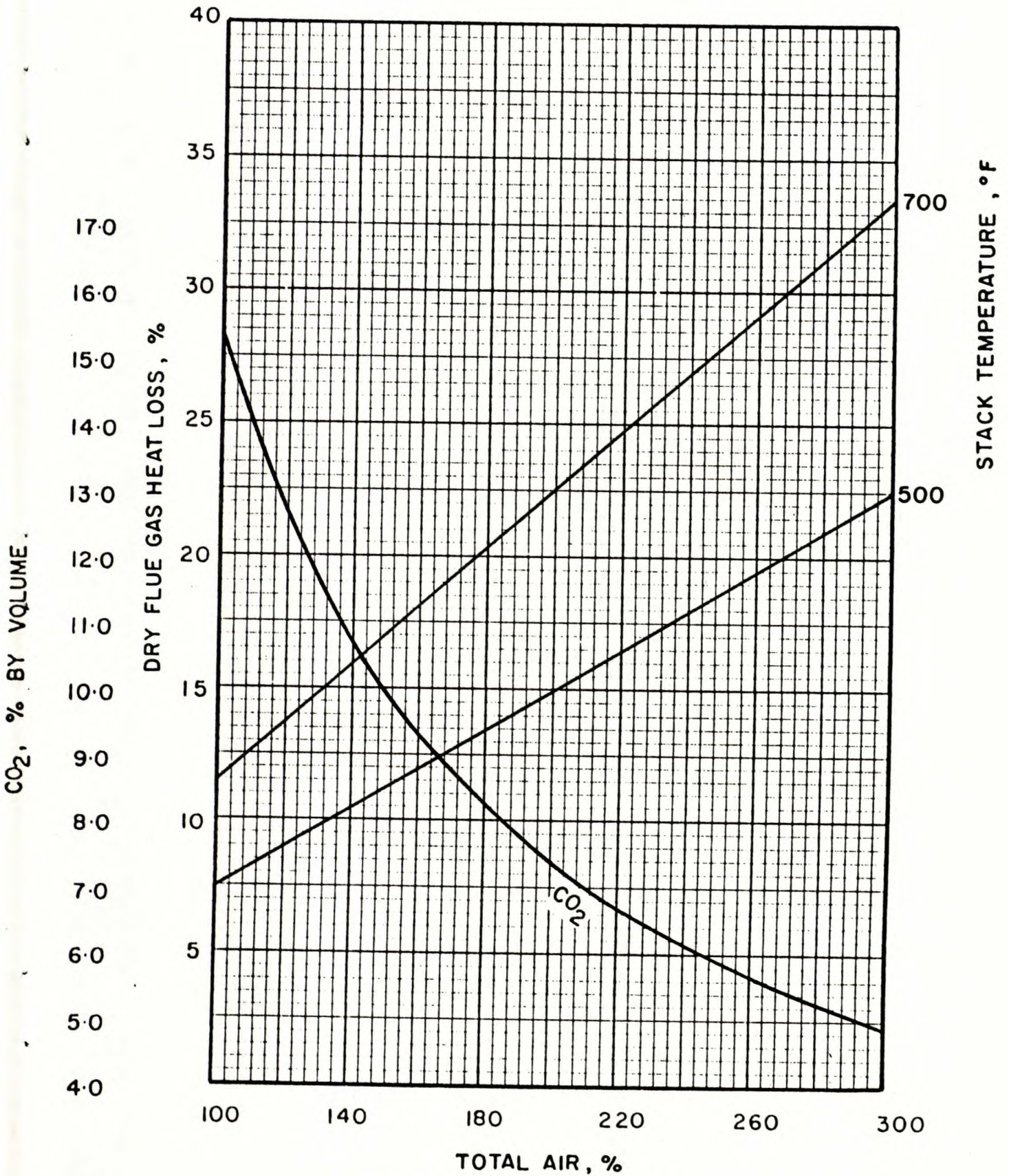


FIGURE 17 Dry Flue-Gas Losses

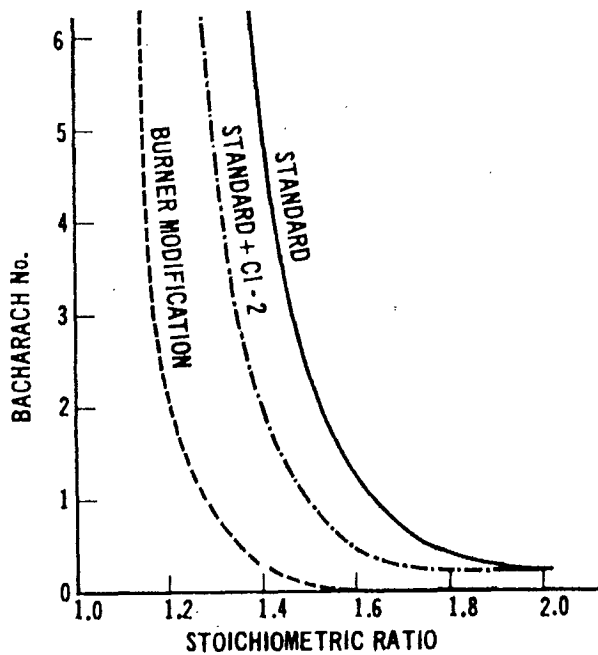
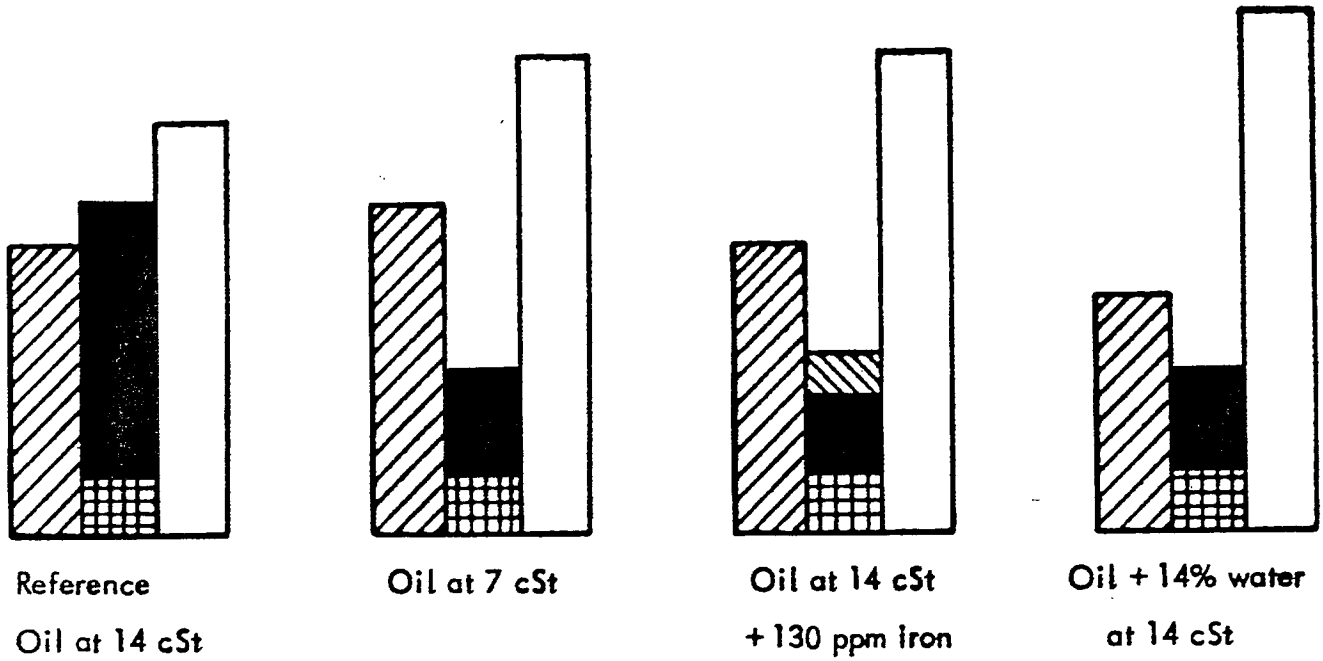







FIGURE 18 The Effect of a Fuel Additive on Burner Performance

Concentration relative
to norm.

1.0 -
0.5 -
0.0 -



-  Nitric oxide
-  Oil ash
-  Carbon
-  Iron oxide
-  Sulphuric acid

} Particulates

Norm concentration 500 vpm
 Norm concentration $2 \times 0.11 \text{ g.Nm}^{-3}$
 Norm concentration 20 vpm

FIGURE 19 A Comparison of Methods of Reducing Particulate and Nitric Oxide Emissions from a Residual Fuel-oil Flame

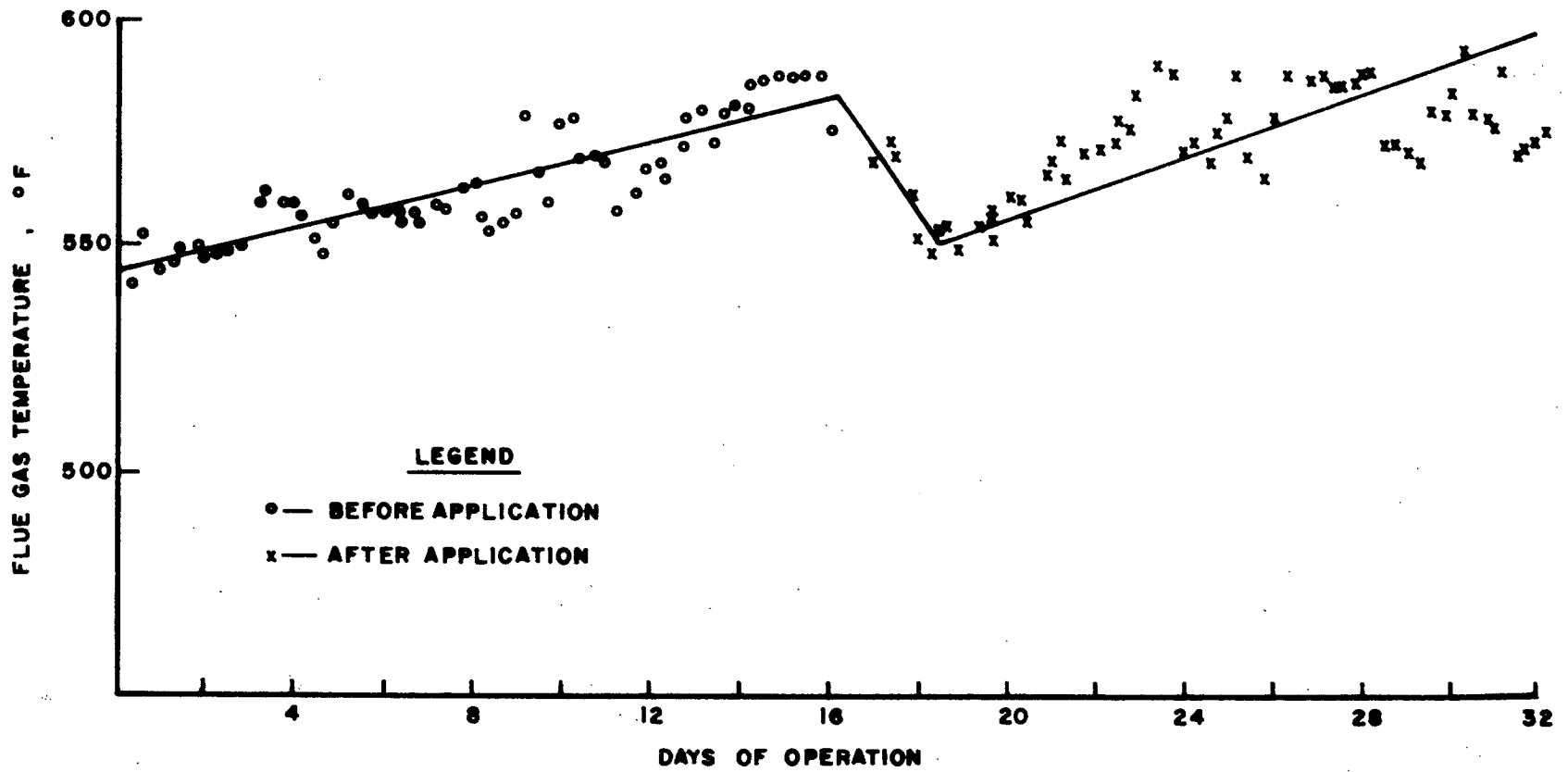


FIGURE 20 The Effect of a Commercial Soot Remover on the Performance of a Warm-Air Furnace

APPENDIX

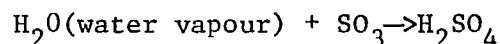
LOW TEMPERATURE CORROSION

IN COMBUSTION SYSTEMS

The text of this Appendix appeared in "A Combustion Handbook for Canadian Fuels, Vol I - Oil" by F.D. Friedrich. It is reproduced here by kind permission of the author.

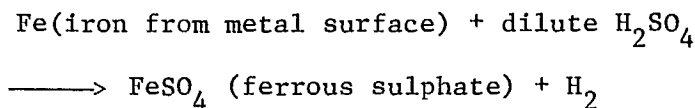
The Mechanism of Low-Temperature Corrosion

Although SO_3 is a gas, it combines readily with water vapour to form sulphuric acid vapour.

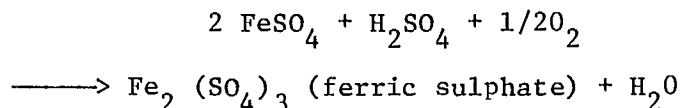


Since the flue gas from combustion of oil contains substantial quantities of water vapour, the above reaction can take place quite readily and, if the acid vapour is cooled by low-temperature-metal surfaces, it may condense on the surfaces as liquid sulphuric acid and be diluted by additional condensation of moisture from the flue-gas. In general, dilute sulphuric acid is more corrosive than highly concentrated sulphuric acid.

Corrosion may then proceed according to the following equation:



In the presence of additional sulphuric acid and oxygen, the ferrous sulphate may be converted to ferric sulphate as follows:



Once formed, ferric sulphate $\text{Fe}_2 (\text{SO}_4)_3$ can accelerate corrosion by combining with moisture to produce additional H_2SO_4 and by acting as a catalyst to promote oxidation from SO_2 to SO_3 .

The amount of water vapour which can be held in a gas, such as air or flue-gas, increases with increasing temperature. For any given concentration of water vapour in a gas, the water dewpoint is defined as that temperature at which the gas is saturated. If the gas is cooled below this temperature, some of the water vapour must condense. For combustion gases from oil, the water dewpoint is usually about 110°F . However, if small quantities of sulphuric acid vapour are present, condensation of sulphuric acid will occur at a temperature well above the water dewpoint. For a given mixture of gas and sulphuric acid vapour, the highest temperature at which acid condenses is commonly called the acid dewpoint.

It should be kept in mind that metals are attacked by sulphuric acid only when it is in the liquid phase. As long as it remains in vapour form, no corrosion occurs. Thus the acid dewpoint, in denoting the maximum temperature at which acid will condense, signifies the maximum temperature at which low-temperature corrosion may occur. The acid dewpoint for an oil containing 2.5% sulphur may be about 270°F . Medium- and high-pressure steam boilers without economizers or air heaters usually have their gas-swept surfaces at temperatures well above the acid dewpoint and thus are safe from low-temperature corrosion. On the other hand, high-temperature-water generators, which frequently have return-water temperatures of 250°F or lower, and boilers equipped with economizers or air heaters, may have large heat-exchange surfaces at temperature below the acid dewpoint, and low-temperature corrosion becomes a serious problem.

Prevention of Low-Temperature Corrosion

There are several ways in which low-temperature corrosion can be reduced or prevented, and the main ones will be discussed briefly in the following paragraphs. Most of them offer practical solutions only under special circumstances, but the use of acid-neutralizing additives has broad application to oil-fired combustion systems.

The most obvious way of avoiding corrosion by sulphuric acid is to burn a fuel that contains little or no sulphur, such as No. 2 fuel oil or natural gas. In many cases, of course, this is uneconomical or infeasible.

It will be recalled that the acid dewpoint signifies the maximum temperature at which low-temperature corrosion may occur. Obviously, low-temperature corrosion can be avoided by maintaining all gas-swept metal surfaces at temperatures above the acid dewpoint. For residual oil containing about 2.7% sulphur, the acid dewpoint is not likely to exceed 275°F. In this case, the minimum requirements to provide freedom from low-temperature corrosion will be an operating pressure of 75 psig for steam boilers and a minimum return temperature of 275°F for high-temperature-water generators. This is assuming that there are no air heaters or economizers and that the sulphur content of the oil does not increase. A more reasonable safety margin is provided by an operating pressure of 100 psig or a minimum return temperature of 300°F. Preventing corrosion by maintaining high surface temperature is well-suited to small and medium-sized installations in the design stage, but is usually not feasible for existing installations and is uneconomical for large boilers which use auxiliary heat-recovery surface to achieve high efficiency.

A fact, often overlooked, is the ability of soot to trap SO_3 vapour by absorption. This potentially corrosive soot may then adhere to metal surfaces, and while corrosion will not occur as long as the surface is above the acid dewpoint, corrosion will occur when the generator is subsequently taken out of service and allowed to cool. To avoid this, burners should be carefully maintained to minimize soot formation, and generator surfaces should be thoroughly water-washed at the beginning of any extended shutdown period.

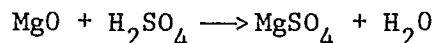
Research has clearly established that, at very low levels of excess air, little SO_3 is formed in the flame and corrosion is negligible. Large installations burning liquid or gaseous fuels under steady load conditions are making increasing use of this fact and avoid corrosion by operating with 0.5% to 1% oxygen in the flue-gas. However, to operate at low excess air without danger of explosions requires accurate, reliable burner and control systems, and it may take a few years to develop systems suitable for small boilers or boilers subjected to rapidly fluctuating loads.

Stainless steel has the greatest potential as a corrosion-resistant material in boilers and auxiliary heat-transfer equipment, but its case is limited by its high cost. Cast iron is substantially more resistant to corrosion than steel, but because of its strength properties its use is limited to low-stressed components such as economizers. Pyrex tubes are sometimes used in air heaters. Because they maintain their original smooth finish, they have a self-cleaning tendency which offsets the lower heat-transfer characteristics of glass. However, they are more prone to damage by furnace puffs than are metal tubes.

Additives to improve combustion or prevent corrosion have had a long and turbulent history. While very few additive manufacturers have been able to prove their claims by quantitative tests under controlled conditions, research over the past few years has clearly demonstrated that certain additive formulations are capable of eliminating low-temperature corrosion from low-ash fuels.

One additive, developed by the Canadian Combustion Research Laboratory for use with residual fuel-oil, consists of particles of magnesia (MgO) and alumina (Al₂O₃) ranging in size from 1 to 7 microns, suspended in a light-oil carrier, or more recently in a water carrier, with a surfactant and a dispersant. A commercial metering pump of moderate cost may be used to feed the additive directly into the oil line to the burners and, at the optimum dosage rate, which was experimentally established to be 1 lb additive to 1500 lb oil, the cost of treatment is modest.

The additive reacts with sulphuric acid according to the equation:



producing harmless magnesium sulphate (MgSO₄) and water. While only a portion of the sulphuric acid vapour is neutralized in the gas stream, the additive particles, because of their small size, tend to migrate to the walls of the gas passages and deposit in a thin layer which neutralizes the condensing the acid before it can attack the metal

The additive has also been formulated as a water-base paint which can periodically be brushed or sprayed on the tube-sheets and exposed surfaces of small, fire-tube boilers, thus providing a protective layer which neutralizes the sulphuric acid as it condenses.