Combustion Fundamentals An Engineering Approach to the Design of Industrial Incinerators

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INTRODUCTION

The design of an industrial incinerator must center around the energy converter of the system or the combustion process. Combustion is the principal function of an incinerator. Although other aspects such as the waste handling, gathering, ash disposal, and controls are important, it is the combustion process that is paramount.

There are two ways that the combustion process can be designed. Either of these two ways is a perfectly good and accepted way of achieving engineering design. The first and most common way is that of empiricism. Simply speaking, we have built one before and we have learned by correcting our mistakes how to achieve a good design. We are therefore safe to continue that design with minor experimenting here and there of new ideas for orderly evolution. Empiricism has always preceded the second way of design which is by the use of rational engineering fundamentals. Eventually, the rational fundamental engineering approach overtakes empiricism and this is what this paper is all about.

EQUILIBRIUM

The principal reactions of combustion are generally considered to be as follows:

$$C + O_2 = CO_2$$

$$2H_2 + O_2 = 2H_2O$$

Many engineers assume that these reactions proceed entirely to the right and expect their equipment to perform accordingly. Such is not the case. These reactions do not proceed entirely to the right; furthermore they are not the only reactions which take place. The combustion process is much more extensive and complex at the high temperatures encountered in combustion. The nitrogen in the air may react to some degree and various radicals containing carbon, hydrogen, oxygen, and nitrogen may be produced. If the waste feed contains other elements, such as chlorine, sulfur, or phosphorous, the combustion process and resulting products will be still more complex.

In the empirical approach, one must construct a furnace, operate it with a particular fuel, take test data, and determine what the actual products of combustion are. One must then burn that particular fuel under the same circumstances as the test furnace to be sure that the results of combustion will be the same. If one is to burn other fuels, construct a unit of different size, or operate a unit in a different fashion, then new test data must be taken to validate what the products of combustion will be. After sufficient experience has been obtained, one may be able to predict with some accuracy what is going to happen but proof will always depend upon validating the results.

In the rational approach, one predicts what the products of combustion will be under certain the-

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oretical conditions. This can be predicted in two ways. First, it can be predicted by the application of equilibrium constants that have of themselves been determined by experience. Second, equilibrium can be determined by assuming that a process is not rate limited; that is, the reaction can proceed as far as it will ever go and all the products of combustion are those which will result in the minimum level of free energy (Gibbs-Helmholtz Function). It is not the purpose of this paper to discuss either way of calculating equilibrium. This appears in the literature. The Research Committee for Industrial Wastes of the American Society of Mechanical Engineers has been granted a research grant from the Engineering Foundation and has prepared a monograph which covers this subject, in sufficient detail to make the actual calculation of equilibrium readily available to all incinerator designers.

Rather, it is the purpose of this paper to point out the advantages of designing for equilibrium and to cite a few case histories which can illustrate the problems.

The products of combustion from an equilibrium calculation will not necessarily be those that will occur in an actual combustion reaction. There are two reasons for this. First, nonequilibrium conditions may exist. Many physical things may be taking place in the flame to cause anything but equilibrium conditions. Some of the flame may be cooled by impingement on a cold surface, or the flame may be laminar with rich mixtures at one point and with lean air-fuel ratios at another. Frequently, in chemical processes and perhaps in incinerator processes, this can be a desirable situation. If a wanted byproduct can only be produced by operating under nonequilibrium conditions, then obviously it is desirable to operate this way. The second reason that equilibrium may not be obtained is that there may not be sufficient time. Each of the many reactions involved proceeds at a given rate which is dependent on many factors, temperature in particular. It is now known that most of the products of combustion are formed right in the combustion flame zone and that residence times in this zone is very short. While the products of combustion may change or can be altered after the flame zone, the reaction rates usually slow down to such an extent that catalysis or more residence time is required than is physically possible to provide.

In incinerators one is generally trying to convert a solid, liquid, or gaseous waste to harmless gases, in most cases carbon dioxide and water vapor. Unfortunately, some incineration processes produce carbon, carbon monoxide, nitrogen oxides, cyanides, and if chlorine is present in the waste feed, phosgene. In general, these noxious materials are produced by burning with improper air, permitting too high flame temperatures, or burning under nonequilibrium combustion. The effects of burning with improper air are well known; in this paper we are stressing equilibrium combustion.

In short, the results of nonequilibrium combustion are generally undesirable for incinerator operation. The results of equilibrium operation are very desirable. Why not then design to equilibrium rather than continue to use empirical designs that produce nonequilibrium?

Achieving this worthwhile goal will not be easy but the methods and ways are beginning to be utilized and efforts should be made to accelerate rational design methods.

THE COMBUSTION OF CELLULOSE

To illustrate the utility of equilibrium calculations, let us consider the burning of cellulose which is a frequently encountered waste material. One of the most important factors in determining equilibria is temperature. To determine temperature, of course, it is necessary to know the heat of combustion, or the heats of formation of the products and reactants and, in addition, the starting conditions. Actually, finding the heat of combustion of cellulose is not easy. The work of Jessup and Prosen [Ref. 1] is comparatively recent and is one of the few references on the heat of formation and heat of combustion of cellulose. Many heats of formation are given in the monograph published by the ASME Research Committee on Industrial Wastes.

Table I presents the equilibrium compositions of products from combustion of cellulose with varying amounts of air ranging from -100 to +500 percent excess air. These are the equilibrium compositions at the adiabatic flame temperature; i.e., it is assumed that there is no heat transferred to or from the combustion zone. Figure 1 shows the adiabatic flame temperature as a function of excess air. It is important to know this temperature because, as will be shown, the temperature has an effect on the formation of the products of combustion. The equilibrium concentrations of the individual combustion products are logarithmatically plotted in Figure 2 as a direct function of excess air. As might be expected, one finds large concentrations of the major constituents – carbon dioxide, carbon monoxide, water, nitrogen, and oxygen. It is the variation of

TABLE I — EQUILIBRIUM PRODUCTS OF CELLULOSE AND AIR AT ADIABATIC TEMPERATURES

EQUILIBRIUM PRODUCTS (% OR PPM) AT ADIABATIC CONDITIONS

Excess Air %	C*	CH_4	CO	CO_2	H_2	H_2O	NH_3	N_2	H	HO	NO	O	O_2	NO_2
-100	61.67%	11.71%	4.32%	23.26%	27.40%	33.30%	–	–	–	–	–	–	–	–
- 80	8.28%	1.44%	20.96%	12.31%	25.44%	7.49%	71 ppm	32.34%	–	–	–	–	–	–
- 60	–	–	21.44%	8.52%	14.43%	10.53%	4 ppm	45.08%	–	–	–	–	–	–
- 40	–	–	14.03%	10.42%	5.44%	14.93%	–	55.17%	70 ppm	12 ppm	–	–	–	–
- 20	–	–	6.65%	14.00%	1.54%	15.62%	–	62.10%	337 ppm	405 ppm	99 ppm	6 ppm	27 ppm	–
0	–	–	1.19%	16.53%	0.20%	14.44%	–	66.57%	237 ppm	2417 ppm	0.20%	191 ppm	0.59%	–
20	–	–	0.15%	15.09%	272 ppm	12.59%	–	68.65%	33 ppm	1724 ppm	0.31%	149 ppm	2.98%	2 ppm
40	–	–	229 ppm	13.30%	47 ppm	11.06%	–	70.03%	4 ppm	782 ppm	0.26%	51 ppm	5.25%	3 ppm
60	–	–	40 ppm	11.82%	10 ppm	9.83%	–	71.07%	–	334 ppm	0.19%	15 ppm	7.05%	3 ppm
80	–	–	7 ppm	10.63%	2 ppm	8.85%	–	71.88%	–	143 ppm	0.13%	4 ppm	8.49%	3 ppm
100	–	–	2 ppm	9.65%	–	8.04%	–	72.55%	–	62 ppm	882 ppm	1 ppm	9.66%	3 ppm
120	–	–	–	8.84%	–	7.36%	–	73.10%	–	28 ppm	597 ppm	–	10.64%	3 ppm
140	–	–	–	8.15%	–	6.79%	–	73.56%	–	13 ppm	407 ppm	–	11.45%	2 ppm
160	–	–	–	7.56%	–	6.30%	–	73.96%	–	6 ppm	278 ppm	–	12.15%	2 ppm
180	–	–	–	7.06%	–	5.88%	–	74.30%	–	3 ppm	192 ppm	–	12.75%	2 ppm
200	–	–	–	6.61%	–	5.51%	–	74.59%	–	1 ppm	133 ppm	–	13.27%	2 ppm
250	–	–	–	5.71%	–	4.76%	–	75.19%	–	–	55 ppm	–	14.33%	2 ppm
300	–	–	–	5.02%	–	4.19%	–	75.64%	–	–	24 ppm	–	15.15%	1 ppm
350	–	–	–	4.49%	–	3.75%	–	75.99%	–	–	11 ppm	–	15.77%	1 ppm
400	–	–	–	4.05%	–	3.38%	–	76.28%	–	–	5 ppm	–	16.29%	1 ppm
450	–	–	–	3.70%	–	3.08%	–	76.51%	–	–	2 ppm	–	16.71%	1 ppm
500	–	–	–	3.36%	–	2.80%	–	76.73%	–	–	1 ppm	–	17.10%	–

*NOTE: All % and ppm on volume basis except C which is mols solids per 100 mols of gases.

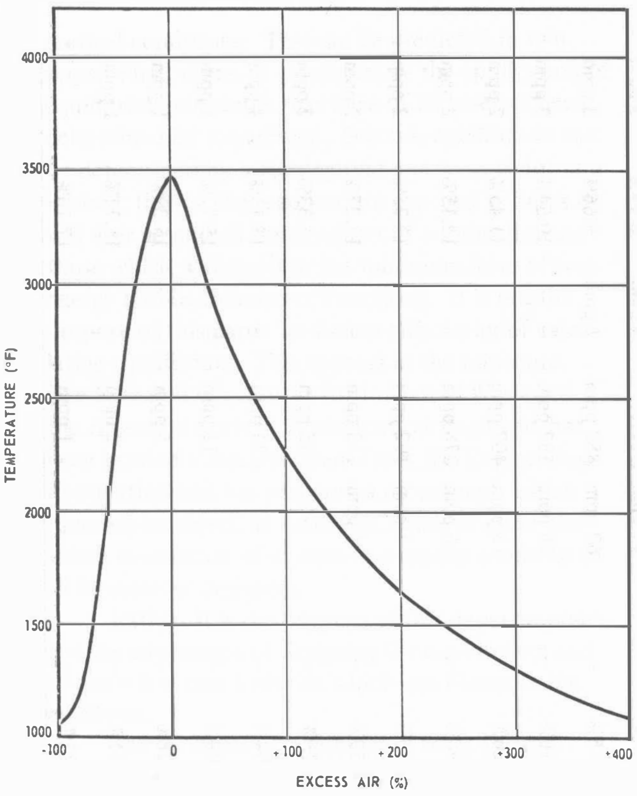

FIG. 1

the minor constituents that is more important here. Notice that the carbon, hydrogen, and oxygen of the cellulose and the oxygen and nitrogen from the atmosphere have yielded minor constituents including nitrous oxide. It is interesting to note that although carbon and nitrogen are present, there is no cyanide formed. Cyanide has been measured in the effluent from municipal incinerators; we surmise that it must result from nonequilibrium combustion.

As mentioned, temperature is a major factor in determining the composition of combustion products. While the temperature is set largely by the composition of the fuel and the air-to-fuel ratio, it may be varied to some degree by heat transfer to or from the combustion zone. This effect may be taken into account in equilibrium calculations.

Table II and Figure 3 show the equilibrium concentrations of products from the combustion of cellulose at a constant temperature of 2000°F. The same products have appeared in the adiabatic case (Figure 2). Note, however, that the concentration of nitrous oxide, which is of major concern with respect to air pollution, is much lower. Figure 4 shows the equilibrium concentration of NO as a function of excess air at different temperatures.

A similar calculation could be made at any other temperature. At 1500°F, there is still less

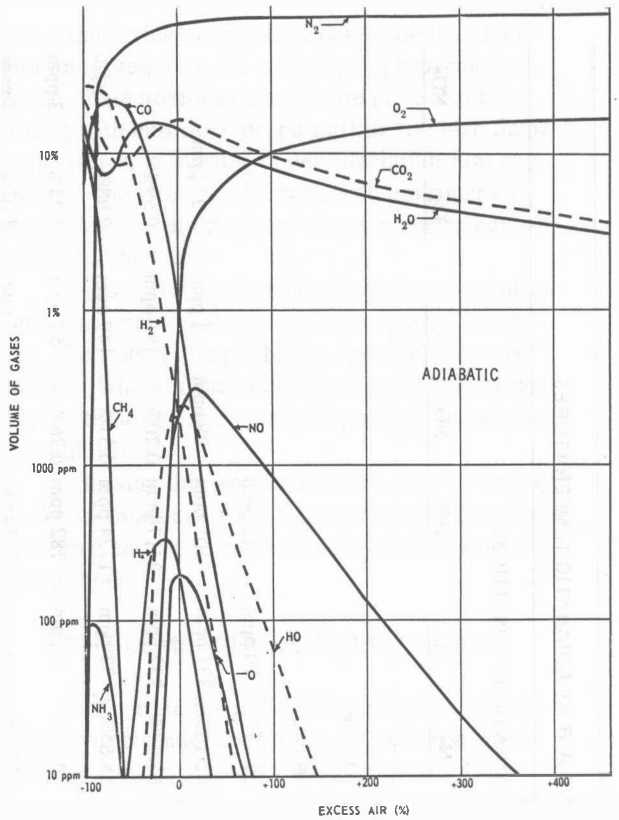

FIG. 2

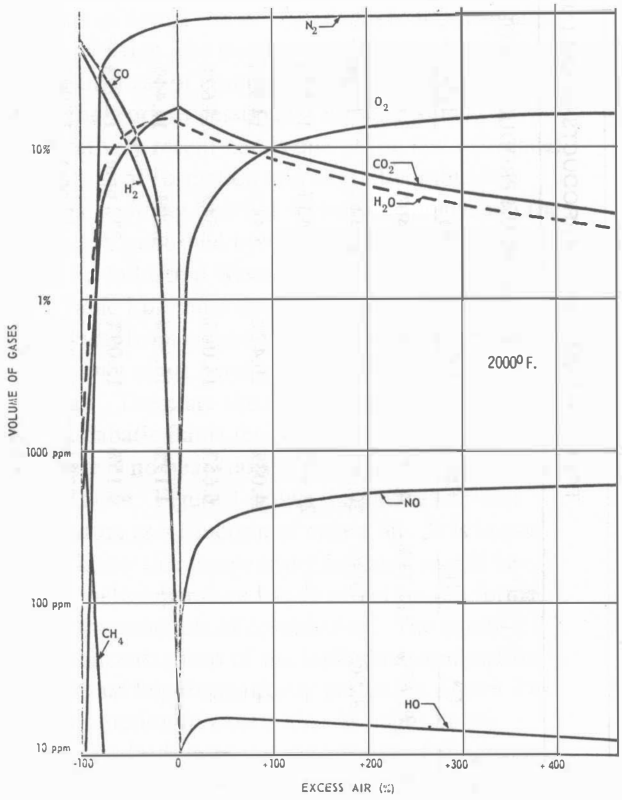

FIG. 3

TABLE II – EQUILIBRIUM PRODUCTS OF CELLULOSE AND AIR AT 2000°F

							EQUILIBRIUM PRODUCTS (% OR PPM) AT 2000°F							
Excess Air %	C*	CH_4	CO	CO_2	H_2	H_2O	H	NH_3	N_2	HO	NO	O_2	NO_2	HCN
-100	10.11%	0.13%	50.00%	623 ppm	49.80%	0.13%	–	–	–	–	–	–	–	–
- 80	–	3 ppm	35.10%	3.58%	26.73%	5.49%	2 ppm	7 ppm	29.09%	–	–	–	–	1 ppm
- 60	–	–	21.73%	8.23%	14.15%	10.81%	1 ppm	3 ppm	45.08%	–	–	–	–	–
- 40	–	–	12.51%	11.94%	6.97%	13.41%	1 ppm	1 ppm	55.17%	–	–	–	–	–
- 20	–	–	5.53%	15.12%	2.64%	14.57%	–	–	62.13%	–	–	–	–	–
0	–	–	4 ppm	17.87%	2 ppm	14.89%	–	–	67.19%	6 ppm	30 ppm	512 ppm	–	–
20	–	–	–	15.27%	–	12.72%	–	–	68.89%	16 ppm	233 ppm	3.09%	1 ppm	–
40	–	–	–	13.32%	–	11.10%	–	–	70.17%	17 ppm	310 ppm	5.37%	1 ppm	–
60	–	–	–	11.82%	–	9.85%	–	–	71.15%	17 ppm	360 ppm	7.14%	2 ppm	–
80	–	–	–	10.63%	–	8.86%	–	–	71.93%	17 ppm	396 ppm	8.53%	2 ppm	–
100	–	–	–	9.65%	–	8.04%	–	–	72.58%	17 ppm	424 ppm	9.67%	2 ppm	–
120	–	–	–	8.84%	–	7.36%	–	–	73.11%	16 ppm	446 ppm	10.64%	3 ppm	–
140	–	–	–	8.15%	–	6.79%	–	–	73.56%	16 ppm	464 ppm	11.45%	3 ppm	–
160	–	–	–	7.56%	–	6.30%	–	–	73.95%	16 ppm	479 ppm	12.14%	3 ppm	–
180	–	–	–	7.06%	–	5.88%	–	–	74.28%	15 ppm	492 ppm	12.73%	3 ppm	–
200	–	–	–	6.61%	–	5.51%	–	–	74.57%	15 ppm	503 ppm	13.26%	3 ppm	–
250	–	–	–	5.71%	–	4.76%	–	–	75.16%	14 ppm	525 ppm	14.31%	4 ppm	–
300	–	–	–	5.02%	–	4.19%	–	–	75.62%	13 ppm	541 ppm	15.12%	4 ppm	–
350	–	–	–	4.49%	–	3.74%	–	–	75.96%	13 ppm	553 ppm	15.74%	4 ppm	–
400	–	–	–	4.05%	–	3.38%	–	–	76.25%	12 ppm	563 ppm	16.26%	4 ppm	–
450	–	–	–	3.70%	–	3.08%	–	–	76.44%	12 ppm	571 ppm	16.68%	4 ppm	–
500	–	–	–	3.36%	–	2.80%	–	–	76.70%	11 ppm	579 ppm	17.07%	4 ppm	–

*NOTE: All % and ppm on volume basis except C which is mols solids per 100 mols of gases.

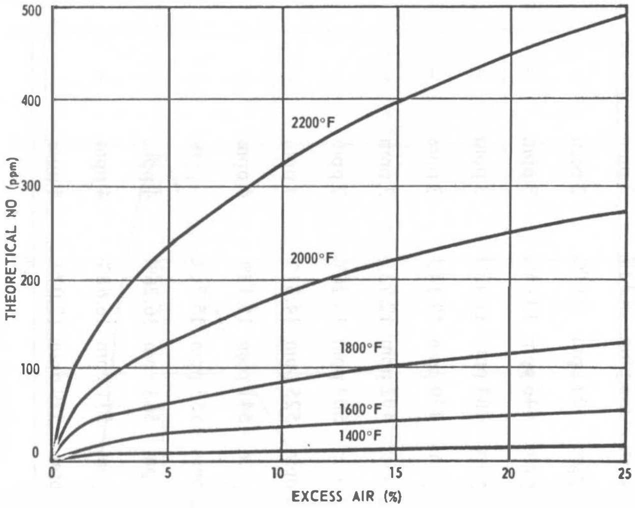

FIG. 4

nitrous oxide, and it would appear that this temperature is an even better operating temperature than 2000° F. This conclusion is not necessarily true, however, because the reaction rates decrease with temperature and are apt to be too slow to permit the attainment of equilibrium without catalysis.

This particular area is again one where considerable improvement in knowledge is needed, but it does not mean that the rational approach cannot be applied to this area. Almost any reaction at 1800° F or higher will be fast enough to reach equilibrium.

The combustion of cellulose, while relatively simple, is used here to illustrate that the products of combustion can be predicted and the conditions selected which will optimize the combustion situation.

NITROUS OXIDES

A paper by Manny and Skopp [2] has been published covering a survey of the literature on the formation of oxides of nitrogen. This is an outstanding paper and any comments of this author are not intended to denigrate the overall worthiness of this excellent treatise. The paper, however, concerned itself entirely with the empirical approach. Although Figure 4 has been previously published [3, 4, 5] showing the equilibrium production of nitrous oxides, it was overlooked by the authors of this excellent paper. We wish to present here an even further study of equilibrium and oxides of nitrogen production as shown in Figure 5. The range is carried into greater values of excess air and to higher temperatures. Of interest, is the necessity to operate equipment fuel-rich at the higher temperatures to abate NO. This is something that empiricism has taught; but no one,

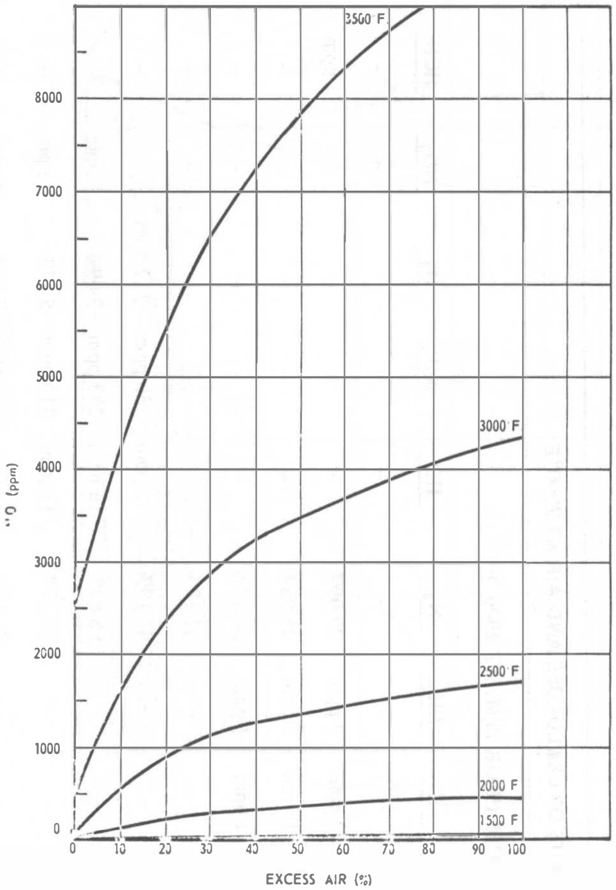

FIG. 5

to this author's knowledge, has calculated. If the authors had recognized the equilibrium approach, they would not perhaps have made some of the conclusions that they did make.

For example, they concluded that natural gas would produce less oxides of nitrogen than oil and that oil would produce less oxides of nitrogen than coal. Yet they freely confessed that there were many cases where the converse was true. Even based on this assumption, they argued that the main thing that one can do to reduce oxides of nitrogen is to convert from coal to oil to gas. This is not the whole story. It is not the chemical composition of the fuel that has any appreciable bearing on the oxides of nitrogen formed if (1) similar conditions of excess air and temperature exist and (2) adequate residence time to achieve equilibrium is provided. There is too much nitrogen available in the air for the combustion for any nitrobodies in the fuel to make significant differences under equilibrium conditions. The excess air and temperature of combustion under equilibrium conditions are far more significant factors. Most reported data of oxides of nitrogen, when evaluated by the excess air and temperature conditions, will fall very nicely on the curves of Figures 4 and 5. For example, the work of Chaikivsky & Siegmund [6] does this.

Equilibrium studies can therefore direct one in the proper direction to accomplish a goal and avoid groping about or arriving at erroneous conclusions. We cannot select our fuels for incinerators. We must burn whatever is there and produce minimum nitrous oxides under these conditions. Equilibrium can show us a rational way to design.

ACHIEVING EQUILIBRIUM

In earlier papers, discussing equilibrium combustion [3 and 5], the author stressed that burners which could operate stoichiometrically would demonstrate that they could achieve equilibrium. While this was and is a valid statement, the statement was incomplete. The complete statement is that such burners can achieve equilibrium when operated under the same circumstances and conditions. This is not to indicate that the original statement was not correct. Within the scope of the author's experience at the time it was written, it was correct. The chief area that has caused the author to revise that statement is that area where the heating value of waste is very low and the volatilization load very high. A burner which may burn #6 fuel oil stoichiometrically at equilibrium may be an utter failure when attempting to burn a 1 percent dispersion of #6 fuel oil in water with natural gas as an auxiliary fuel. Similarly, a large burner, which burns the aqueous solution quite satisfactorily, may be a failure if reduced in scale.

The reason for this is quite well known. Every manufacturer of liquid burners knows that if fuel oil is allowed to impinge upon a refractory or surface, it will produce carbon. Carbon will be rapidly formed by most burners because a localized rich operating fuel-air ratio will occur. Under this condition, carbon will form. The same condition can occur in an acceptable burner that will burn a hydrocarbon stoichiometrically if an excessive vaporizing load is added to the unit. It is not enough to have sufficient heat available to obtain the vaporization. The fundamental laws of heat transfer are applicable and proper physical conditions must exist for the heat transfer to take place. Where water is present in large quantities, the droplets of water can serve to.act as shields for other droplets of water. While a spray pattern which has its surface near the source of heat can evaporate before it meets a wall, it may well be that the surface shield of water droplets have prevented sufficient heat to have reached the next layer of water droplets so that they have not volatilized before they are impinged upon a surface. Once the droplets are impinged upon a surface, they coalesce and all benefits of fine atomization are lost. If the droplets contain materials such as sulfates or nitrobodies that it is desired to abate, the impingement and subsequent coalescence into larger droplets can only result in the nonequilibrium destruction of these items.

One must therefore add to the requirements for equilibrium burners, previously known (that is, the well-stirred reactor), the condition that materials that require a great deal of heat transfer to be volatilized must be added in such a fashion that they can burn in the well-stirred reactor while receiving sufficient heat to volatilize quickly.

SUMMARY

The author has tried to show that better incinerators can result when empiricism gives way to a rational engineering fundamentals approach. He will be the first one to admit that the rational engineering fundamentals are not fully developed or widely disseminated. This is no reason that the task should not be undertaken and the known fundamentals applied wherever possible. For awhile empiricism must be combined with the fundamental approach if good incinerators are to be developed. However, it is the obligation of every conscientious incinerator designer to use those fundamentals that are available whenever it is to his and his customer's advantage to do so.

For many years the theory of combustion, as it has been known, has had little practical application. With the development of such practical parameters as Creighton-Thring and swirl numbers and the recent efforts of the developers of heat transfer theory to solve practical furnace problems, the gap between the engineers and theoreticians has been closed. It is the obligation of the engineers to cooperate and further encourage the closing of this gap so that empiricism may give way to a rational engineering approach for better incinerators.

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