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CATALYTIC OXIDATION OF FUELS FOR NO_x CONTROL FROM AREA SOURCES

Industrial Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

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CATALYTIC OXIDATION OF FUELS FOR NO_x CONTROL FROM AREA SOURCES

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"...the incandescent solid must not be considered a mere idler or looker-on at the crowd of reacting molecules; actually it galvanized into life the dormant affinities, with the result that the stately minuet of ordinary flame combustion gave place to the wild intoxication of the Venusberg."

from "Surface Combustion,"
Engineering, Vol. 93, May 10,
1912, p. 632.

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SECTION 1

SUMMARY

The use of catalysts in place of conventional burners for promoting hydrocarbon oxidation reactions appears to have advantages in the control of emissions. The operating conditions of these catalytic combustors are limited by the catalyst bed temperature capability, and the temperature obtained through normal one-stage, low excess air operation that is necessary for efficiency reasons is outside the current temperature capability of catalyst systems. It is therefore necessary to consider other system techniques such as bed cooling, exhaust gas recirculation, or staged combustion to hold the bed temperature down. The purpose of this study is to update the knowledge on catalytic combustion, and to assess the potential and problems of catalytic combustors for stationary combustion systems. Earlier reviews examined the use of catalytic combustors in point sources, such as utility boilers. This study is concerned with stationary area sources, where emissions would be distributed somewhat uniformly over a wide area. Based on a review of the state-of-the-art of catalytic combustion concepts, an assessment has been made of their applicability to gas- and oil-fired home heaters and commercial and industrial boilers. As used in this study, "catalytic combustion" refers to devices which employ special additives (usually precious metals) to enhance the heterogeneous activity of the surface. This section gives a summary of the study results and the overall study conclusions.

1.1 STUDY RESULTS

The major results of the investigation are summarized below.

Area Source Characterization

- The most popular means of heating homes and commercial buildings is through the use of central, forced-warm-air, gas- or oil-fired furnaces. Initial catalytic oxidation redesign and/or retrofit efforts for residential applications should be directed toward this type of equipment due to the clean fuels used and the relative simplicity of the redesign effort.
- The design of warm-air furnaces is based largely on empiricism and prototype development, experience, and testing. No theoretical barriers appear to exist to a catalytic redesign or retrofit program.
- The excess combustion air levels in a warm-air furnace are necessarily high (20 – 50 percent for gas-fired furnaces, 25 – 100 percent for oil-fired furnaces) in order to keep the heat exchanger metal temperature below 900°F. A catalytic redesign or retrofit should be aimed at achieving sufficiently low combustion temperatures by means other than increasing excess air, since flue losses increase as the mass of flue gas increases, thereby lowering overall system thermal efficiency.
- The fuels supplied to residential and commercial heating equipment, including warm air furnaces and cast iron boilers, are predominantly natural gas and distillate oil. This will be an asset to new catalytic oxidation concepts since they require clean fuels.
- Cyclic-based emissions from oil-fired warm-air furnaces can, in many cases, account for most of the total CO, UHC, and smoke emissions. The design of a substitute catalytic concept should be aimed at eliminating these ignition peaks, as well as the reduction in efficiency caused by the on-off mode of operation.
- Scotch firetube industrial boilers appear to offer some advantages to a catalytic retrofit effort due to their unique internal, first pass furnace volume.

Catalytic Combustion Review

- The overall success of a catalytic combustion system in reducing CO and UHC to low levels is a function of both heterogeneous and gas-phase reactions; surface reactions alone appear to be unable to achieve the desired low levels.
- Newly developed high-temperature catalyst support materials that are capable of maintaining their structural and thermal integrity at temperatures up to 3000°F are necessary for high system efficiency unless methods for cooling the catalyst bed are used. However, current catalyst systems

are limited by the catalyst coating to much lower temperatures than the supports. An example is platinum, where the catalytic activity decreases by 30 percent at a temperature of 1800°F, and by 75 percent at a temperature of 2200°F.

- The most promising catalyst materials are the noble metals, such as platinum and palladium, because of their high activity and relatively low activation temperature.
- Currently, there are no commercially available catalysts for application to catalytic combustion.
- Metal oxides have activities which approach those of the noble metals, but have significantly higher light-off temperatures, probably limiting their use to spinel structures.
- The principal catalyst poisons for natural gas and light distillate oils will probably be phosphorous, sulfur, and certain halides. Their effect on a variety of catalysts is not known.
- The existing applications of catalytic oxidation concepts in industry, such as in nitric acid plant tail gas cleanup, industrial odor control, small catalytic heaters, and automotive oxidation catalyst systems, are generally in the low-temperature range of applicability. The applicability of this technology to high-temperature catalytic combustion is therefore quite limited, since the problems of catalyst sintering and thermal degradation of the support are avoided at low temperatures (i.e., <1400°F).
- Research is presently being conducted in the area of high-temperature catalytic combustion for application to gas turbine engines. This research is done with extremely fuel-lean conditions, making it difficult to relate directly to domestic, commercial, and industrial space heaters, where near-stoichiometric conditions are desirable.
- Operation of stationary heating and steam generating systems with low overall excess air tends to optimize overall system thermal efficiency. Two-stage combusion, wherein the first stage is run fuel-rich and secondary air is added in a catalytic second stage to complete the combustion, has been shown to be effective for utility and industrial boilers in controlling NO_x emissions. However, proper design is necessary to also minimize CO and UHC, and to keep the system fuel-air ratio near stoichiometric. Staging should be examined carefully for application to catalytic combustor technology.

- Because of the necessity of avoiding local "hot spots" in the catalyst bed, premixed fuel-air systems are needed for catalytic combustors. To prevent blockage of the passages in a catalyst bed, liquid fuels must be prevaporized. The problems associated with fuels introduction to the catalyst bed are formidable ones that require careful attention.
- At the present time, it is assumed that the catalyst bed temperature must be held below 2800°F to minimize the formation of NO_x. Further research work should be undertaken to establish this maximum allowable temperature.
- Current research programs have all been conducted at catalyst bed temperatures well below 2800°F (i.e., 2400°F), and have all demonstrated a successful minimization of NO_x formation.
- Because much of the research concerning catalytic oxidation is proprietary information and therefore not available to the general research community, an experimental program which examines catalyst-support performance and addresses the application of these catalysts in various combustor-heat exchanger systems is needed. Information on the proper methodology to follow in selecting a catalyst is also unavailable from catalyst manufacturers, and needs to be addressed.

Application of Catalytic Combustion to Area Sources

- Flue gas recirculation with a single stage catalytic combustor appears to be one of the most viable retrofit and/or redesign applications.
- Due to the limited furnace volume, low heat transfer coefficient, and cyclic nature, gas-fired home furnaces exhibit several problems for retrofit of a catalytic combustor. These problems appear to be solvable, but redesign appears to be a more viable solution.
- The necessity for preheated air for some catalyst-fuel combinations to activate the catalyst bed must be taken into consideration in any final design.
- Oil-fired units present formidable problems for retrofit, including oil vaporization, startup, and air preheating. Due to the complexity of these problems, catalytic retrofit of oil-fired units is not recommended.
- In order to keep system efficiency high, special control circuitry for on-off operation may be required. This system would include a sequencing control for air/fuel operations and a safety control.

- Because of the many possible choices open to a designer for catalytic combustor retrofit and/or redesign, preliminary conceptual designs for gas- and oil-fired warm air furnaces and commercial and industrial boilers have been made as a part of this study.
- Since the size of the catalytic combustor required for a given application is unknown due to a basic lack of knowledge of the catalyst characteristics, wash coat, support, and bed depth required for an oxidation reaction to go to completion, any attempt at doing a cost analysis of a retrofit or redesign catalytic combustor could lead to erroneous conclusions regarding cost.
- The application of catalytic combustion may be more feasible for large-size units because of the larger initial cost, generally more sophisticated controls, better supervision of equipment, and less limitations on heat transfer.

1.2 CONCLUSIONS

The results of this study indicate that the catalytic combustion concept is feasible for gas- and oil-fired warm air furnaces, and commercial and industrial boilers. At the present time, catalyst availability for systems of interest to catalytic oxidation studies is unknown, however. Oil-fired units pose special problems in terms of fuel vaporization, startup, and air preheating.

It is recommended that a comprehensive testing program be undertaken to support the conclusions stated above. Because the bulk of the knowledge concerning catalyst preparation and performance lies in the proprietary realm, and is thus unavailable generally, this information must be generated and disseminated in an open manner before catalytic combustion can be successfully evaluated as a combustion modification concept. Therefore, the following program is recommended:

- Screening tests of various catalyst-support combinations with a variety of fuels, in order to determine activation energies and kinetic rate constants.
- Development of a mathematical model for combined homogeneous/heterogeneous combustion, which will be capable of predicting the performance of a catalytic bed. This model will make use of the data obtained in the screening tests.
- Tests which demonstrate the feasibility of catalytic combustion in flue gas recirculation, catalyst bed cooling, and two-stage combustion concepts. Since the goal of low NO_x emissions is dependent on holding the bed temperature down, the mechanisms of active bed cooling must be studied in detail.

- Prototype design and development of catalytic furnaces using flue gas recirculation, catalyst bed cooling, and/or two-stage combustion. Since little data of any value presently exists to aid the designer in sizing a catalytic combustor, this data must be obtained experimentally before further prototype design is attempted.

SECTION 2

INTRODUCTION

More than 150 years ago Davy discovered that platinum wires could promote combustion reactions in flammable mixtures, and that the resulting reactions appeared to take place on the surface of the wires, "without flame" and with the high radiative fluxes associated with the solid surface emittance rather than the low emittance of the combustion products (Reference 1). Subsequent study and investigation followed a number of paths reviewed by Spalding in Reference 2. Of this work, a substantial fraction which might be termed "fundamental studies of heterogeneous catalysis" has attempted to

- Identify specific heterogeneous reactions
- Quantify reaction kinetics for these reactions
- Define the mechanisms by which the solid surface promotes or accelerates oxidation reactions and identify catalyst properties leading to high activity.

A second fraction which can be labeled "computation" has dealt with theories and analyses which mathematically

- Describe the diffusion of reactants to the promoting surface and the diffusion of products away from it, in the bulk aerodynamic flow around the surface
- Describe the diffusion of reactants and products in pores (if any) of rough or permeable surfaces
- Link these descriptions to calculations of the catalytic reactions at the promoting surface
- Predict, by appropriate numerical techniques, the combined heat and mass transfer events in systems with convection, diffusion, and both homogeneous and heterogeneous chemical reactions.

A final third fraction can be termed "reduction to practice", which includes attempts to construct and employ practical devices exploiting heterogeneous combustion. As is frequently the case in combustion, work in this area has proceeded with very little

reference to achievements in fundamentals and computation. Experiments throughout the 1800's demonstrated that various materials promoted heterogeneous combustion reactions to various degrees, and that with increasing surface temperatures the number of materials with the ability to promote reactions increased. Numerous investigators attempted to make practical use of this knowledge. The earliest successful devices exploited heterogeneous combustion to provide more efficient lamps. The best example is the mantle lantern or Auer light, still sold in great numbers as a "camping lantern", in which combustion takes place on the ash residue of a fiber bag mantle surrounding the fuel/air orifice. This mantle ash contains oxides, including cerium oxide and thorium oxide, which in addition to constraining radiation emission to desirable lines in the visible spectrum, contribute to the catalytic activity of the mantle (Reference 3). The outmoded theatrical chalk light employed a simpler and less sophisticated surface combustion concept, but also achieved high radiance levels.

Concepts close to the original experiments of Davy have been used as passive ignition devices and as combustible detectors, particularly in the form of hydrogen leak detectors. Related applications along this line include catalytic fume abatement devices and automotive catalytic converters, both depending on precious metals to oxidize low concentrations of combustibles in gas streams.

After extensive practical experimentation, Bone publicized various high temperature applications of surface combustion, using for the most part conventional ceramic materials (References 4, 5). He built and tested surface combustion furnaces, boilers, and permeable panels. This line of investigation has not, however, proven very fruitful, although some commercial equipment of this type is available (Reference 6). This is due primarily to the complexity and expense of the required air/fuel mixing and distribution equipment, and the relative scarcity of industrial applications either requiring (or even able to accept) high radiative fluxes. Surface combustion radiant panels are used as space heaters (although such panels require careful engineering and often precious metal additives to function as true heterogeneous combustors). Catalytic tent heaters operating at quite low temperatures constitute one familiar example in this class.

The range of commercial devices has recently led to some specialization of terminology in a field where formerly several terms were used interchangeably. The term "radiant burner" refers to burner types employing a refractory surface situated within or near the flame so as to provide for radiant heat transfer from the flame area. Heterogeneous combustion occurs in these devices to some degree, but generally does not dominate the process and homogeneous combustion constitutes most of the reaction mechanism. "Surface combustors" employ refractory in a similar manner but use special provisions of air/fuel distribution to maximize the amount of heterogeneous combustion occurring. "Catalytic combustors" employ special additives (usually precious metals) to enhance the heterogeneous activity of the surface.

There are several reasons for the recent upsurge of interest in catalytic combustion. Use of the diffusion flame for combustion appears to place a limit on the lower level of control that can be achieved economically for clean fuels (approximately 25 – 30 ppm of NO_x for small sources), and catalytic combustion appears to be able to reach lower levels of NO_x control (perhaps <10 ppm). In addition, catalytic combustion is soot-free, and the potential of high combustion efficiency for the overall system is present if the excess air can be limited in some way such as two-stage combustion, flue gas recirculation, or cooling of the catalyst bed.

A recent study by the Control Systems Laboratory of the EPA reported the results of tests conducted on commercially available catalytic heaters, to determine the potential of catalytic combustion for pollution-free domestic heating applications based on camper heaters (Rerference 56). This study found that while NO_x emissions were very low from nearly all the heaters, UHC emissions were higher than those of conventional domestic heating units and CO emission levels were extremely high in some cases. It was concluded that more research was necessary before catalytic heating could be considered a viable domestic heating alternative.

The EPA has classified pollutant sources as "area" sources (relatively few emissions from a large number of sources distributed over a wide area, e.g., home furnaces), "line" sources (e.g., highways), or "point" sources (a large amount of emissions emanating from a single source, e.g., utility boilers). The Aerospace Corporation, under an EPA contract, reviewed the state-of-the-art of surface and catalytic combustion concepts in 1973, and assessed the applicability of these concepts to large utility boilers and stationary gas turbines (Reference 7). It was concluded that catalytic combustors might be applicable to both existing and new stationary gas turbines, but it was unlikely that catalytic combustors could be economically installed in utility boilers.

This study, then, was undertaken to assess the present state-of-the-art in catalysis and in catalytic combustion, to assess the feasibility of catalytic combustion for the control of NO_x emissions from stationary sources, and to define the problems that would be encountered in the redesign and/or retrofit of catalytic combustors for stationary sources. Recommendations of the most promising applications for area source combustors as presented, based on cost and technical factors.

SECTION 3

CHARACTERIZATION OF STATIONARY COMBUSTION SOURCES

This section has four subsections as follows:

- General considerations, in which the nature of the residential, commercial, and industrial area source sectors are described, current cost and sophistication restraints are discussed, and the various types of equipment are introduced
- A description of the design and operating characteristics of warm air furnaces and boilers
- Air pollutant emission characteristics
- Conclusions

This discussion provides the background information required for a future catalytic combustion redesign or retrofit effort.

3.1 GENERAL CONSIDERATIONS

Emissions of nitrogen oxides from fuel combustion account for over 98 percent of the nation's total of 20 million tons per year. This contribution is almost evenly divided between mobile sources and stationary sources. Reducing emissions from the latter is the thrust of the present study.

The options available for controlling these NO_x emissions include fuel modification, flue gas treatment, modification of operating conditions, or use of alternate processes. The first three of these methods have, in the recent past, been vigorously investigated and one of them, combustion modification, has proven largely successful for the more prolific NO_x emitters. In order to extend the reduction capability of such sources as well as to bring those sources which do not respond to the simpler reduction options into compliance with future emission regulations, alternate processes must be explored. One of these, catalytic combustion, is the focus of this report.

The catalytic approach may offer significant NO_x, CO, and unburned hydrocarbon emission reduction potential due to a possible low operating temperature as well as a concurrent promotion of oxidation reactions. An assessment of the applicability of catalytic concepts to gas turbines and utility boilers was performed by

the Aerospace Corporation in 1973 (Reference 7). This report concluded that catalytic oxidation might be applicable to gas turbines, but that application to a utility boiler might require a new system design. The report also indicated that only gaseous fuels and light, sulfur-free hydrocarbons could be used in catalytic systems due to system requirements and catalyst poisoning difficulties. Since these fuels are used predominantly in area sources, which may also be more amenable to redesign, it is necessary to extend consideration to these sources.

This section of the present study will begin the task of assessing the applicability of catalytic combustion to area sources by discussing their design, operating and emission characteristics and by noting which of these factors may be critical for catalytic concepts. The area sources of concern include residential and commercial comfort heating equipment and industrial boilers.

3.1.1 Residential Sector

Figure 3-1 gives a breakdown of the major types of residential heating equipment. The prevalent designs are the warm air furnace and hydronic systems, as shown in Table 3-1. According to data obtained from the Gas Applicance Manufacturers Association (GAMA), the trend in the last 10 years has been toward gas-fired forced warm air systems. The 1970 U.S. Census data substantiates this by indicating that for houses built prior to 1939 almost 30 percent of the warm air furnaces are oil-fired compared to approximately 15 percent for houses built during the period 1960-1970. This overall trend toward the use of gas-fired equipment is favorable to programs involving the use of catalytic oxidation processes since they have been identified as requiring clean fuels.

Equipment characterization and system concept evaluation will, therefore, concentrate on gas-fired central furnaces and steam or hot water units, the latter overlapping to some extent on the commercial heating sector (that is, cast iron boilers are used for both residential and commercial heating applications).

3.1.2 Commercial Sector

The two major categories of commercial comfort heating equipment are warm air furnaces and boilers, as illustrated in Figure 3-2. The warm air furnace design concept resembles that used for residential heating purposes except that the larger-scale equipment dictates that the unit usually be mounted on the roof of the building. Boilers include water tube, fire tube, and cast iron types, all of which usually employ only one burner.

The distribution of equipment types for heating commercial buildings varies around the country. On the West Coast, or in other moderate climates, about 85 percent of the heating units are warm air furnaces. If comfort heating is the only

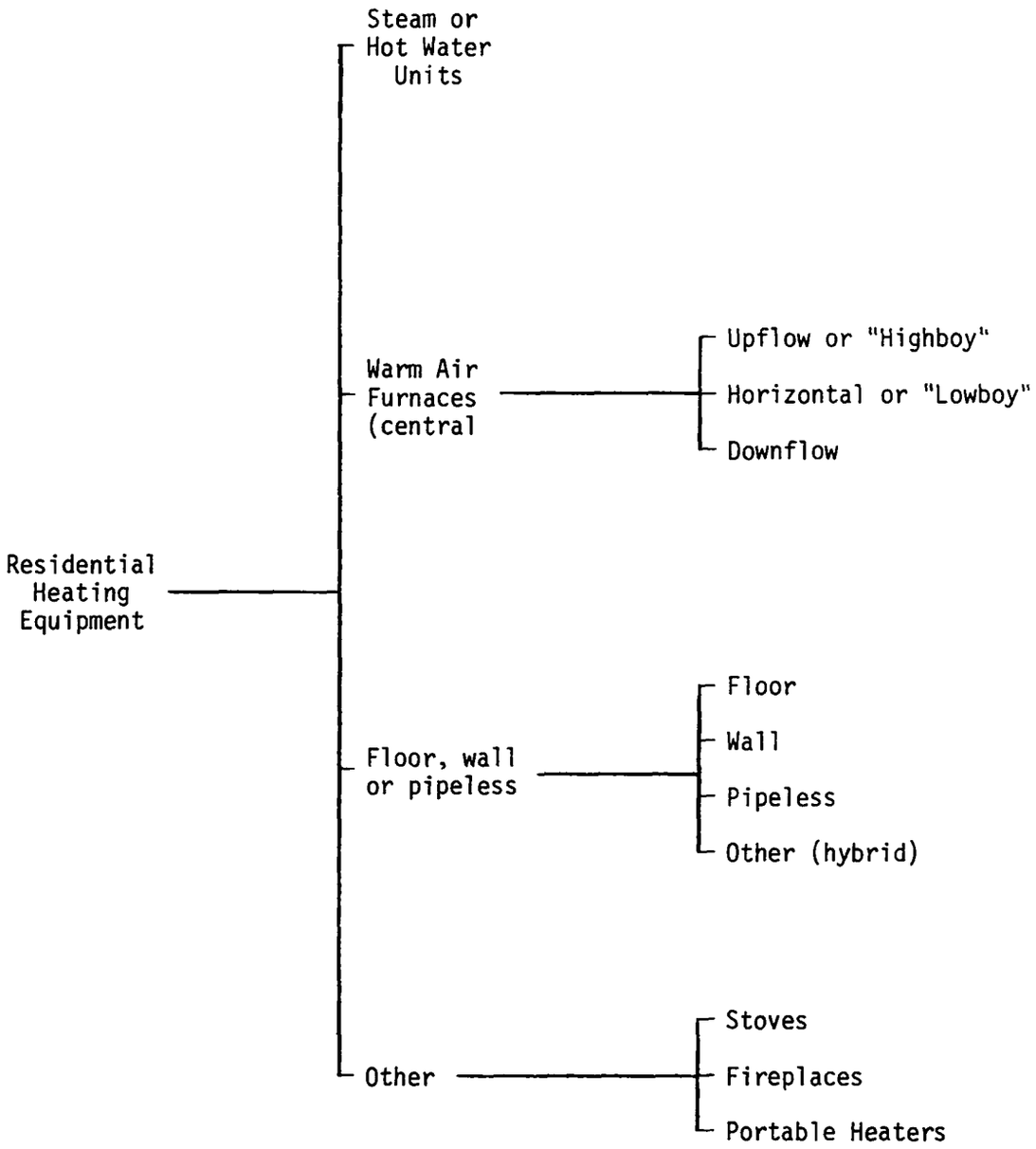


Figure 3-1. Residential heating equipment types.

TABLE 3-1. DISTRIBUTION OF RESIDENTIAL HEATING SYSTEMS FROM THE 1970 U.S. CENSUS

Equipment Type and Fuel Rank	Percent of National Total	Rank
Warm Air Furnace		
Gas	31.56	1
Fuel Oil	10.37	4
Coal or Coke	1.00	
Wood	Negligible	
Electricity	Negligible	
Bottled, Tank, or LP Gas	2.04	9
Other Fuel	0.08	
Steam or Hot Water		
Gas	8.78	5
Fuel Oil	12.29	2
Coal or Coke	1.02	
Wood	Negligible	
Electricity	Negligible	
Bottled, Tank, or LP Gas	0.28	
Other Fuel	0.36	
Floor, Wall, or Pipeless		
Gas	7.79	6
Fuel Oil	0.98	
Coal	0.10	
Wood	Negligible	
Electricity	Negligible	
Bottled, Tank, or LP Gas	0.65	
Other Fuel	0.01	
Other Heating Equipment		
Gas	12.06	3
Fuel Oil	4.67	7
Coal	1.00	
Wood	1.36	10
Electricity	Negligible	
Bottled, Tank, or LP Gas	3.57	8
Other Fuel	0.01	
TOTAL	99.98	

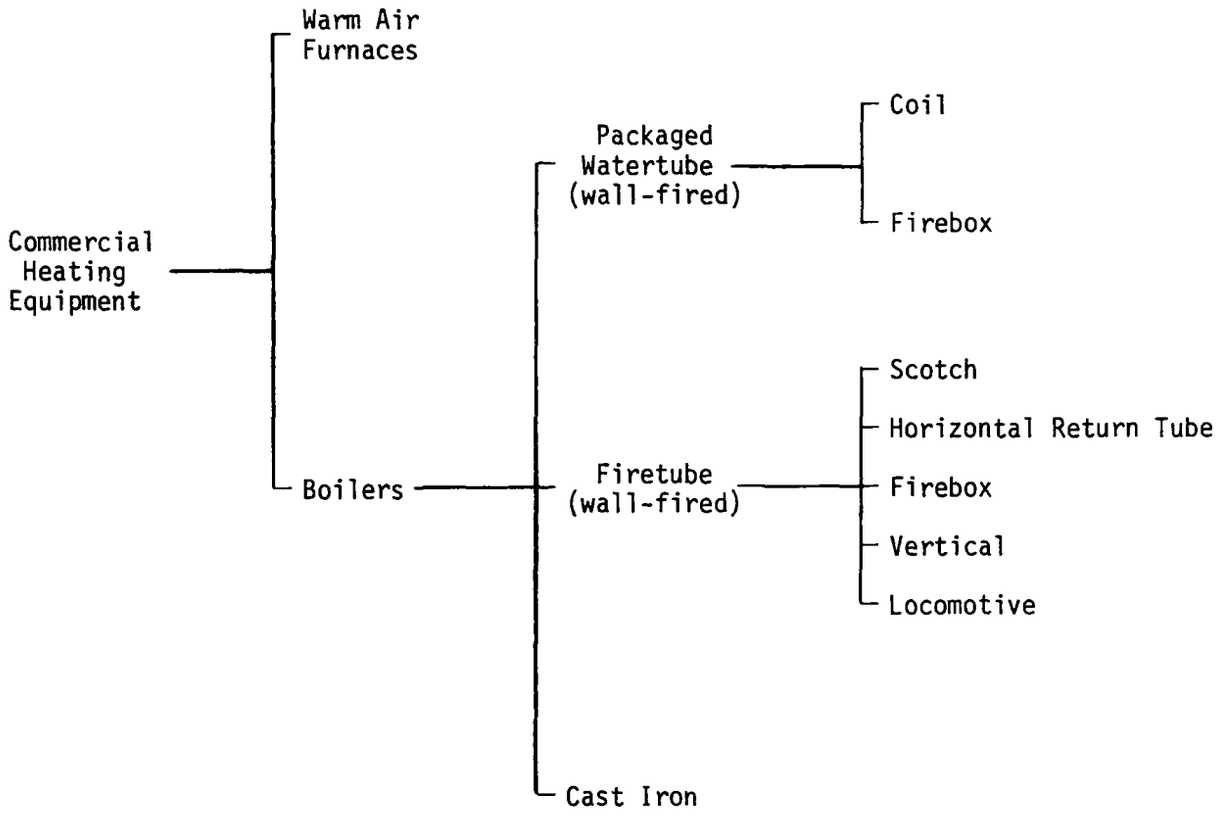


Figure 3-2. Commercial heating equipment types.

requirement and if mildly fluctuating delivered air temperatures can be tolerated, warm air furnaces are chosen over boilers. In addition, a warm air furnace has a lower initial cost than that of a boiler, and the latter requires a more elaborate piping system. Highrise buildings, however, almost always require boilers due to a demand for different kinds of heated fluids.

The predominant fuels burned in warm air furnaces are distillate fuel oil and natural gas. As for residential heating equipment of this type, it appears that excellent opportunities exist for the application of retrofit or new-design catalytic concepts to commercial warm air furnaces. The best approach would be to choose a typical commercially-available furnace for intensive analysis. Of the myriad manufacturers, Lennox appears to produce moderately-priced and popular equipment of representative design, and would be suitable for this purpose.

Fuels burned in boilers used for heating commercial buildings include distillate and residual fuel oil, natural gas, and, to a small degree, process gas. Natural gas and distillate oil dominate. The type of boiler chosen for a given commercial heating application depends mostly on the size of boiler required or its function. Generally speaking, cast iron sectional boilers are used for supplying most low pressure steam or hot water in a small to medium size application. Fire tube boilers, all of which are packaged, are available in sizes up to 25 x 10^6 Btu/hr, while packaged water tube boilers range in capacity between 10 x 10^6 and 250 x 10^6 Btu/hr. Most fire tube or water tube boilers are offered with dual fuel burners (gas and oil).

3.1.3 Industrial Sector

The types of heating equipment utilized in the industrial source sector are divided, as with commercial heating equipment, between warm air furnaces and boilers. Figure 3-3 depicts the relationship between these basic types. In industrial buildings where there is no requirement for hot water or steam, about 90 percent of the heating sources are warm air furnaces or radiant heaters. These furnaces are identical to those used in commercial heating applications. In most industrial buildings, however, the processes in operation on the premises demand the availability of hot water and/or steam. A variety of boiler types are used for these purposes.

Firetube boilers, as shown in Figure 3-4, comprise the first category. These packaged units are essentially the same as the commercial heating units described previously, but include additional, very rare, types of stoker-fired HRT and firebox boilers. These are, of course, coal-fired, and may not be germane in the context of a catalytic retrofit program. Distillate oil and natural gas are the most common fuels delivered to the remaining types of boilers.

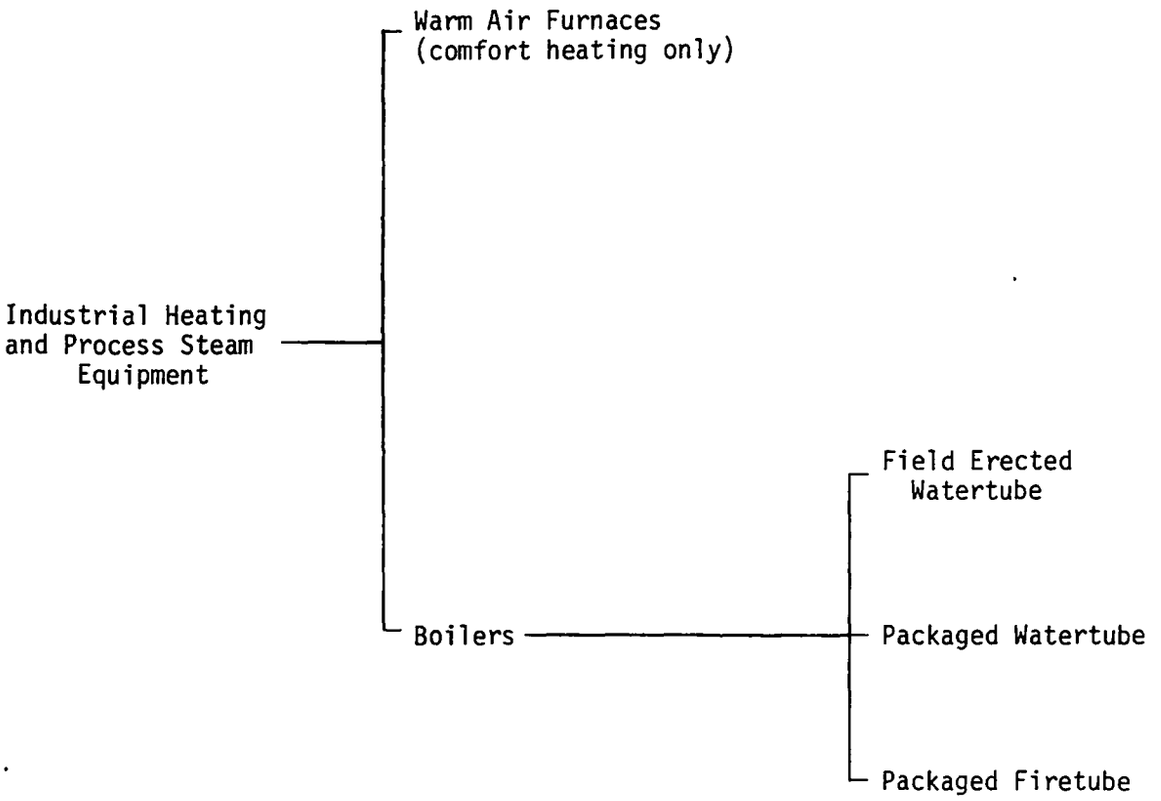


Figure 3-3. Industrial heating and process steam equipment — basic types.

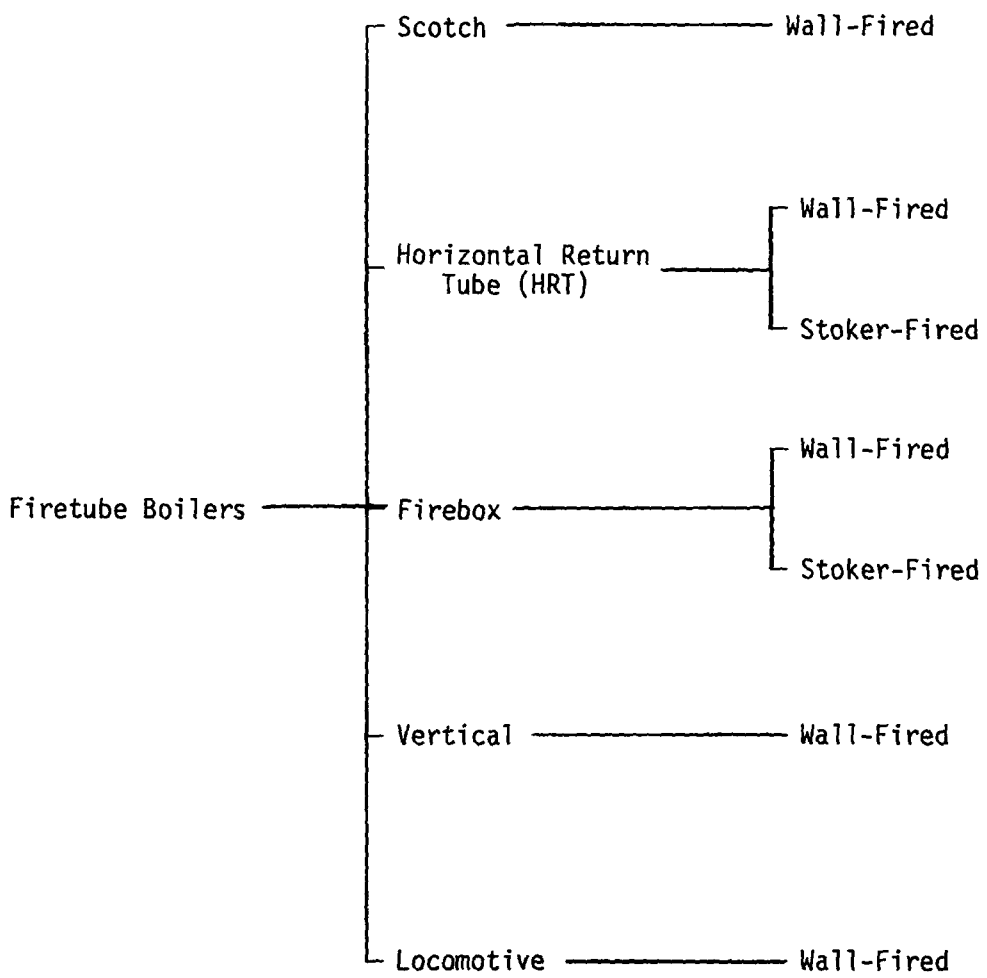


Figure 3-4. Industrial heating and process steam equipment – firetube boiler types.

Watertube boilers comprise the remaining types of industrial boilers, and are available in packaged or field-erected form. A breakdown of the former type is shown in Figure 3-5, while Figure 3-6 illustrates the variety of field-erected boilers. Both types are commonly one-or two-burner, multi-fuel (including residual oil) facilities. Most packaged watertube boilers range in capacity from 10 x 10^6 to 250 x 10^6 Btu/hr, while field-erected units are available in sizes above 100 x 10^6 Btu/hr and designs that are similar to full-scale utility boilers at very large capacitites.

The remainder of this section is devoted to a more detailed discussion of the combustion equipment types comprising the source sectors described above, and is divided into separate discussions on warm air furnaces and boilers (steam and hydronic).

3.2 EQUIPMENT AND OPERATING CHARACTERISTICS

3.2.1 Warm Air Furnaces

A warm air furnace is a self-enclosed appliance used for heating air for a house or building. It discharges hot air directly into the space being heated or more commonly through ducts which transport the warm air to the area to be heated. Some furnaces operate by gravity (buoyancy forces), but the majority are forced air systems, using a pressure blower to move the air through the ducts and back to the furnace (References 8, 9, 10).

The furnace consists of a burner with related piping and controls, a heat exchanger, and a blower for forced air systems. The furnace package is enclosed in a rectangular steel casing. The heat exchanger compartment is insulated to improve efficiency and to limit the outer casing temperature for personnel safety. The combustion takes place in the primary combustion space of the metal-walled heat exchanger. The combustion products pass through secondary flue gas passageways of the heat exchanger and exit through a flue to the atmosphere. The air to be heated circulates over the outside of the heat exchanger to the warm air discharge. The air discharged is heated to 100°F to 150°F. Furnaces are fired by natural gas and distillate oil and (rarely) by coal.

Domestic or residential warm air furnaces are usually defined as furnaces whose capacities are under 300 x 10^3 Btu/hr and are generally classified into four types:

- Downflow, in which the blower is mounted above the heat exchanger, the flue gas discharges at the side or top and the warm air discharges from the bottom of the unit (counter-flow). Figure 3-7 shows a typical gas-fired downflow unit, while Figures 3-8 and 3-9 show counterpart oil-fired furnaces utilizing two different heat exchanger designs.
- Upflow or "high-boy", which is similar to downflow except that the blower is mounted below the heat exchanger and both the warm air and flue gas

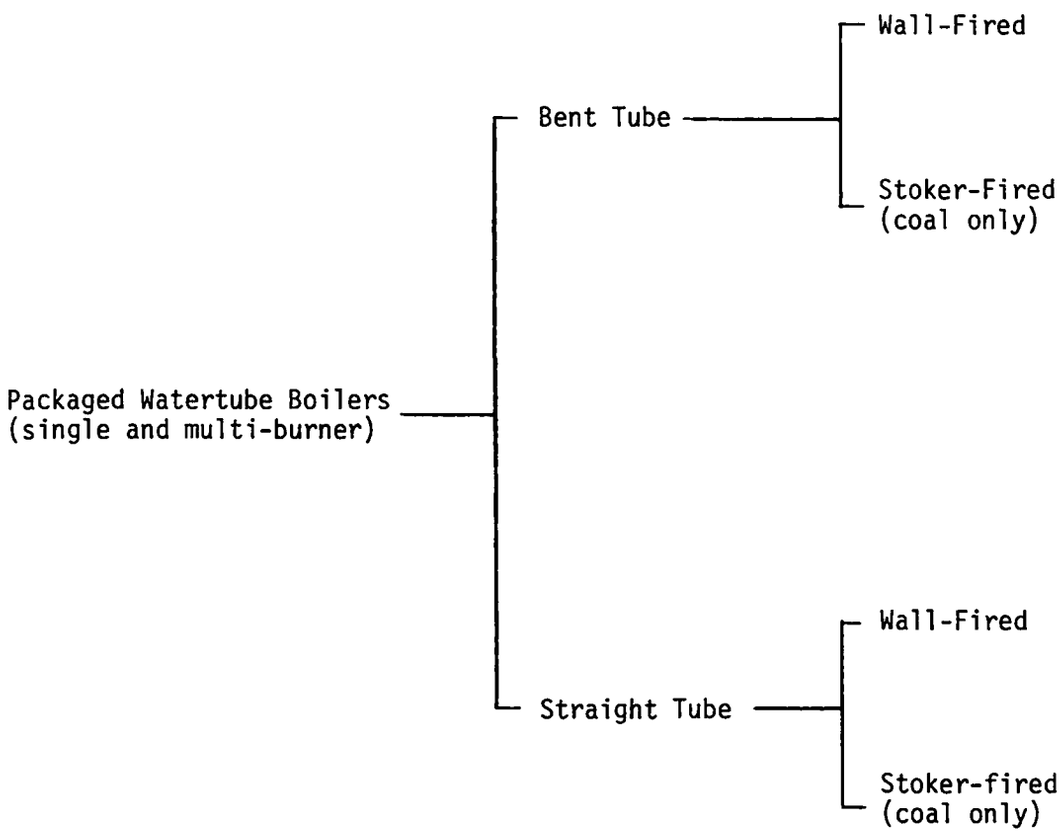


Figure 3-5. Industrial heating and process steam equipment — packaged watertube boiler types.

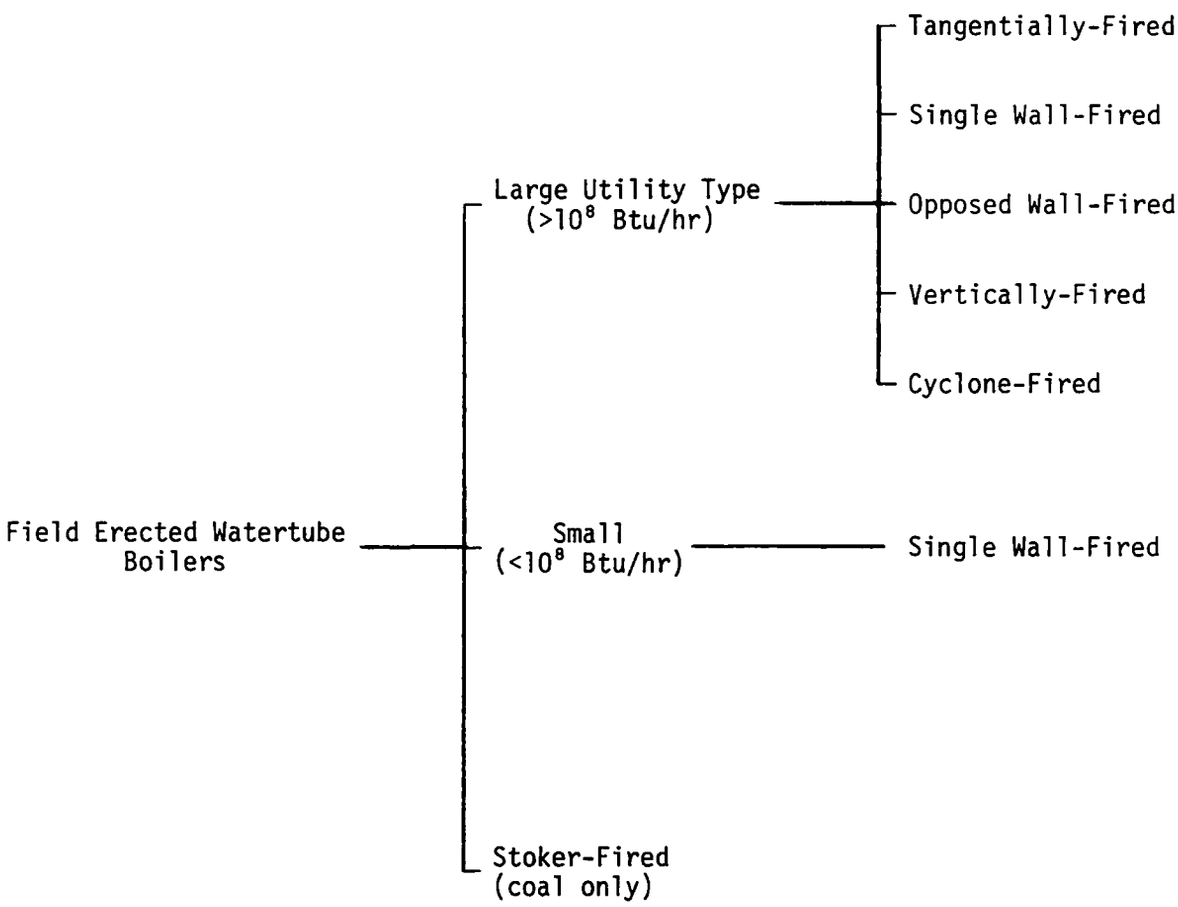


Figure 3-6. Industrial heating and process steam equipment — field erected watertube boiler types.

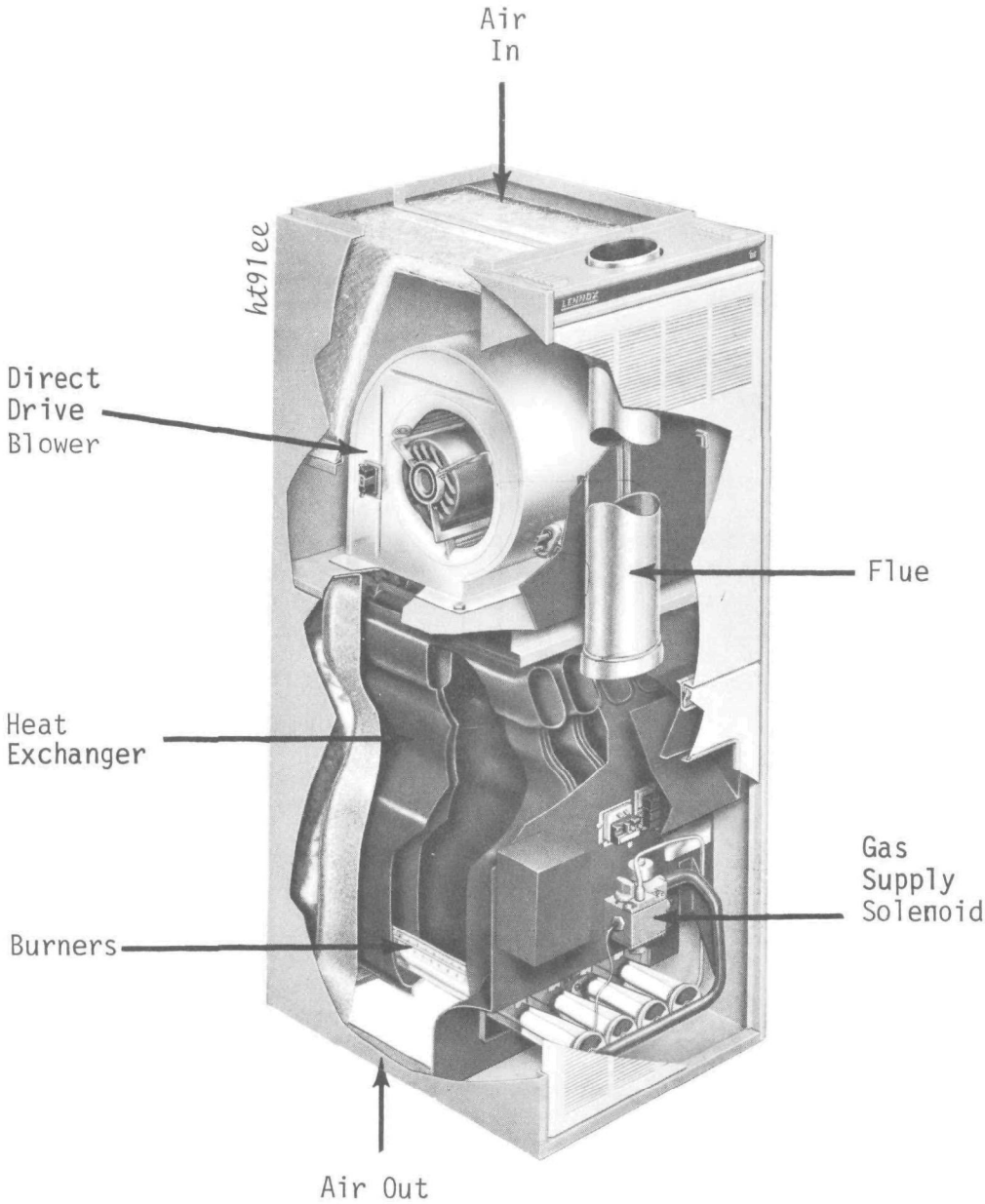


Figure 3-7. Forced warm air gas-fired furnace — downflow (note: Figures 3-7 through 3-13 courtesy of the Lennox Co.).

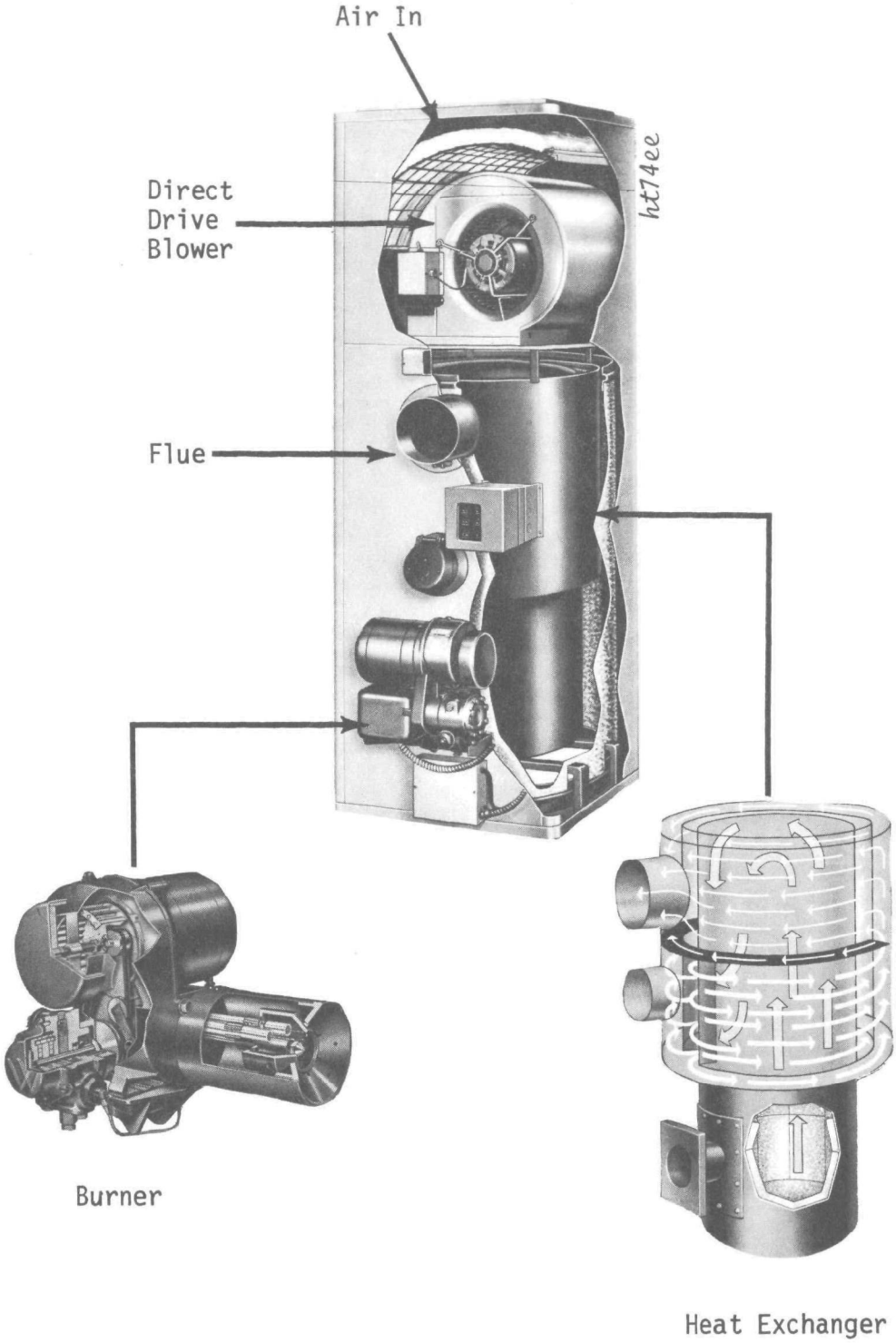


Figure 3-8. Forced warm air oil-fired furnace — downflow.

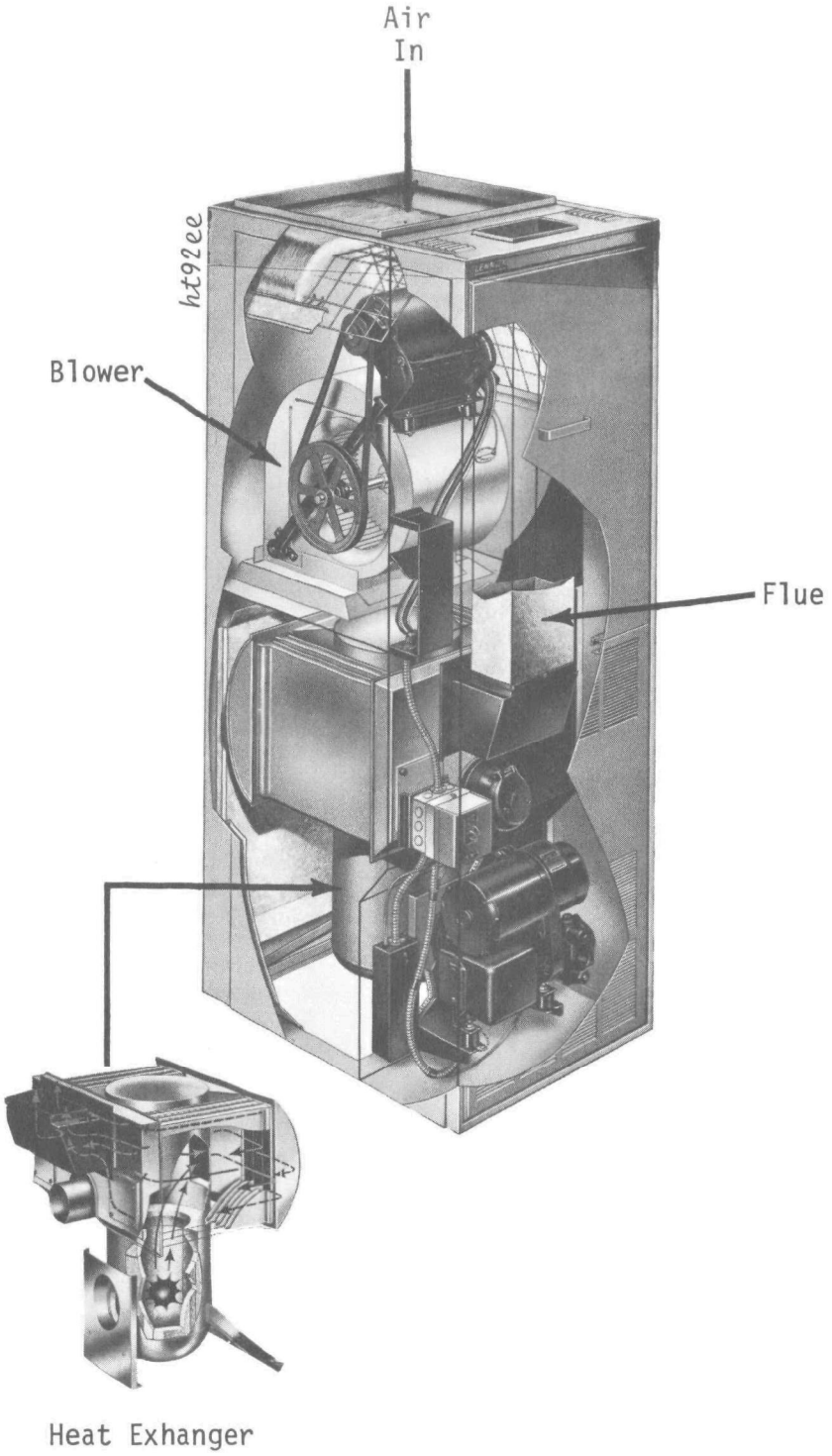


Figure 3-9. Forced warm air oil-fired — downflow, with compact heat exchanger.

discharge from the top of the unit (co-flow). Gas-fired furnaces of this type mounted with direct and belt-driven blowers are shown in Figure 3-10. Figure 3-11 illustrates the same furnace design fired by oil.

- Horizontal, in which the blower is mounted next to the heat exchanger, the flue gas discharging at the top and the warm air at the end of the unit (Figures 3-12 and 3-13).
- Basement or "low-boy", which is very similar to the horizontal unit except that the flue gas discharges at the side and the warm air from the top. In addition, the heat exchanger may be higher and narrower than for a horizontal furnace.

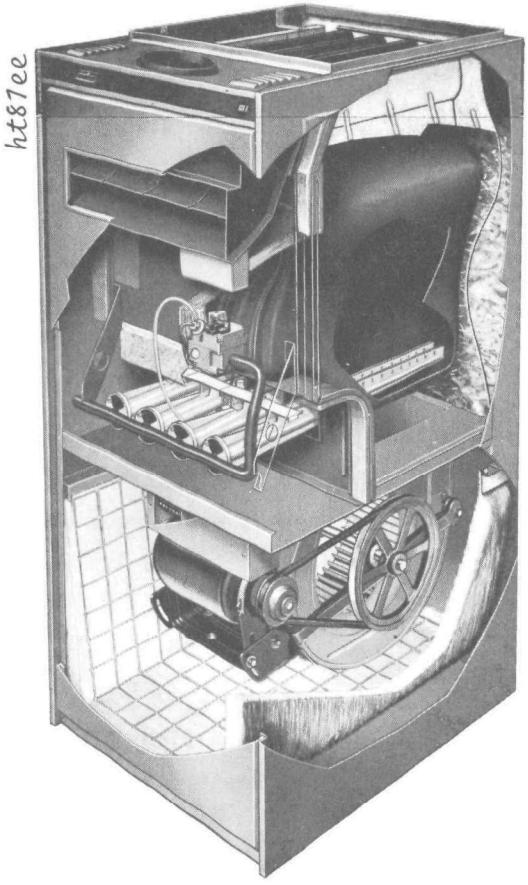
All of these units are available in a wide range of capacities. The choice of the appropriate type is based most often on available installation space. For example, horizontal units are intended for use in situations where headroom is limited, such as in attics or crawl spaces.

Sub-types of warm air furnaces include space heaters and unit heaters. A warm air furnace is known as a space heater or unit heater when it discharges directly into the space being heated and has no ducts. By definition of the American Gas Association, a unit heater is non-residential (larger than domestic). While domestic heaters may be used in commercial installations, commercial or industrial size heaters are seldom used in domestic applications.

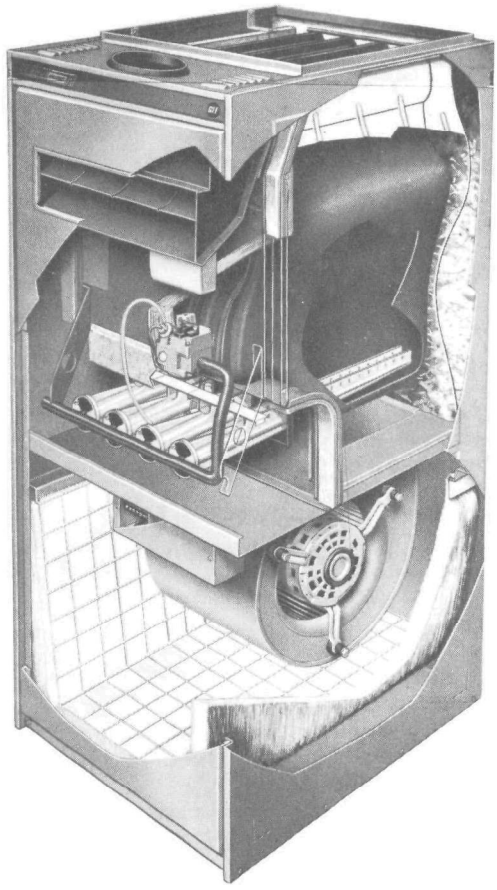
Space heaters are designed as room heaters, wall furnaces and floor furnaces. A room heater is a self-contained, free standing, gas-fired air heater installed in the space being heated. It may employ gravity or forced air circulation and be vented or unvented. Wall furnaces are similar but are designed to be mounted in a wall and are vented. A floor furnace is mounted under a floor with a grill at floor level. Unit heaters may be free-standing floor units or may be designed for suspension from the ceiling.

The heat exchanger in a warm air furnace can have a single combustion chamber, usually cylindrical, or a series of individual sections. The single combustion chamber is used with a single port oil-fired burner, as shown in Figure 3-8. It is usually lined with insulating refractory or felt insulation but can be fabricated from a temperature resistant alloy steel. The sectional type is used with multiple gas-fired burners which are cross-connected to use a single port. This type is illustrated in Figure 3-7. The exchanger sections are connected at the bottom and at the top to a common flue gas breeching. Construction may be of alloy steel, stainless steel or sometimes aluminized steel.

Two types of blowers are found on modern forced warm air furnaces: direct drive and belt drive. Direct drive blowers are of the multiple speed type and usually

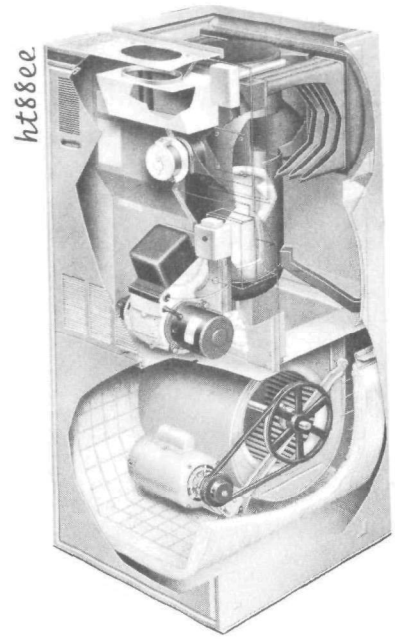


Belt drive blower

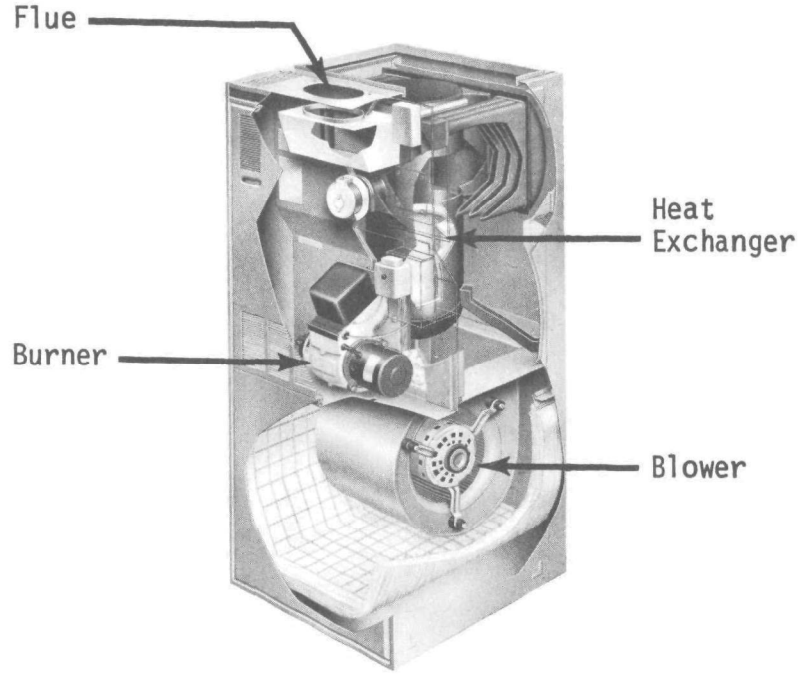


Direct drive blower

Figure 3-10. Forced warm air gas-fired furnace — upflow.



Belt drive blower



Direct drive blower

Figure 3-11. Forced warm air oil-fired furnace — upflow.

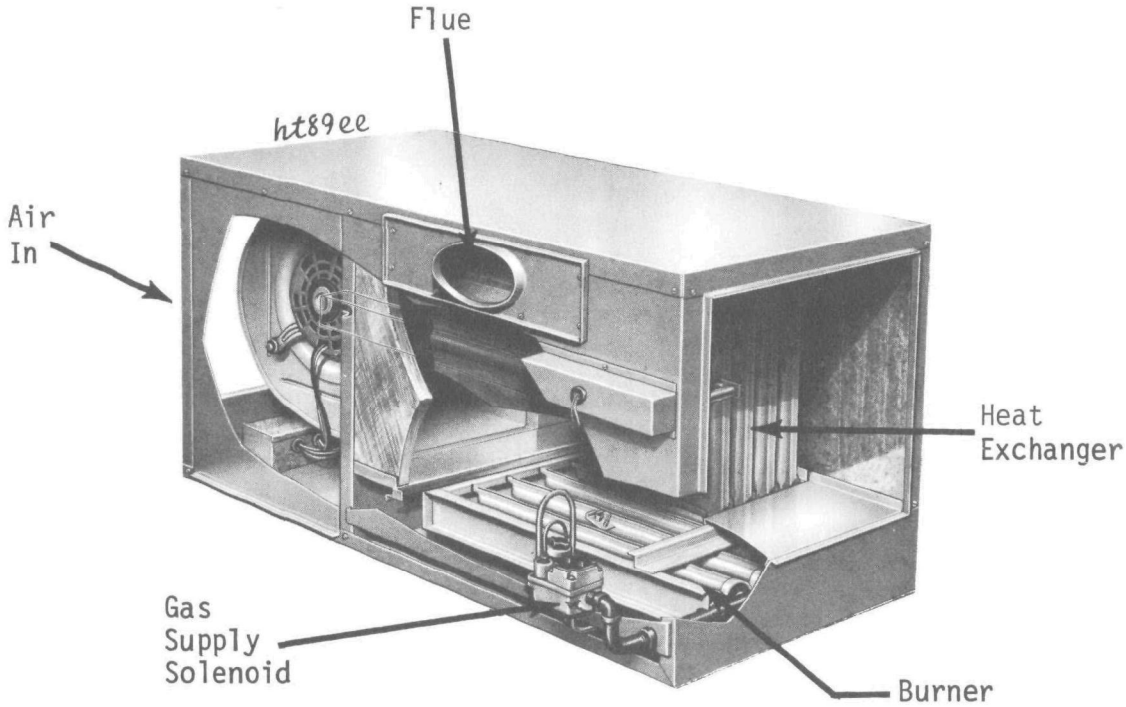


Figure 3-12. Forced warm air gas-fired furnace — horizontal.

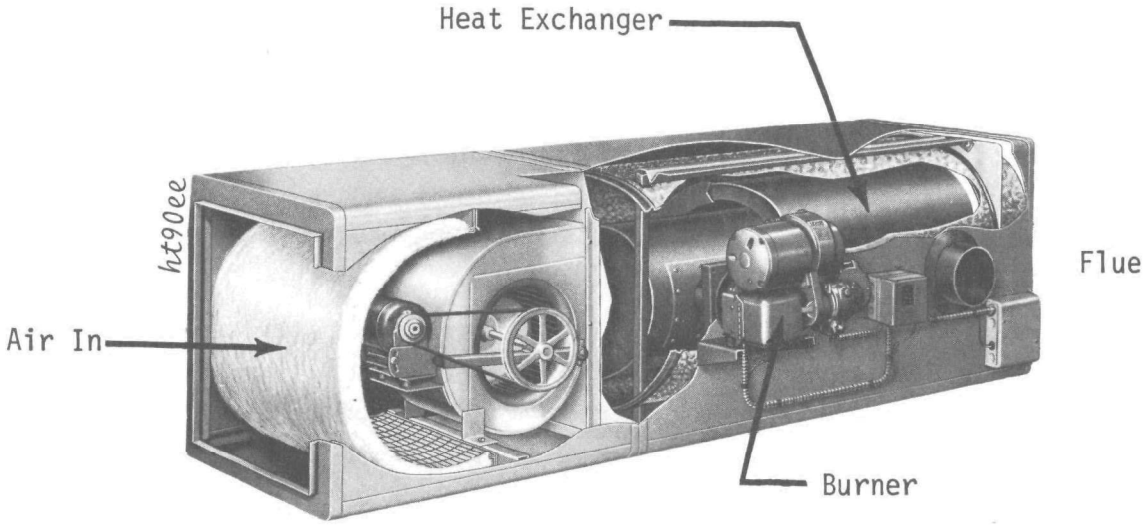


Figure 3-13. Forced warm air oil-fired furnace — horizontal.

are found on combination heating and cooling furnaces. However, they are also used on heating furnaces only. When properly connected electrically, the blower will run at slower speeds in the winter months and at a faster speed during the summer months.

Belt drive blowers operate at one speed, which is dependent on the adjustment of the pulley system. This speed is set by the servicemen during furnace installation, and can have a major impact on efficiency if done improperly.

The gas burners on residential-size warm air furnaces are naturally aspirated types consisting of three to four venturis, with distribution pipes consisting of rows of small orifices (Figure 3-7). The primary air is drawn into the venturi by the gas pressure and premixes with the gas prior to ignition. The primary air/fuel ratio can be controlled by small shutters at the end of each venturi. Secondary air from the furnace room enters around the burners to reduce the overall flame temperature and allow complete combustion. Units always utilize draft diverters which dilute the flue gas stream and prevent downdrafts from blowing out the pilot.

Typical operating conditions of a domestic-size warm air furnace (100,000 Btu/hr) are given in Table 3-2. The wide range in excess air levels is due to variations in installations and meteorological conditions. The combustion chamber pressures are quite low due to the naturally aspirated burners. Consequently, the heat transfer open area on the flue gas side is quite large to prevent excessive pressure drop. This results in the fairly low heat transfer coefficients on the hot side, as shown in Table 3-2, which necessitates fairly large surface areas. An overall heat transfer coefficient of 2.7 Btu/hr-ft^2-°F is recommended by ASHRAE.

Gas-fired furnaces rely on the stack to create sufficient draft to draw the secondary air through the furnace. Manufacturers frequently claim that reducing the stack temperature below 300°F will result in insufficient draft for the burners and cause condensation in the stack.

In all, the design procedure of gas-fired forced warm air furnaces is largely empirical and relies on testing and modifications of experimental units to meet AGA/ANSI standards.

Oil-fired forced warm air furnaces look very similar to the gas-fired units from the outside and are now being made with overall volumes not much greater than the gas-fired versions. There are considerable differences internally, however. The heat is supplied by a gun type oil burner of the type pictured in Figure 3-8. These burners consist of a combustion air blower, motor, damper, fuel pump, spark ignition system, main air tube and swirlers, and fuel nozzle. The fuel flow rate is determined by the oil nozzle orifice size, and the total air flow rate by the blower and damper. The proper air/fuel ratio is adjusted using the damper until the optimum CO and smoke levels are achieved.

TABLE 3-2. DESIGN POINT CHARACTERISTICS OF A TYPICAL 10^5 BTU/HR FORCED WARM AIR GAS-FIRED FURNACE*

Excess Combustion Air: 20% to 50%
Flue Exit Diameter: 3-1/2" to 5"
Heat Exchange Area: ~ 30 to 35 ft^2
Overall Heat Transfer Coefficient: 2 to 3 Btu/hr-ft^2-°F
Exit Flue Gas Temperature (Before Draft Diverter): 450°F to 650°F
Draft Diverter Dilution Air Flow Percent of Flue: 20% to 50%
Combustion Chamber Pressure: ± 0.2" W.G.
Recirculating Air Flowrate (scfm): 800 to 1200 scfm
Temperature Rise on Air Side: 70°F to 75°F
Maximum Gas Side Heat Exchanger Metal Temperature: 900°F
Overall Steady State Efficiency: 75% to 80%
Common Operating Mode: on/off
Ignition System: Pilot flame
Draft System: Natural

*Data is compiled from discussion with manufacturers and from References 10, 11, 12, 13, 14.

The burner is mounted in a refractory or refractory-felt lined combustion chamber which is cooled by air circulating through the house. From the combustion chamber the flue gas passes through a heat exchanger, as discussed previously, and finally out the stack. The absence of a pilot flame and the use of a forced draft system precludes the need for a draft diverter in the flue. The burner blower may supply the full pressure to exhaust the gas from the stack or it may rely partially on the buoyancy forces downstream of the stack. Table 3-3 lists typical operating conditions for this type of furnace.

As for gas-fired furnaces, the design procedure is quite empirical and relies on prototype development, experience, and testing. Standards for construction and thermal efficiency are set by Underwriters Laboratory and ANSI.

One of the most important attributes of a conventional warm air furnace is the cyclical operating mode. This often contributes to an overall thermal efficiency of significantly less than the AGA standard 80 percent. A 1970 study by Stricker (Reference 15) attempted to measure the efficiencies of gas- and oil-fired warm air furnaces in the "as-found" condition in the field over a 6-month period. Figures 3-14 and 3-15 from this study show the typical temperature rise on the air side during a cycle. The fire is extinguished at the maximum temperature rise, and it is at this point that the peak, or certified, efficiency is probably achieved. For the remainder of the cycle the air blower remains on but the flue gas temperatures and flow rates have dropped. Perhaps what is more important and not shown on this curve is that the burner has been firing for several seconds prior to cooling air blower start-up. Again, this means that there is a significant period of time when there is very little flow on the air side, implying inefficient heat exchange. Of course, some of this heat is stored as heat capacitance in the furnace structure to be recovered eventually, but much of it escapes out the stack under inefficient conditions.

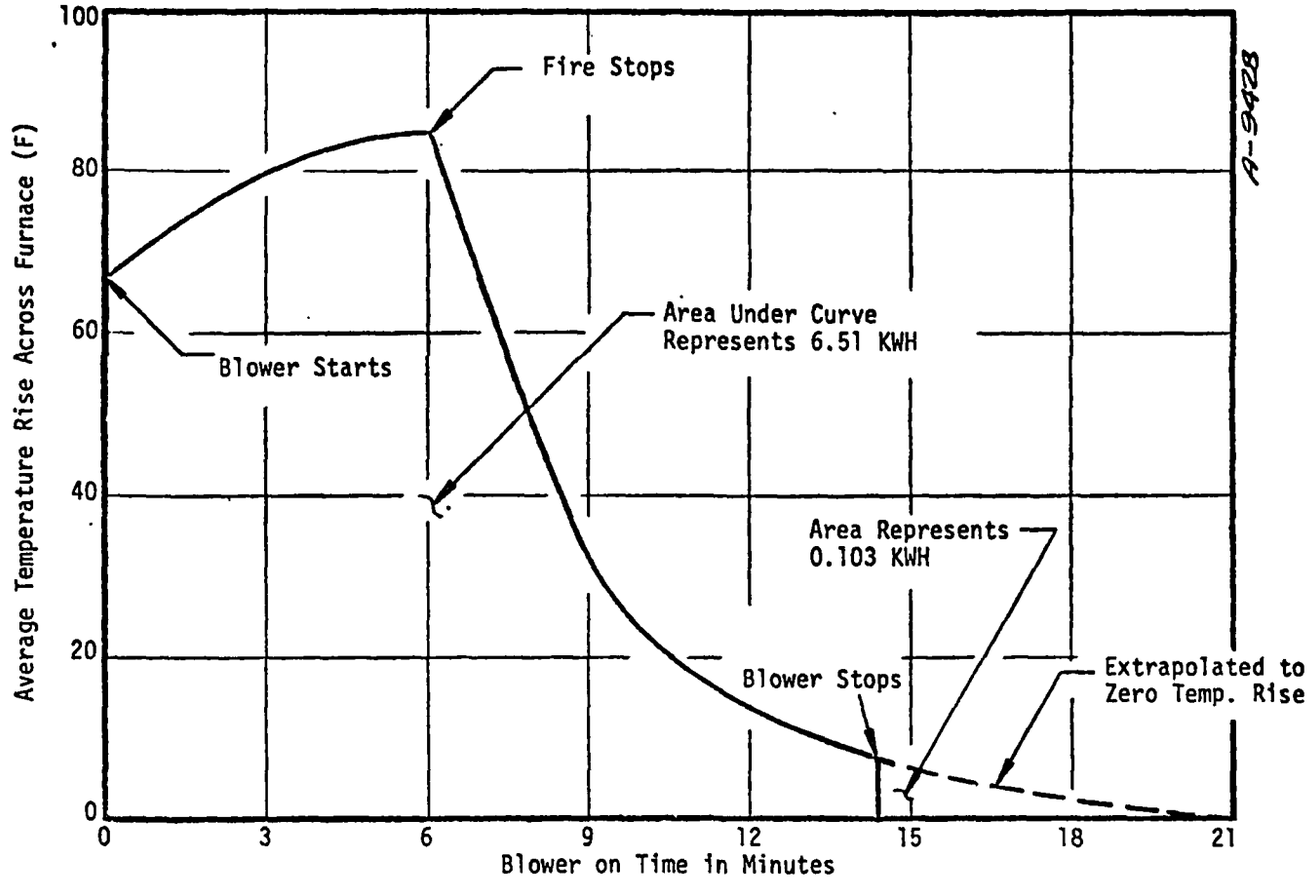
One type of warm air furnace that bears further discussion is the roof-mounted commercial-size unit. The designs of these units vary considerably among manufacturers, relative to the domestic sector. The apparent standardization of the latter is due mainly to the large sales volume as well as an extremely competitive market place. These conditions differ sufficiently in the commercial heating sector to allow some design innovations, especially in gas-fired units.

The burners in these units tend to be inherently more versatile. One such unit, used in rooftop furnaces manufactured by The Trane Company, consists of a "Series NP Maxon Burner" with a 25 to 1 turndown capability.

Novel heat exchangers are also more common in these units, such as the "Mutiloy" type found on General Electric products. This heat exchanger is composed of a bundle of parallel stainless steel fire tubes with numerous small cooling fins welded to the outside.

TABLE 3-3. DESIGN POINT CHARACTERISTICS OF TYPICAL 10^5 BTU/HR WARM AIR OIL-FIRED FURNACE

Excess Combustion Air: 25% to 100%
Flue Exit Diameter: 5" to 7" (round)
Heat Exchange Area: 20 ft^2 to 30 ft^2
Overall Heat Transfer Coefficient: 2 to 3 Btu/hr-ft^2-°F
Exit Flue Gas Temperature: 500°F to 900°F (older units)
Combustion Chamber Pressure: 0.05" W.G. to 0.2" W.G.
Recirculating Air Flow: 800 to 1300 scfm
Temperature Rise on Air Side: 75°F to 80°F
Maximum Gas Side Heat Exchanger Metal Temperature: 900°F
Overall Steady State Efficiency: 70% to 80%
Common Operating Mode: on/off
Ignition System: Spark
Draft System: Forced


Average Temperature Rise Across Furnace (F)
100
80
60
40
20
0
0
3
6
9
12
15
18
21
Blower on Time in Minutes
Fire Stops
Blower Starts
Area Under Curve
Represents 6.51 KWH
Area Represents
0.103 KWH
Blower Stops
Extrapolated to
Zero Temp. Rise

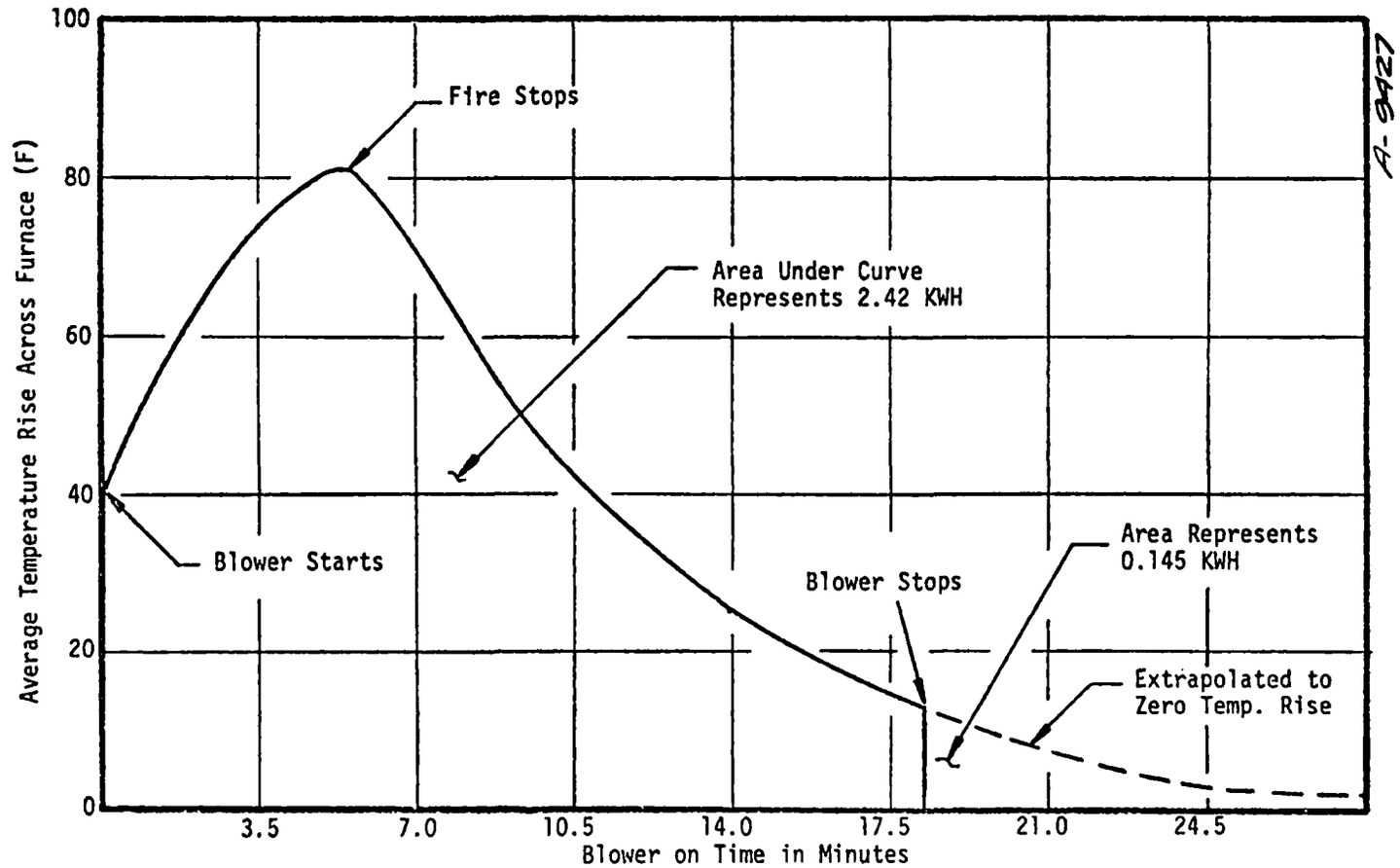


Figure 3-15. Temperature rise across an oil-fired warm air furnace during a typical cycle.

Higher quality materials of construction and larger interior volumes are other factors that distinguish commercial-size from domestic-size furnaces.

3.2.2 Boilers

A boiler is a device designed to generate steam or hot water by transmitting heat from an external combustion source to water in a container (References 9, 16, 17). Heat for the production of steam or hot water is obtained from the combustion of a fuel by a burner in a furnace or fire box. The energy released by combustion is absorbed by the water and its vapor which are contained in the boiler. The boiler heat transfer surfaces usually consist of steel tubes that are exposed to, or carry, the hot combustion gases. Boilers designed to produce steam utilize a uniquely-designed pressure vessel in which saturated steam is separated from the steam-water mixture.

Most of today's boilers are internally fired, that is, the furnace volume is an integral part of the unit and is often surrounded by water-cooled surfaces. Boilers that have additional water-cooled surfaces, such as superheaters, air heaters and economizers, are steam generators. However, the term "boiler" is applied to both steam and hydronic, or hot water, units.

Boilers are marketed as packaged, shop-assembled or field-erected units. Packaged boilers are equipped and shipped complete with fuel-burning equipment, mechanical draft equipment, automatic controls and accessories. They were introduced in the early 1940's and have since gained wide acceptance. Both firetube and smaller watertube units are available in packaged form. Firetube units range in size from below 10^7 Btu/hr to 25 x 10^6 Btu/hr. Ratings of industrial watertube units overlap those of the firetube boilers, with nearly all of the units less than 500 x 10^6 Btu/hr. Generally, above 250 x 10^6 Btu/hr, watertube boilers are field erected.

The principal types of industrial and commercial boilers in use today are the cast iron, firetube and watertube boilers. Table 3-4 gives a breakdown of industrial boiler types by percentage of the entire boiler population. This information is a "best estimate" of the number of watertube and firetube boilers in service based on the total capacity of the type in operation about 1972. Table 3-5 shows a breakdown by fuel capability. Table 3-6 presents estimated installation trends between 1930 and 1990. The major points to be noted from these tables are:

- A higher portion of packaged boilers in the smaller sizes and field-erected boilers in the larger sizes
- More firetube and cast iron boilers in the smaller sizes and watertube boilers in the larger sizes

TABLE 3-4. POPULATION BREAKDOWN BY BOILER TYPES (PERCENTAGE BASIS) FOR ALL COMMERCIAL-INDUSTRIAL BOILERS IN SERVICE IN U.S. IN MID-1974 (Reference 18)

RATED CAPACITY, SIZE RANGE		Commercial			Industrial			
	10^6 Btu/hr or 10^3 lb stm/hr				10-16	17-100	101-250	251-500
	Boiler Horsepower	10-50	51-100	101-300	301-500			
WATER TUBE								
Industrial Type $>10^4$ # Steam/hr					(22)	(79)	(100)	(100)
Packaged					15	55	25	0.5
Field erected					7	24	75	99.5
Commercial Type $<10^4$ # Steam/hr		(6)	(8)	(5)				
Coil		2	3	2				
Firebox		1	1	1				
Other		3	4	2				
FIRE TUBE								
Packaged Scotch		15	20	30	30	10		
Firebox		25	25	30	25	10		
Vertical		1	0.5	nil				
Horizontal Return Tubular (HRT)		5	10	15	20	1		
Misc. (Locomotive type, etc.)		2	3	5	3	nil		
CAST IRON		45	33	15				
MISC. (Tubeless, etc.)		1	0.5	nil				
TOTAL COMMERCIAL-INDUSTRIAL BOILERS		100%	100%	100%	100%	100%	100%	

TABLE 3-5. POPULATION BREAKDOWN BY FUEL CAPABILITY (PERCENTAGE BASIS) FOR ALL COMMERCIAL-INDUSTRIAL BOILERS IN SERVICE IN MID-1974 (Reference 18)

RATED CAPACITY, SIZE RANGE	Commercial			Industrial			
10^6 Btu/hr or 10^3 lb stm/hr				10-16	17-100	101-250	251-500
Boiler Horsepower	10-50	51-100	101-300	301-500			
FUELS							
Oil Only	42	42	40	35	35	30	22
Gas Only	50	50	50	45	35	22	22
Coal Only	2	1	1	3	10	18	22
Oil & Gas and Gas & Oil	5	6	8	16	18	26	23
Oil & Coal and Coal & Oil						0.5	3
Gas & Coal and Coal & Gas						0.5	3
Misc. Fuels (alone or with alternate fuels)	1	1	1	1	2	3	5
Total	100%	100%	100%	100%	100%	100%	100%
OIL							
Distillate, No. 2	95	85	50	10	2	2	2
Resid	(5)	(15)	(50)	(90)	(98)	(98)	(98)
No. 4 and Light No. 5 (No preheat)	4.5	14	30	20	2	nil	nil
Heavy No. 5 and No. 6 (Preheated)	0.5	1	20	70	96	98	98
Total Oil	100%	100%	100%	100%	100%	100%	100%

TABLE 3-6. ESTIMATED TRENDS OF BOILER TYPES (PERCENTAGE BASIS) FOR ALL COMMERCIAL-INDUSTRIAL BOILERS INSTALLED IN YEARS NOTED (Reference 18)

RATED CAPACITY, SIZE RANGE		Commercial												Industrial															
	10^6 Btu/hr or 10^3 lb stm/hr													10-16				17-100				101-250				251-500			
	Boiler Horsepower	10-50				51-100				101-300				301-500															
		'30	'50	'70	'90	'30	'50	'70	'90	'30	'50	'70	'90	'30	'50	'70	'90	'30	'50	'70	'90	'30	'50	'70	'90	'30	'50	'70	'90
WATER TUBE																													
Industrial Type > 10^4 # Steam/Hr														(25)	(17)	(19)	(20)	(94)	(97)	(94)	(90)	(100)	(100)	(100)	(100)	(100)	(100)	(100)	(100)
Packaged														0	2	18	20	0	8	80	89	0	0	80	90	0	0	1	20
Field erected														25	15	1	0	94	89	14	1	100	100	20	10	100	100	99	80
Commercial Type < 10^4 # Steam/Hr		(13)	(15)	(16)	(21)	(13)	(16)	(16)	(12)	(5)	(11)	(10)	(14)																
Coil		nil	2	3	5	nil	3	5	4	nil	3	4	5																
Firebox		8	5	3	1	8	5	3	1	3	3	4	5																
Other		5	8	10	15	5	8	8	7	2	5	2	4																
FIRE-TUBE																													
Packaged Scotch		nil	10	11	10	1	14	22	26	2	21	41	40	nil	35	40	45	nil	2	5	9								
Firebox		6	11	18	20	20	15	17	23	20	30	35	30	20	40	40	35	1	1	1	1								
Vertical		5	6	6	6	3	5	3	2	5	2	nil	nil																
Horizontal Return Tubular (HRT)		5	1	nil	nil	5	2	nil	nil	60	25	1	nil	50	5	nil	nil	5	4	nil	nil								
Misc. (Locomotive type, etc.)		8	5	3	2	5	1	1	1	8	5	2	nil	5	3	1	nil	nil	nil	nil	nil								
CAST IRON		60	50	45	40	50	45	40	36	nil	5	10	15																
MISC (TUBELESS, ETC)		3	2	1	1	3	2	1	nil	nil	1	1	1																
TOTAL COMMERCIAL-INDUSTRIAL BOILERS		100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
		%				%				%				%				%				%				%			

- The expanding role of packaged Scotch firetube boilers for commercial and small industrial applications.

The characteristics of these boilers are described individually below.

3.2.2.1 Cast Iron Boilers – Capacities up to 13.5 x 10^6 Btu/hr (References 8, 9)

One class of domestic and small commercial boilers sold today have heat exchangers that are constructed of cast iron. They are designed for supplying low pressure steam (15 psig maximum) or hot water (40 psig maximum) and are used primarily for air or water heating systems.

These boilers usually consist of an assembly of vertical cast iron sections. Water enters at the bottom of the sections and hot water or steam exits at the top. The products of combustion are conducted through labyrinth passages cast into the sections. The capacity of a sectional boiler may be varied by the addition or deletion of sections.

Cast iron boilers tend to be more expensive than steel firetube boilers, but they are more reliable, longer lived, and require less maintenance. One disadvantage of cast iron boilers is that the sections tend to deform and take a permanent set due to thermal expansion which can lead to flue gas leaks at the joints and around the doors.

Figure 3-16 shows a typical gas-fired cast iron boiler. New units are usually considerably more expensive than forced air systems and are, therefore, now being made only in the larger size ranges of 130,000 Btu/hr and higher. However. old units are still prevalent in the Northeastern and Northcentral regions of the country. The natural gas supply systems on the newly-designed units are quite similar to the warm air furnace, utilizing naturally aspirated burners.

Heat transfer area is governed by the gas side transfer coefficient which is once again limited by the pressure drop requirements of the burners.

Figure 3-17 shows an oil-fired cast iron boiler. Again, although quite common in older homes in the Northcentral and Northeast states, these units are now quite costly and are limited to the larger size ranges. These boilers are similar in some respects to oil-fired warm air furnaces in that they employ a refractory-lined combustion chamber followed by the heat exchange surface. No draft diverter is required.

It has been reported that poor matching of burner and combustion chamber requirements frequently occurs between the burner manufacturer and furnace manufacturer

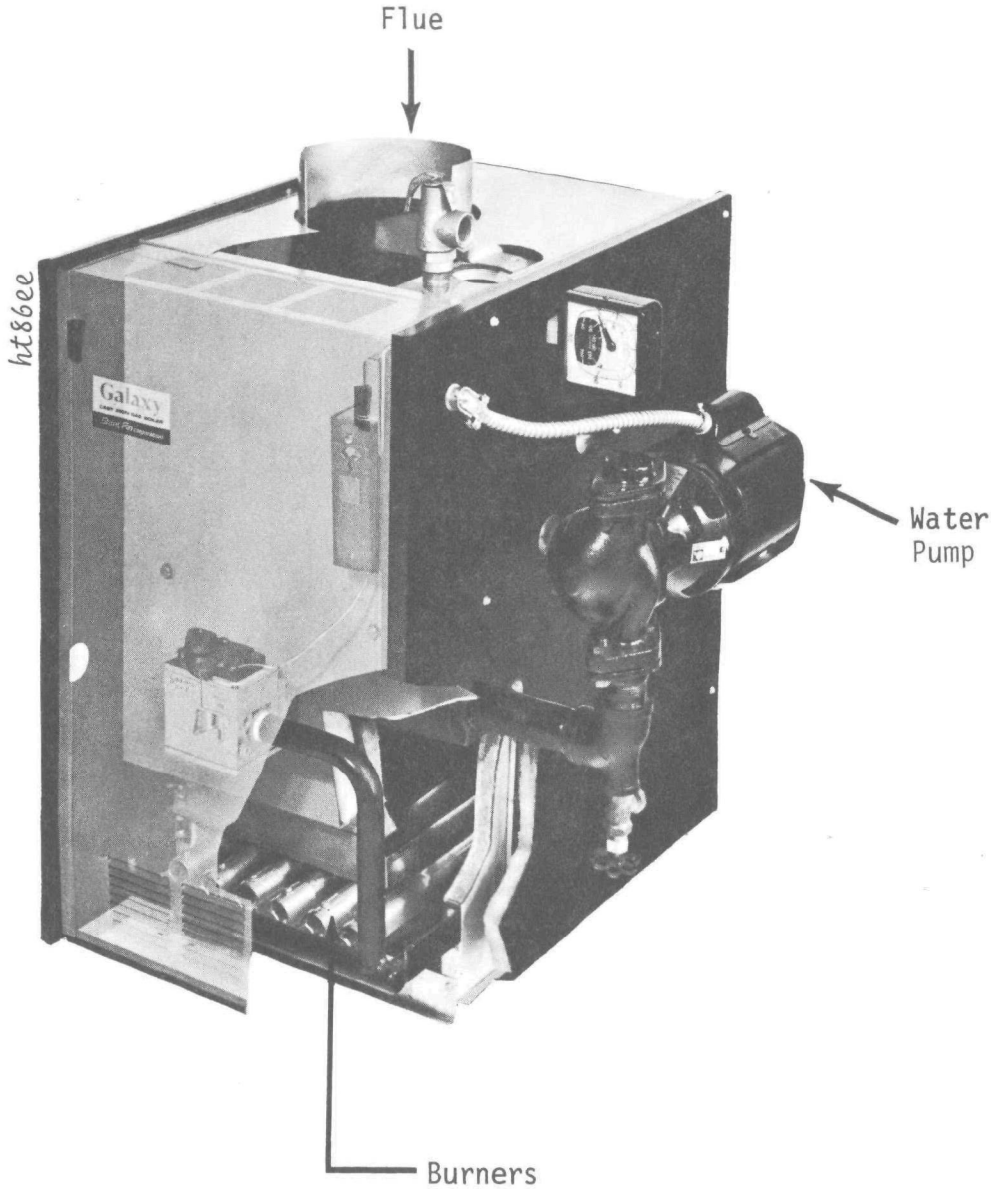


Figure 3-16. Gas-fired cast iron boiler (courtesy of Slant-Fin Corporation).

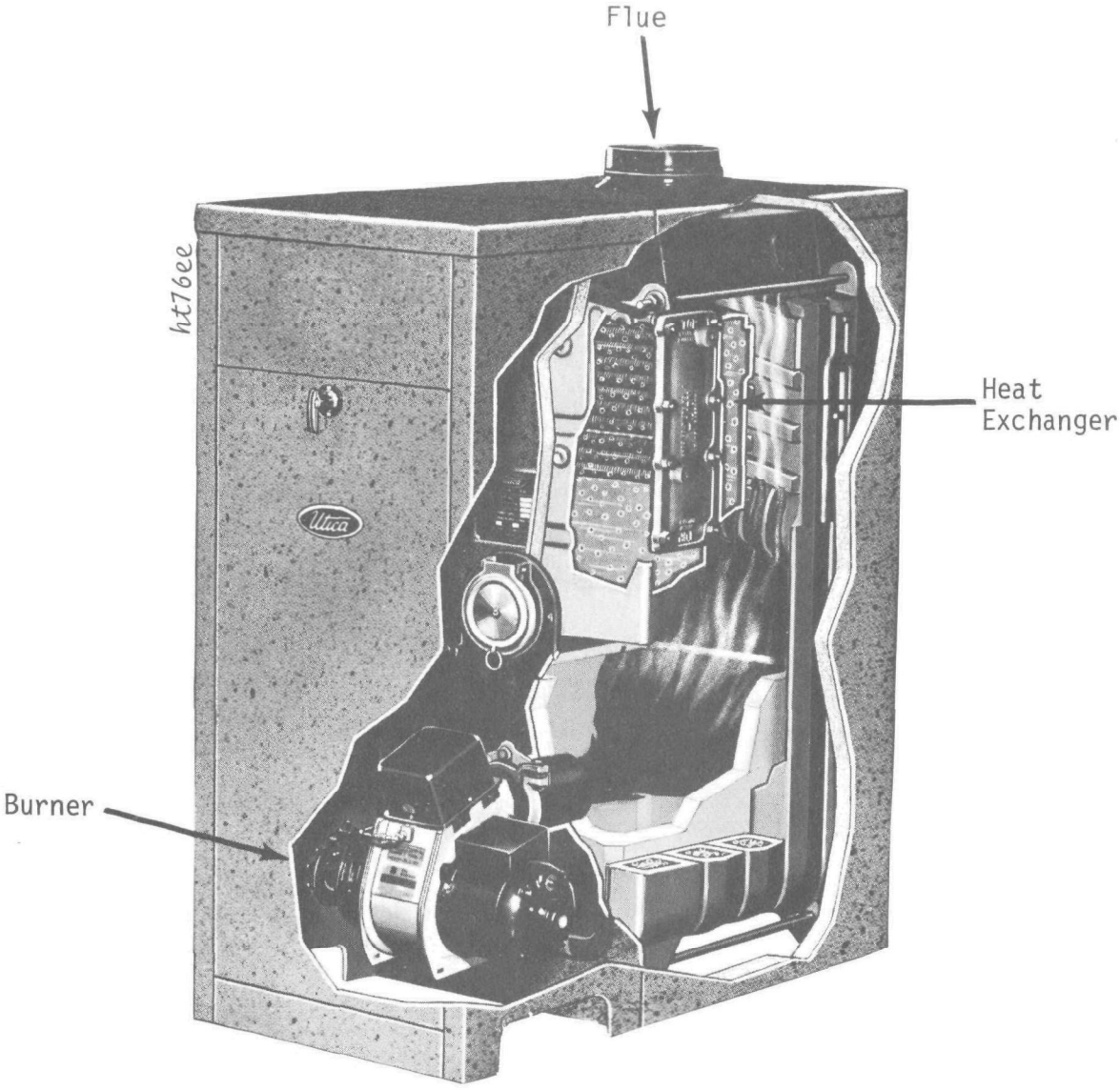


Figure 3-17. Oil-fired cast iron boiler (courtesy of the Utica Radiation Company).

(Reference 19). Typically, considerable leakage of secondary air into the firebox is allowed, which serves to lower the flame temperature. In many cases this is necessary to prevent damage to the combustion chamber, but leakage probably results in overall lower furnace efficiency. Typical operating conditions and design factors for both oil- and gas-fired systems are given in Table 3-7.

Cast iron boilers are rated by The Hydronics Institute (IBR ratings). They must be designed and constructed in accordance with the ASME Code, Section IV, Heating Boilers. The IBR Testing and Rating Code specifies the test conditions and such things as minimum efficiency, percentage of carbon dioxide in the flue gas, flue gas temperature and smoke reading. The ratings cover a range of 48 x 10^3 Btu/hr to 13.5 x 10^6 Btu/hr.

3.2.2.2 Firetube Boilers — Capacities up to 25 x 10^6 Btu/hr (References 9, 16, 17, 20, 21)

In a firetube boiler the products of combustion are directed through the tubes which are submerged in water. The tubes are normally straight and may be horizontal, inclined, or vertical with one or more passes. They are held in place inside the boiler shell by tubesheets at either end of the bundle. Except for small domestic units, many of which are vertical, most units have horizontal tubes. Firetubes have large water storage capacity which effectively dampens wide fluctuations in steam demand. Firetube boilers are more efficient than simple shell boilers because heat is absorbed by the tubes as well as the shell.

All units must be designed in accordance with the ASME, Section I, Power Boiler Code, or Section IV, Heating Boiler Code. Firetube boilers are rated by the Steel Boiler Institute Division of The Hydronics Institute. The ratings are based on tests, the results of which are reviewed by the Institute. There are three general classifications:

Schedule 1: Residential and Commercial

- Natural draft up to 1.8 x 10^6 Btu/hr
- Mechanical draft from 1.8 x 10^6 to 23 x 10^6 Btu/hr

Schedule 2: Commercial and Industrial

- Natural draft up to 18 x 10^6 Btu/hr
- Mechanical draft from 800 x 10^3 to 22 x 10^6 Btu/hr

Schedule 3: Commercial and Industrial

- Mechanical draft up to 23 x 10^6 Btu/hr

(All ratings given are SBI gross output.)

TABLE 3-7. CHARACTERISTICS OF TYPICAL 10^5 BTU/HR GAS- AND OIL-FIRED CAST IRON BOILERS

	Gas	Oil
Recirculating Water Flows (gpm):	3 15	3 15
Excess Air (percent):	30 - 500	30 100
Flue Exit Diameter (inches):	3-1/2 - 5	3-1/2 5
Exit Flue Gas Temp (Upstream Draft Diverter)(°F):	500 - 600	400 - 600
Exit Flue Gas Temp (Downstream Draft Diverter)(°F):	300 400	--
Combustion Chamber Pressure (" W.G.):	0.05 2	0.2
Temperature Rise on Water Side (°F):	10 40	10 - 40
Overall Steady State Efficiency (percent):	75 - 80	70 - 75

Firetube boilers are used where steam demands are relatively small. The principal uses of firetube boilers are for heating systems, for industrial process steam, or as portable boilers. The heating boilers are restricted to 15 psig steam pressure or 30 psig hot water pressure. The power boilers are limited to about 250 psig steam pressure.

Most firetube boilers are now constructed with an internal furnace. The internal furnace is substantially surrounded by water-cooled surfaces. The internal furnace in a firebox firetube boiler, described below, is surrounded by water-cooled surfaces except at the bottom.

There are many firetube boilers in operation which have been constructed with an external furnace, usually of brick construction. The brickset type is not very suitable if water scale or silt is to be expected. The water leg design, normally incorporated into the internal furnace concept, is much better for poor boiler water conditions. Water circulation is enhanced, and suspended solids can be conveniently drained off and the system purged.

The types of firetube boilers are:

- Horizontal Return Tubular (capacities up to 22 x 10^6 Btu/hr)

The horizontal return tubular (HRT) is a two-pass (one under shell, and one through the tubes) power boiler. It was formerly the most popular type of firetube boiler. At present, approximately 10 percent of all commercial-size boilers are HRT. It has the advantage of low installed cost due to its simple setting (brickset). Water circulation, however, tends to be sluggish, contributing to a boiler efficiency of about 70 percent.

- Locomotive (capacities up to 20 x 10^6 Btu/hr)

This is a single pass firetube firebox boiler. It has an internal water jacketed furnace and is used primarily as a portable power source. It requires unusually long firetubes to prevent excessive exit gas temperatures. Water circulation is better than with an HRT boiler, but it is still poor. Boiler efficiencies of slightly less than 70 percent are normal.

- Firebox (capacities up to 20 x 10^6 Btu/hr)

The two major types of firebox boilers are the short and the compact, the former employing two passes and the latter three. These units are constructed with an internal, steel encased, water-jacketed firebox. This design makes for very good circulation and the boiler attains efficiencies of about 80 percent. Since the furnace size is limited, properly matching burner flame length and combustion volume is a critical factor. The greatest advantage of this type of boiler is its efficiency and the minimum floor space required for installation.

- Vertical (capacities up to 3.5 x 10^6 Btu/hr)

Vertical boilers are normally single-pass boilers and are used for power boiler applications and as residential hot water and steam boilers. As a power boiler, its most important use is as a portable steam source for construction work. Boiler efficiencies are about 70 percent. Power boilers are designed for up to 3.5 x 10^6 Btu/hr, and high head room is required for these units. They have a limited steam release surface and since the upper ends of the tubes are steam-cooled, a slow start-up is essential to prevent tube damage by overheating.

- Scotch (capacities up to 25 x 10^6 Btu/hr)

This type of boiler was developed 30 years ago based on the Scotch marine boiler and has since become one of the most popular firetube boilers, as indicated previously in Table 3-4. In addition, Table 3-6 shows an increasing trend toward the use of this boiler type.

Figure 3-18 shows a typical oil-fired Scotch boiler. Its design emphasizes compactness and limited head room requirements, and attains efficiencies of about 80 percent. It is capable of gas, oil, or combination firing. Inside shell diameters are normally limited to about 95 inches and operating pressures to 250 psig, although some units are designed for 600 psig.

Characteristics of a typical Scotch boiler are given in Table 3-8. They can have either two, three, or four passes. The burner flame is contained in an elongated, water-cooled combustion chamber which also acts as the first pass. This characteristic is unique to this type of boiler. The rear wall of the furnace is either refractory-lined ("dry-back") or water-cooled ("wet-back") in the larger versions. Due to the relatively small diameter firetubes and concomitant large pressure drop, they require provision for mechanical draft.

Most Scotch boilers are designed with a minimum amount of heating surface. In most cases, five square feet of heating surfaces are required to produce one boiler horsepower. Improved heat transfer is attained by:

- Keeping the flue gas velocity high throughout the boiler by routing the gas through a steadily diminishing number of constant-diameter firetubes per pass
- The installation of "turbulators" in the firetubes
- Improving water side circulation by internal baffling and other means.

Due to their compact design and multiple tube passes, the packaged Scotch boiler is more difficult to clean than other firetube boilers.

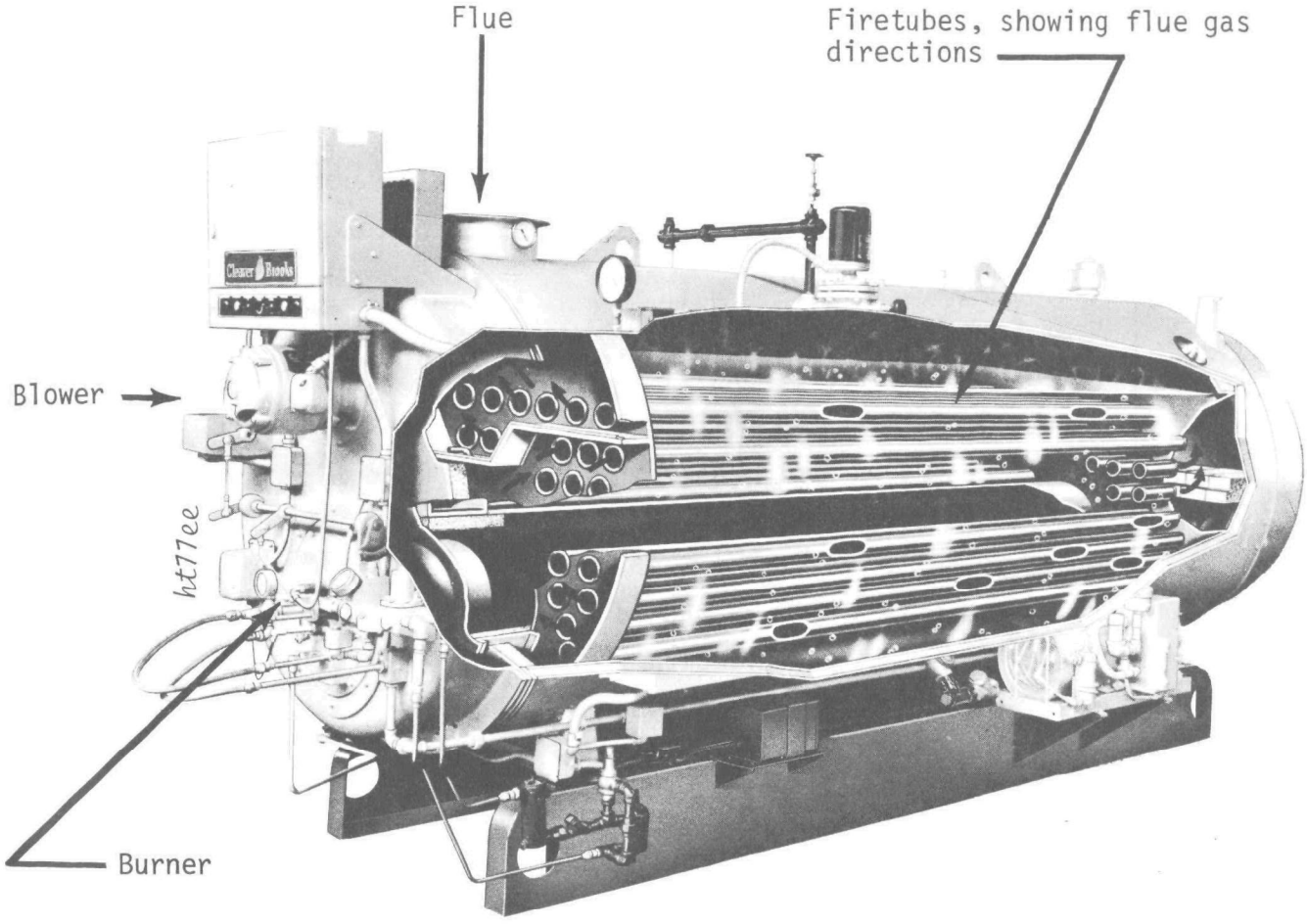


Figure 3-18. 4-pass scotch firetube boiler, (courtesy of the Cleaver Brooks Company).

TABLE 3-8. CHARACTERISTICS OF A TYPICAL 4×10^5 BTU/HR (80 BHP) PACKAGED SCOTCH FIRETUBE BOILER

Excess Air: 5% to 20%
Heat Exchange Area: 400 ft^2
Combustion Chamber Dimensions: D = 1 to 2 ft, L = 10 to 12 ft
Firetube Diameter: 1 to 2 inches
Common Operating Mode: on/off and partial load
Ignition System: Spark
Draft System: Forced
Maximum Gas Side Heat Exchanger Temperature: 900°F
Overall Steady State Efficiency: 80%
Exit Flue Gas Temperature: 450°F to 650°F
Natural Gas Fuel Consumption: 3350 ft^3/hr
Light Fuel Oil Consumption: 24 gal/hr

3.2.2.3 Watertube Boilers — Capacities to 500 x 10^6 Btu/hr (References 9, 16, 21)

Above a capacity of 16 x 10^6 Btu/hr, industrial boilers are almost exclusively of the watertube type. They also dominate the market where design pressure exceeds 150 psig.

Watertube boilers can be either field-erected or packaged. Common sizes for the former type fall between 50 x 10^6 and 500 x 10^6 Btu/hr, while 10^7 to 250 x 10^6 is the capacity range for the latter. Larger packaged boilers, above 450 x 10^6 Btu/hr, are currently being designed but are not yet common.

Since the industrial-sized watertube packaged boiler was first introduced in the early 1940's, they have become very popular. In the period of 1930-1950, almost 95 percent of the 10^7 to 100 x 10^6 Btu/hr units were field-erected. However, it is anticipated that by 1990 about 99 percent of this class will be packaged. Similarly, until 1950 all of the watertube boilers in the range of 100 x 10^6 to 500 x 10^6 Btu/hr were field-erected. Forecasts, such as Table 3-6, indicate that by 1990 about 90 percent of the sizes up to 250 x 10^6 Btu/hr will be packaged.

As the name implies, watertube boilers are designed to flow water through the heat transfer tubes, instead of combustion products as in the firetube design. Because of the smaller diameter pressurized components and the advantage using tubes gives in accommodating expansion, they are better able to contain the pressure and afford an inherently safer design.

Field-erected boilers are usually balanced draft and therefore require both forced draft and induced draft fans. Field-erected boilers are commonly fired with coal, gas and/or oil. Many such boilers exist today but very few new applications have capacities lower than 200 x 10^6 Btu/hr, except for pulverized or stoker coal-fired units. This is because of the packaged boiler's domination of the oil- and gas-fired boiler market, which is in turn due to their low capital cost in the sizes between 12 x 10^6 and 200 x 10^6 Btu/hr.

Packaged watertube boilers are used for gas and oil firing applications. They are not used for coal firing because they have much smaller furnace volumes than are permissible. They are designed to be rail-shipped as a complete, single package with minimum fieldwork. The furnaces are also designed to operate under positive pressure versus the balanced or slightly negative pressure found in coal-fired boilers.

Boiler efficiencies attained in watertube boilers are about 80 percent without heat recovery. Watertube boilers are designed in accordance with the ASME Code and must conform with state and local ordinances.

The two general types of watertube boilers are horizontal-straight and bent tube boilers.

Straight tube boilers are no longer manufactured, having been completely supplanted by firetube boilers in the smaller sizes and bent tube boilers in the intermediate sizes. There are, however, a large number of straight tube boilers still in operation.

The straight tube boiler owed its early popularity to its low draft loss, good tube visibility for inspection and cleaning, ease of tube replacement and low headroom requirements. It is often subject to leaks around the handholes; considerable labor is required to open a sectional header type for inspection; and it has poor water distribution and low circulation rates.

These boilers are normally baffled to create two or three flue gas passes across the water tubes. The tubes are grouped into sections and expanded at the ends into headers. The headers are connected to the drum by downcomers for supplying water to the tubes and by risers for discharging water and steam from the tubes. In some models steel saddles connect the header to the drum. The "horizontal" tubes are inclined at an angle of 5 to 15 degrees for natural circulation of the water. The flue gas is normally moved by a forced circulation fan.

Horizontal straight tube boilers can be subdivided as follows:

- Type of Header

  Box Header

  This is a box-like uptake or downcomer which forms a tube sheet and handhole plate. It is normally braced with staybolts and gives better circulation than a sectional header.

  Sectional Header

  This is formed from many individual forged steel headers. Each header has a riser and a downcomer which connect to the steam drum. The lowest header is known as the mud drum. It acts as a collecting chamber for the sediment, solids or mud, in the boiler water.

- Type of Drum

  Long Drum

  The long drum is located longitudinally and parallel to the horizontal tubes. Since the riser and downcomer (one or many depending on the header type) must be connected to the long drum circumferentially, there is a limit to the number of headers or tubes that can be connected to a single drum. Multiple drums can be used if required. The long drum design is used for units rated from 5×10^6 to 80×10^6 Btu/hr at pressures of 160 to 325 psig.

Cross Drum

The cross drum is mounted at right angles to the tubes. The drum is located above the downcomer with the steam and water risers connected to the drum in longitudinal rows. It provides better steam distribution in the drum than the long drum design and presents no problems in increasing capacity by increasing the unit width. It is used for capacities of 5 x 10^6 to 500 x 10^6 Btu/hr and pressures up to 1450 psig.

- Portable Firebox Boiler

  This is a straight watertube boiler built with a steel encased, bricklined firebox with water cooled walls. The water and steam are contained in an enclosure above the crownsheet. It is designed for 1 x 10^6 to 18 x 10^6 Btu/hr and 15 psig to 250 psig pressure.

Horizontal bent tube boilers, the other major type of watertube boiler, are classified by the number of drums, headroom, and tube configuration, the latter of which is the most important distinguishing factor. The most common tube configurations are:

- O-type with two drums, one upper and one lower, centrally located
- D-type, a modification of the O-type, with the two drums located to the side (top and bottom) of the tube bundle (Figures 3-19 and 3-20)
- A-type which has three drums, two lower drums and an upper, centrally located drum for steam-water separation.

In the bent tube boiler each tube is connected to the steam drum and to at least one lower drum or header. The tubes enter a drum radially and are designed to allow for the anticipated expansion. The furnace is of the waterwall type backed up with refractory. The tubes, which form the furnace waterwall, are an integral part of the boiler. The steam drum contains internals, such as separators and cyclones, to facilitate steam-water separation. Bent tube boilers have the advantage of great design flexibility making them readily adaptable to space limitations by either extending their length or, more practically, the width. They provide good accessibility for inspection and cleaning, which normally entails mechanical cleaning from inside the steam drum.

Most packaged units are oil-, gas- or combination-fired, although there are some coal-fired packaged units. The furnace wall cooling tubes are usually oriented vertically. Vertical furnace tubes are particularly desirable on coal-firing since they are less susceptible to slag adherence.

Heat recovery from the flue gas is practical and often desirable with bent tube boilers, particularly in the intermediate and large sizes. This may consist of

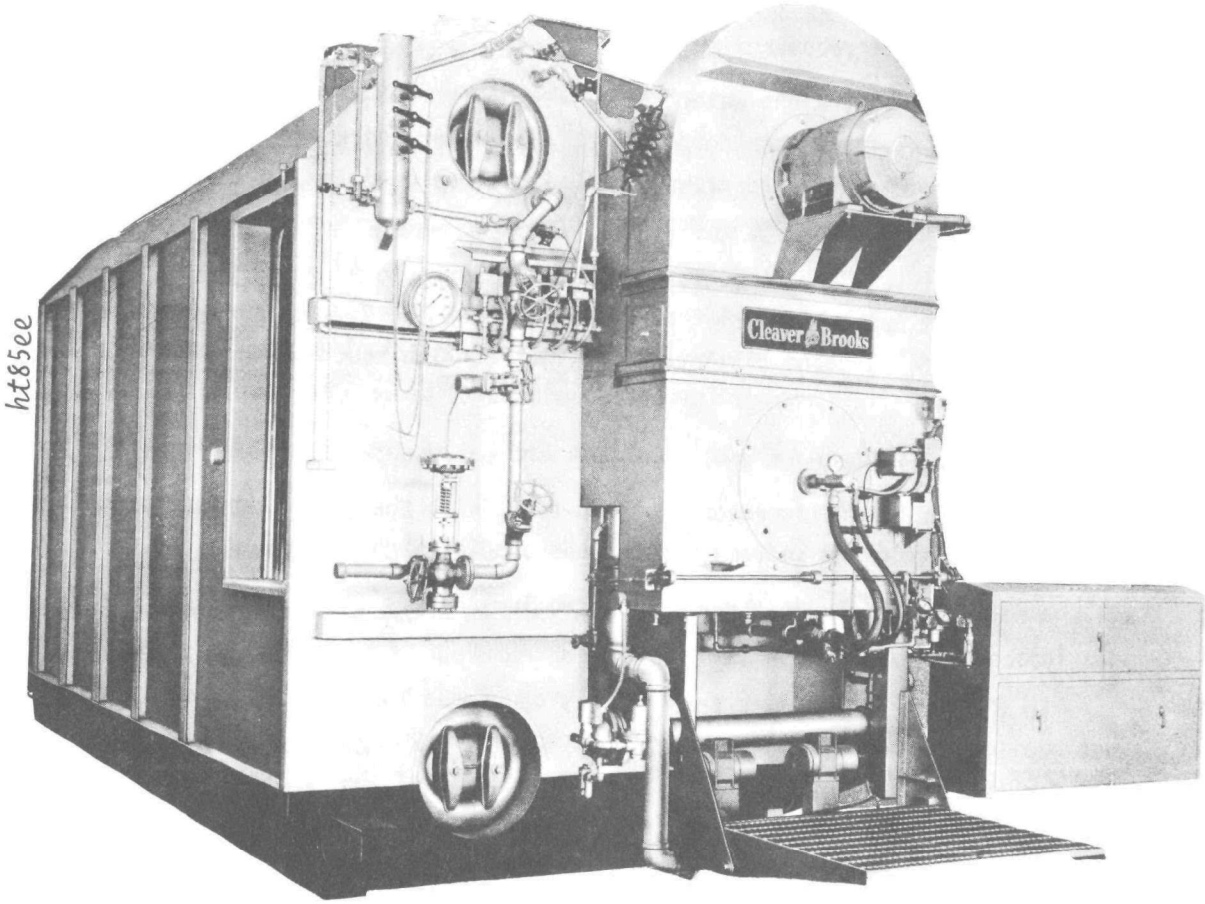


Figure 3-19. 80 x 10^6 Btu/hr combination-fired packaged watertube, D-type boiler (courtesy of the Cleaver-Brooks Co.).

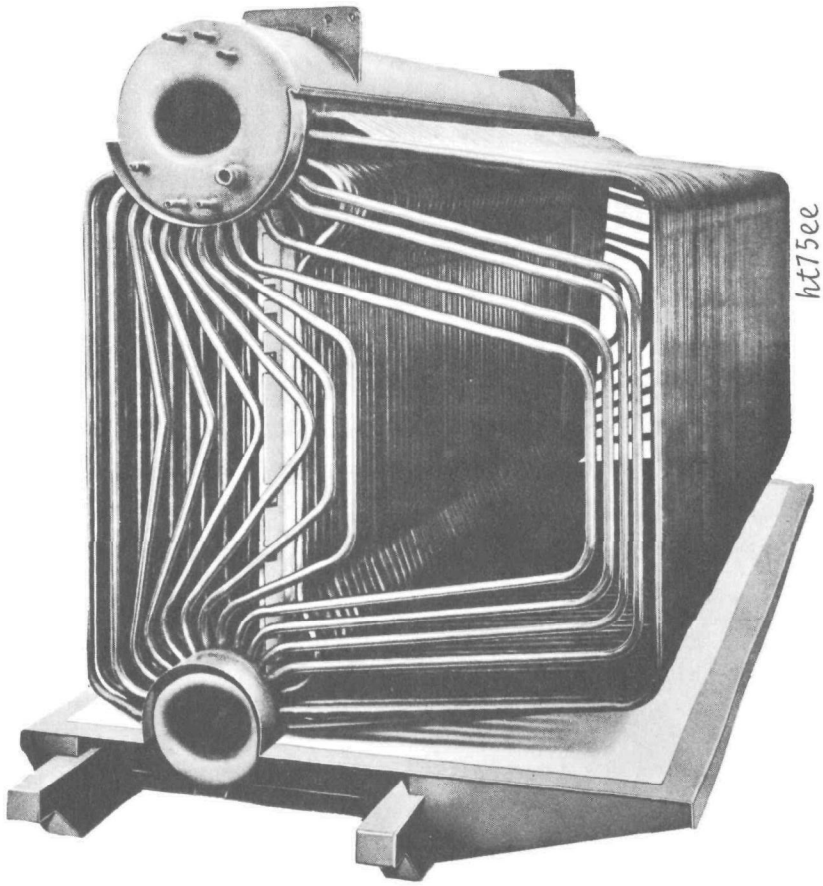


Figure 3-20. D-type bent tube configuration (courtesy of the Cleaver Brooks Co.).

an economizer, which preheats feedwater, an air preheater, to heat combustion air, or both. These may be internally mounted in the boiler, but are more commonly external to the boiler.

The larger industrial-size, field-erected watertube boilers (> 250 x 10^6 Btu/hr) are identical to utility boilers used for generating electrical power. These multi-burner facilities are available in the tangentially-fired design as well as the wall-fired type found in the smaller units.

3.3 AIR POLLUTANT EMISSION CHARACTERISTICS

The preceding subsections of Section 3 described the equipment and operating characteristics of residential, commercial, and industrial combustion-generated air pollution sources. Warm air furnaces and boilers were included in this category. The following discussion will center on a characterization of the pollutant emissions from these sources as well as the conventional means by which such emissions have been reduced.

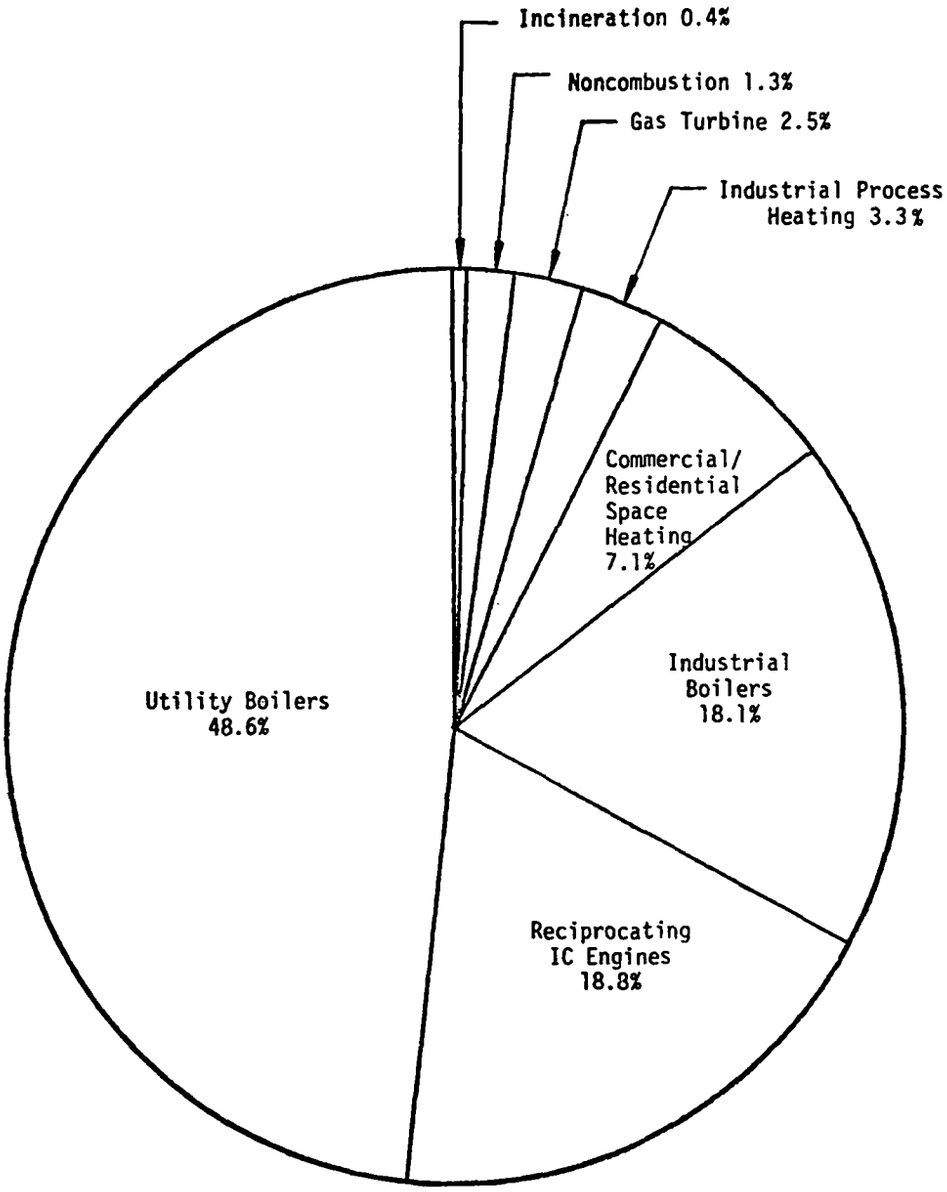
3.3.1 Commercial and Residential Sector

As shown previously in Table 3-1, natural gas and distillate oil-fired heating equipment account for about 80 percent of the residential heating units in the U.S. The actual contribution from fuel combustion in this equipment to the total national air pollutant loading (summation of mass of particulate, SO_x, NO_x, CO, and unburned hydrocarbons) is unclear. One investigator estimated that air pollution from the combination of residential and commercial heating sources constitutes about 10 percent of the national total (Reference 22). This figure, however, may be outdated; the source paper was published in 1964. Fuel usage and emission factors were the basis for this estimate.

Another data dource, the National Emission Data System (NEDS), does not compile information for sources that emit less than 25 tons/year of any pollutant. This limitation causes the exclusion of residential heating from consideration. From all indications, however, this contribution to the nation's total emissions probably falls in the 1 to 10 percent range.

The emissions from commercial and residential space heating for one pollutant species, oxides of nitrogen, have been fairly well established by recent studies. The 1972 data shown in Figure 3-21 gives an estimate of 826,800 tons/year (7.1 percent of total) as the contribution from commercial and residential heating (Reference 23).

The impact of these emissions is greater than a simple weight percent would indicate, however, since the emissions occur in regions of high population density, they are emitted at essentially ground level, and they are seasonal in nature so that there is a concentration of emissions within a 3- to 5-month time span. For these reasons the U.S. Environmental Protection Agency has instigated an emission reduction R&D program.



Estimated NO_x Emissions Tons/Year	Source
5,670,000	Utility Boilers
2,189,000	Reciprocating IC Engines
2,108,000	Industrial Boilers
826,800	Commercial/Residential Heating
390,200	Industrial Process Heating
291,000	Gas Turbines
149,000	Noncombustion
41,000	Incineration
11,665,000	TOTAL

Figure 3-21. Summary of 1972 stationary source NO_x emissions.

To aid in the effort of reducing emissions from this sector, the EPA is conducting research on the reduction of air pollution from various types of residential heaters. Early work was performed on an experimental furnace to determine the basic reduction parameters. Later, commercially available equipment was investigated. The most recent published work from this project appeared in 1974 (Reference 24).

This study, which concentrated on an oil-fired warm air furnace, showed that residence time, flame retention devices, maintenance, and excess air are major factors in the control of emissions, the latter being the dominant one. Emissions of CO, UHC, smoke, and particulates pass through a minimum as excess air is increased from stoichiometric, as shown in Figure 3-22. It is observed that both thermal efficiency and NO emissions behave in the opposite manner: as excess air is increased, they pass through maximum points.

At stoichiometric ratios ranging from 1.2 to 1.5, the NO, HC, and CO emissions from various types of gas-fired burners averaged 0.104, 0.0032, and 0.051 g/10^6 cal input, respectively. Emissions of the same species from equivalent size oil burners were comparable to these levels, with particulates being a problem only from this fuel. Compared to other sources of air pollution, the levels of UHC and CO from properly adjusted furnaces are very low.

Combustion chamber material was found to affect all emissions. Furnaces with steel-lined chambers required higher excess air levels to reach optimum emission levels, thus reducing efficiency. The shape of the combustion chamber had little effect on pollutant generation.

As mentioned in Section 3.2.1 of this report, the on/off mode is the outstanding operating characteristic of warm air furnaces, and is the major efficiency reducing factor. The aforementioned EPA study has since identified the importance of cyclic-based emissions. Work on a model residential heating system indicated that the sizeable peak emissions measured during ignition and shutdown can account for most of the total emissions.

CO and UHC emissions peak at ignition and shutoff as shown qualitatively in Figure 3-23. HC concentration drops to insignificant levels between the peaks, while CO emissions tend to flatten out at a measurable level. Figure 3-24 shows that particulate matter continuously tapers off after the ignition-induced peak. Figure 3-25 shows that, after an initial peak, the NO emission level continues to rise. The operating time of most domestic burners seemingly is not long enough for NO to reach equilibrium levels.

The transient emissions are caused mainly be variations in the combustion chamber temperature. At ignition, a cold refractory will not support complete combustion, producing peaks of CO, UHC, and smoke. These peaks could be eliminated by

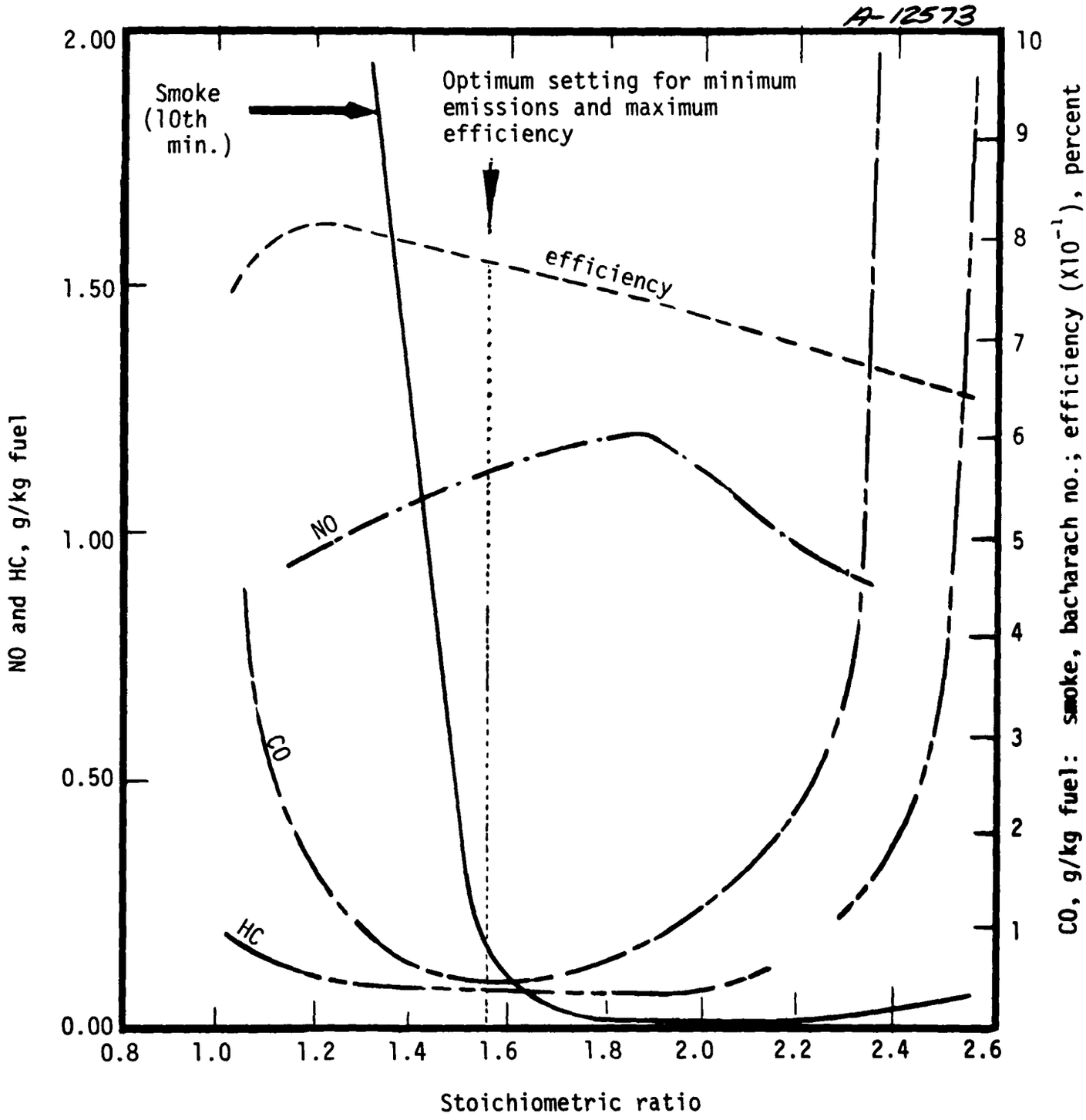


Figure 3-22. General trend of smoke, gaseous emissions, and efficiency versus stoichiometric ratio.

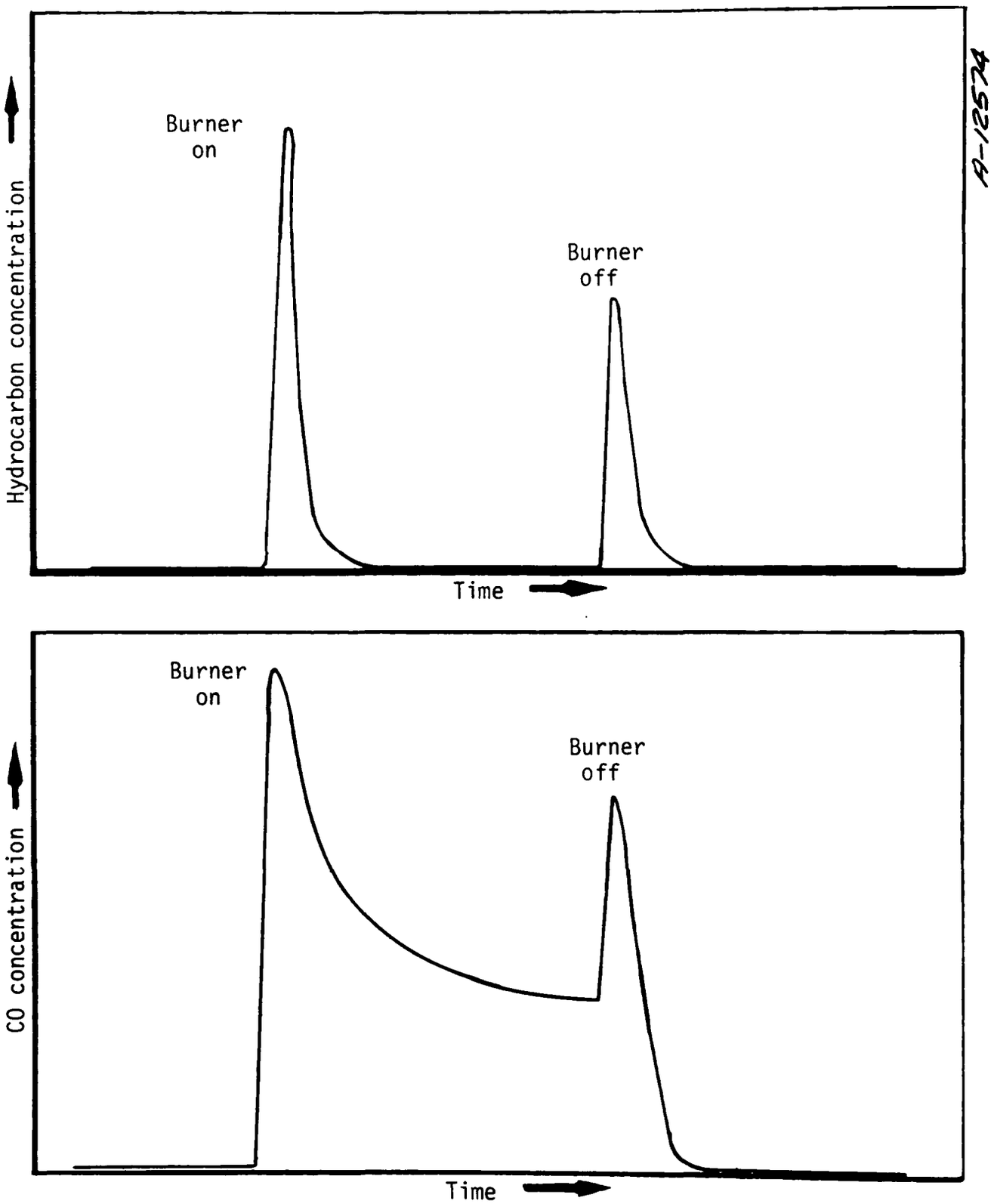


Figure 3-23. Hydrocarbon and carbon monoxide trends during cycle.

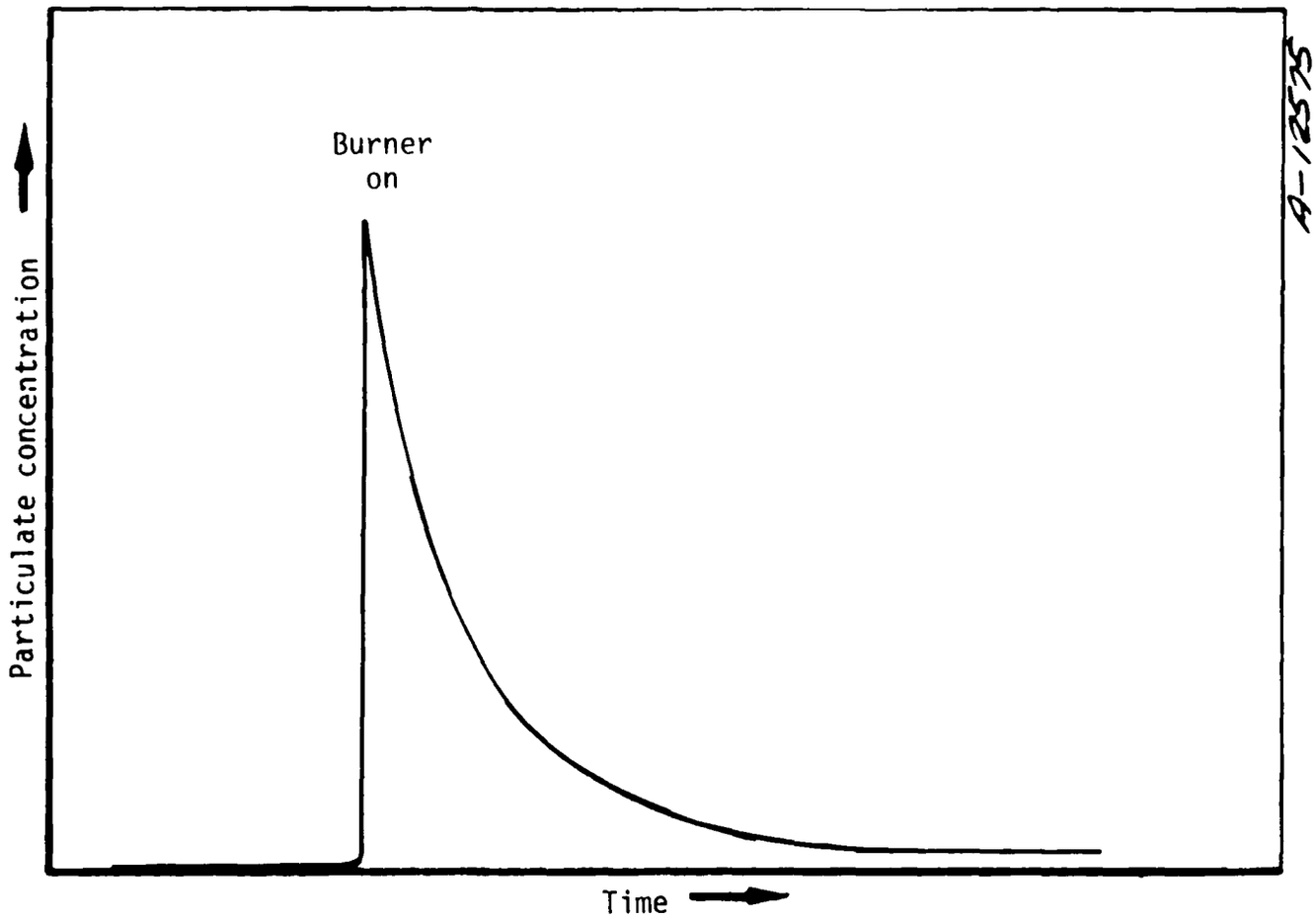


Figure 3-24. Particulate trends during cycle.

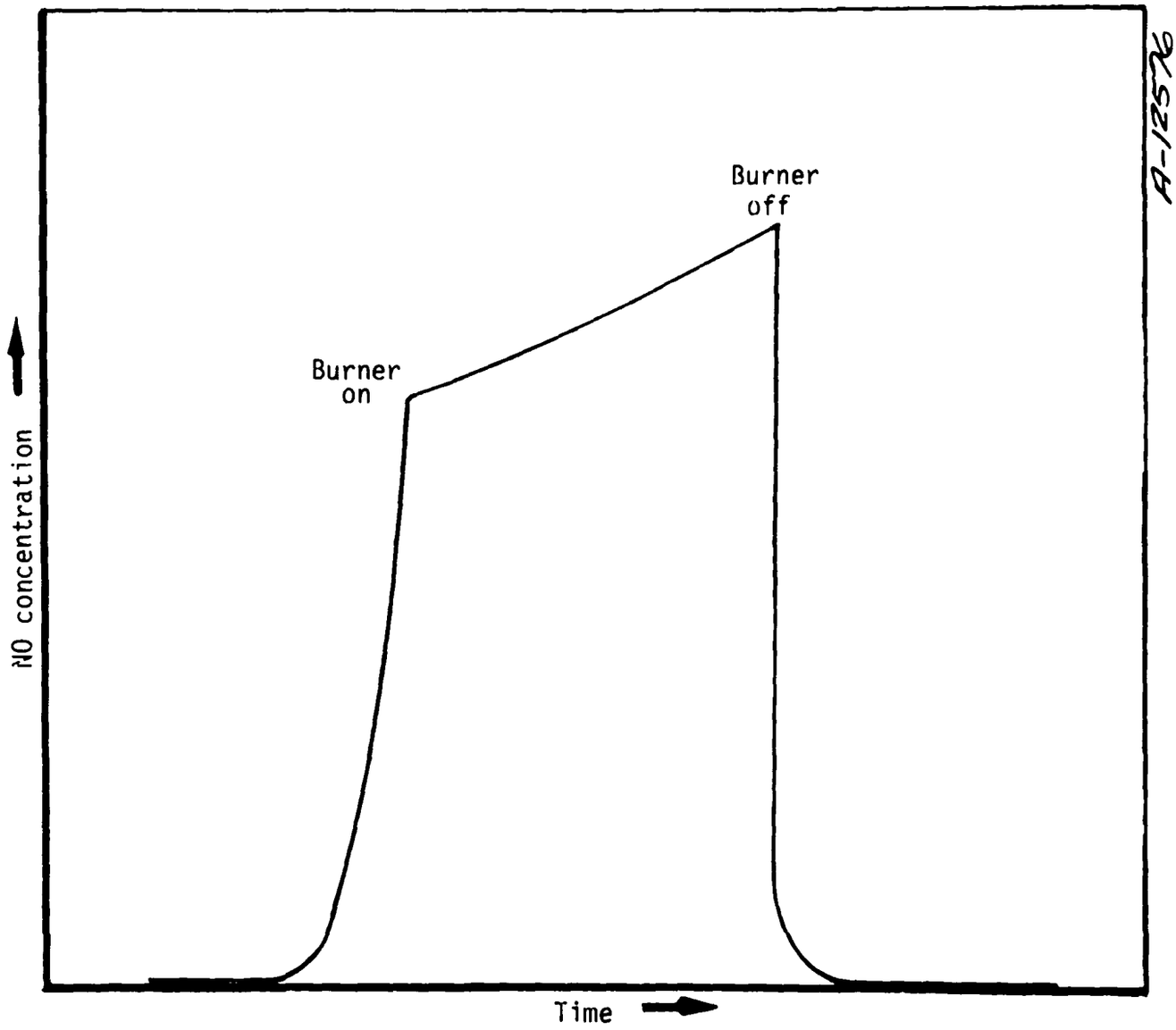


Figure 3-25. Nitric oxide trend during cycle.

keeping the refractory warm during the off-time by a pilot or modulating burner. NO emissions show a continuous increase due to the steadily rising temperature of the combustion chamber walls.

It is important to recognize that cyclic-based emissions mainly affect emissions of CO and UHC, both of which are very low for oil burners in any case. It is hoped that particulate emissions can be reduced by new burner designs.

3.3.2 Industrial Sector

Combustion sources of air pollution in this sector include mainly firetube and watertube boilers in the range of 10^7 to 500 x 10^6 Btu/hr capacity. These boilers contribute the largest portion of air pollution from this sector since, as indicated in Table 3-5, they are fueled mainly by residual oil and coal.

Information on the total pollutant mass emissions from industrial boilers is scarce. As in the case of residential and commercial heating, however, total NO_x emissions have been fairly well documented for this type of equipment and are shown in Figure 3-21. Industrial boilers accounted for 2,108,000 tons/year, or 18.1 percent of the total, of NO_x in 1972.

The most thorough investigation of emissions from industrial boilers was conducted recently by Cato, et al., in 1974 (Reference 25). From tests of a sample of 50 industrial boilers ranging in capacity between 18 x 10^6 and 500 x 10^6 Btu/hr, a wide variation in pollutant concentration was discovered. In the "as found" condition, CO varied from 0 to 1000 ppm, UHC from negligible to about 600 ppm, SO_x from negligible to 1800 ppm, and solid particulates from 0.001 (gas) to 2.8 lb/10^6 Btu fired (coal).

The major objectives of the study were to characterize NO_x emissions from these boilers, as well as to identify the effective reduction methods. Table 3-9 summarizes the effects of various parameters on these NO_x emissions. In general, it was found that typical, existing industrial boilers have limited flexibility to allow combustion modifications for reducing NO_x.

Table 3-10 gives the average NO_x emissions from all the boilers measured under both baseline and low NO_x conditions. The largest degree of success was achieved on natural gas-fired units. For all fuels, however, the most effective techniques were off-stoichiometric combustion, excess air reduction, and burner adjustment.

The reduction of other pollutants from industrial boilers can be achieved by other methods. Fuel switching is an effective means for reducing particulates and SO_x, new burner design for particulates (and NO_x) and burner adjustment and furnace maintenance for reduction of CO and UHC concentrations.

TABLE 3-9. SUMMARY OF THE EFFECT OF VARIATIONS IN PARAMETERS AND OPERATING CONDITIONS ON NO_x EMISSIONS FROM INDUSTRIAL BOILERS

	Natural Gas Fuel	Oil Fuel	Coal Fuel
Burner Heat Release Rate (Btu/hr/burner)	• NO_x emissions increase with increasing burner loading • The relationship between NO_x and burner loading depends on combustion air temperature; the higher the air temperature the more important the burner loading	• NO_x emissions increase with increasing burner loading	• NO_x emissions increase with increasing burner loading
Excess Oxygen	• NO_x emissions not affected by O_2 level for ambient temperature combustion air • NO_x emission decrease with decreasing O_2 level for preheated combustion air	• NO_x emissions decrease with increasing O_2 level • Number 2 oils not as sensitive to O_2 level as No. 5 and 6 oils • Combustion air temperature does not affect NO_x-vs.-O_2 relationship as found with natural gas	• NO_x emissions decrease with decreasing O_2 level and are more sensitive than for either oil or natural gas fuel • Combustion air temperature does not affect NO-vs.-O_2 relationship as found with natural gas
Furnace Heat Release Volume (ft^3/Btu/hr)	• Not an important consideration for natural gas fired boilers	• NO_x emissions decrease as furnace heat release volume increases • Relationship does not appear to be dependent upon oil grade	• NO_x emissions decrease as furnace volume increases • The furnace volume required for carbon burnout depends on the design of the coal burning equipment which may also influence the NO_x-vs.-volume relationship
Combustion Air Temperature	• NO_x emission increase with increasing combustion air temperature • Burner loading influences the relationship between NO_x emissions and air temperature • NO_x emissions for the larger burners increases at a greater rate with increasing air temperature than for the smaller burners	• Not an important consideration for oil fired boilers	• Not an important consideration for coal fired boilers
Fuel Nitrogen Content	Does not apply (except in some waste fuel streams)	• NO_x emissions increase with increasing fuel nitrogen content • The average conversion ratio was 46% (590 ppm/1% fuel N) and the average thermal NO_x was 105 ppm	• Fuel nitrogen content of the coals did not vary significantly and no correlation could be made of nitrogen content with NO_x emissions
Fuel Firing Method	• Nearly all natural gas-fired boilers tested had multiple ring burners • The design of the ring burner is believed to affect NO_x emissions but data are not available from this program to support this thesis • Data from other programs show that air-rich operation of gas spud burners tend to produce higher NO_x emissions than do ring burners	• When properly atomized, the type of oil atomizer did not affect NO_x emissions (air, steam or mechanical) • The operating conditions for a particular atomizer such as fuel oil temperature, atomizer air pressure, etc., at the burner did affect NO_x emissions	• Underfed stokers had the lowest NO_x emissions, a cyclone combustor had the largest NO_x emissions, and spreader stoker and pulverized coal burners had similar intermediate NO_x emissions

TABLE 3-9. CONCLUDED

	Natural Gas Fuel	Oil Fuel	Coal Fuel
Off-Stoichiometric Operation	• NO_x emissions were successfully reduced by burners out of service and air flow adjustments which effect burner stoichiometry • Air register and damper tuning was necessary to avoid excessive CO and hydrocarbons emissions • Successful application of this technique requires sufficient test time to empirically determine boiler adjustments to allow operation at low overall excess O_2 with a burner out of service. The time available in Phase I was insufficient to arrive at optimum adjustments	• NO_x emissions were successfully reduced by burners out of service and air flow adjustments which effect burner stoichiometry • Air register tuning was necessary to reduce smoking which limited excess O_2 levels and NO_x emission reductions • Successful application of this technique requires sufficient test time to empirically determine boiler adjustments to allow operation at low overall excess O_2 with a burner out of service. The time available in Phase I was insufficient to arrive at optimum adjustments • Conversion of fuel nitrogen to NO_x is also reduced by O/S operation. Other studies show reductions in conversion from the normal 40 to 50% to 20 to 30%	• NO_x emissions were successfully reduced by burners out of service and air flow adjustments which effect burner stoichiometry • Air register tuning was necessary to reduce smoking which limited excess O_2 levels and NO_x emission reductions • Successful application of this technique require sufficient test time to empirically determine boiler adjustments to allow operation at low overall excess O_2 with a burner out of service. The time available in Phase I was insufficient to arrive at optimum adjustments • Conversion of fuel nitrogen to NO_x is also reduced by O/S operation. Other studies show reductions in conversion from the normal 40 to 50% to 20 to 30%

TABLE 3-10. AVERAGE NO_x EMISSIONS FROM INDUSTRIAL BOILERS

Fuel	Baseline Operation		Low NO_x Operation		Average % NO_x Reduction
	NO_x (ppm)	O_2 (%)	NO_x (ppm)	O_2 (%)	
Coal	442	9.0	385	6.3	15
#2 Oil	126	5.7	115	2.8	10
#5 Oil	295	5.8	254	4.9	15
#6 Oil	275	6.0	230	5.4	20
Natural Gas	131	5.0	105	5.3	25

3.4 CONCLUSIONS

The following discussion gives the principal conclusions drawn from the preceding characterization of area sources and the impact these conclusions will have on a catalytic combustion redesign or retrofit effort:

- The most popular means of heating homes and commercial buildings is through the use of central, forced warm air, gas- or oil-fired furnaces. Initial catalytic oxidation retrofit or redesign efforts should be directed toward this type of equipment.
- There is very little variation in the design and cost (for the same capacity) among manufacturers of gas- or oil-fired domestic-size warm air furnaces. This is due mainly to the extremely competitive nature of the furnace market.
- The cooling coils for air conditioning installed on many warm air furnaces apparently will not impact retrofit possibilities.
- Commercial-size, roof-mounted furnaces appear to offer advantages to a redesign or retrofit program due to their larger interior volume as well as higher-quality materials of construction.
- The design of these warm air furnaces is based mainly on empiricism and prototype development, experience, and testing. No theoretical barriers appear to exist to a catalytic redesign or retrofit program.
- The excess air levels in a warm air furnace are necessarily greater than 20 percent in order to keep the heat exchanger temperature below 900°F. A catalytic redesign or retrofit should be aimed at achieving sufficiently low combustion temperatures by means other than increasing excess air.
- The fuels supplied to residential and commercial heating equipment, including warm air furnaces and cast iron boilers, are predominantly natural gas and distillate oil. This will be an asset to new catalytic oxidation concepts since they require clean fuels.
- Emissions of CO, UHC, and NO_x are observed from gas-fired residential heating units, all of which can be eliminated by a properly designed catalytic combustor. Particulates and SO_x are normally not present in the effluent from these sources.
- Cyclic-based emissions from oil-fired warm air furnaces can, in many cases, account for most of the CO, UHC, and smoke emissions. In contrast, emissions of NO_x increase steadily during the on-cycle. The design of a substitute catalytic concept should be aimed at eliminating these ignition and shutdown peaks, as well as the reduction in efficiency caused by the on/off mode of operation.

- Scotch firetube industrial boilers appear to offer some advantages to a catalytic retrofit effort due to their unique internal, first pass furnace volume. Strategies for retrofitting or redesigning watertube boilers are less obvious.
- Although the initial attempt to characterize area sources during the present study was successful, further effort should be directed toward compiling more detailed design and operating information on typical units, including industrial process furnaces, before initiating a catalytic redesign or retrofit program.

SECTION 4

RECENT DEVELOPMENTS IN CATALYTIC FUELS OXIDATION CONCEPTS

In this section, the recent developments in catalytic fuels oxidation concepts are discussed in the following order:

- General considerations, where the catalytic combustion process and some of the important system characteristics are described
- Characteristics and properties of catalyst materials, where a review of the support, wash coat, and catalyst materials presently available for use in catalytic combustion is presented
- Existing applications of catalytic combustion, where proven catalytic combustion applications are described
- Research programs in catalytic combustion, wherein current on-going research programs are described
- Conclusions

This discussion provides the background information to assess the state-of-the-art in catalytic combustion.

4.1 GENERAL CONSIDERATIONS

During steady operation, the catalytic combustion process can be described as follows:

- The premixed gases are introduced at a velocity in excess of the flame speed associated with the equivalence ratio and preheat of the mixture (to avoid flashback).
- These gases diffuse to the surface — and presuming the catalyst surface is at sufficient temperature (related to self-ignition temperature) — will react on the active sites at and within this surface.
- Heat will be generated and conducted, radiated or convected away. A portion will serve to heat the bulk gases in the main flow.

- The bulk gases will commence to react in the gas phase as initially sustained by the heat input from the catalyst surface. This combustion is related to the observed light-off in some systems.
- As the combustible gases are consumed, radiative and conductive heat removal will reduce the surface and gas phase temperatures and reactions will slow. Under some conditions this can result in extinction.

The overall success of a catalytic system in reducing hydrocarbons and CO to low levels depends, somewhat ironically, on gas phase reactions. A reduction of unburned hydrocarbons, for example, to low ppm levels probably cannot be achieved by purely surface reactions, even under the assumption of perfect catalytic reaction rates. Under such conditions, the reaction rates are limited not by chemical kinetics but by the rate of mass transfer of the reactants from the bulk gas to the catalyst surface (Reference 26). This rate is fairly low. Idealized analysis identifies a requirement of 2.3 "transfer units" for each order of magnitude reduction of a gas phase combutible by surface contact, and a required length of approximately 100 hydraulic radii for each transfer unit. This would imply far too lengthy a system for most purposes.

Therefore, system design must ensure that gas-phase reactions occur to reduce combustibles to low levels. For most conjectured applications, the temperatures and concentrations in the bulk gas are within the range where gas-phase reactions occur at significant rates. For example, in automative catalytic converters at certain. operating conditions, gas-phase oxidation of hydrocarbons in the bulk stream can produce a net increase in CO (additional flow length is required to provide for further gas-phase and surface reactions to eliminate the CO).

An evaluation of a catalytic combustion system involves a determination of the important operating characteristics of the system. These characteristics include:

- Ignition requirement
- Flashback potential
- Lean and rich flammability limits
- Maximum specific heat release
- Heat removal mechanisms
- Combustion efficiency
- Pollutant potential

These characteristics are discussed in greater detail below.

4.1.1 Ignition Requirement

An important factor for evaluating catalyst performance is the ability of the fuel-air mixture to ignite in the presence of a catalyst. The ignition temperature can be determined by comparing the temperatures of the air-fuel mixture both upstream

of and in the catalyst bed, and beginning with an air temperature well below the self-ignition limit. As the air temperature is raised, an increase in the catalyst bed temperature over that upstream of the bed will indicate the onset of ignition.

The "light-off" temperature is determined by interpreting the unburned hydrocarbon measurements. At the beginning of a test the amount of unburned hydrocarbons will be at a maximum (100 percent). At some point as the inlet air temperature is increased ignition will occur and the amount of unburned hydrocarbons will decrease. The "light-off" temperature can be defined as that inlet temperature at which the catalyst has appreciable activity with regard to oxidizing the reactants. "Appreciable activity" is typically defined as either 50 or 90 percent conversion of hydrocarbons to oxidized species.

Ignition and light-off temperatures are functions of:

- Catalyst (material, area, substrate composition)
- Catalyst bed geometry
- Fuel type
- Space velocity
- Air/fuel ratio
- Pressure
- Dilution

An example of the effect that the catalyst material can have on the ignition temperature of a fuel is shown in Figure 4-1. For this automotive application (Reference 27) a noble metal catalyst exhibits a higher ignition temperature than a base metal catalyst. Light-off temperatures, though, are much lower with the noble metal catalyst when defined at rates of conversion of 60 percent or greater. An example of possible effects due to variations in catalyst content, chemical composition of the substrate, and substrate surface area is shown in Figure 4-2. This figure is from Reference 28 which studied variations of catalysts and substrates on the oxidation of n-heptane. In this case, minimal effect on light-off temperature was found.

Typical catalyst bed geometry effects on light-off temperature are shown in Figure 4-3. This study of n-heptane fume abatement (Reference 29) illustrates that a catalyst on a crossflow ceramic honeycomb substrate has a lower "light-off" temperature than the same catalyst on spherical pellets. Ignition temperature appears to be about the same.

The type of fuel combusted will also affect the catalyst ignition and light-off requirements. Figure 4-4 shows the effect of various fuels on the ignition and light-off temperatures of a palladium catalyst on an alumina substrate. Notice that methane, which is a low-carbon number molecule, has the highest light-off temperatures. It has been concluded that light-off temperature varies inversely with the carbon number of the fuel used.

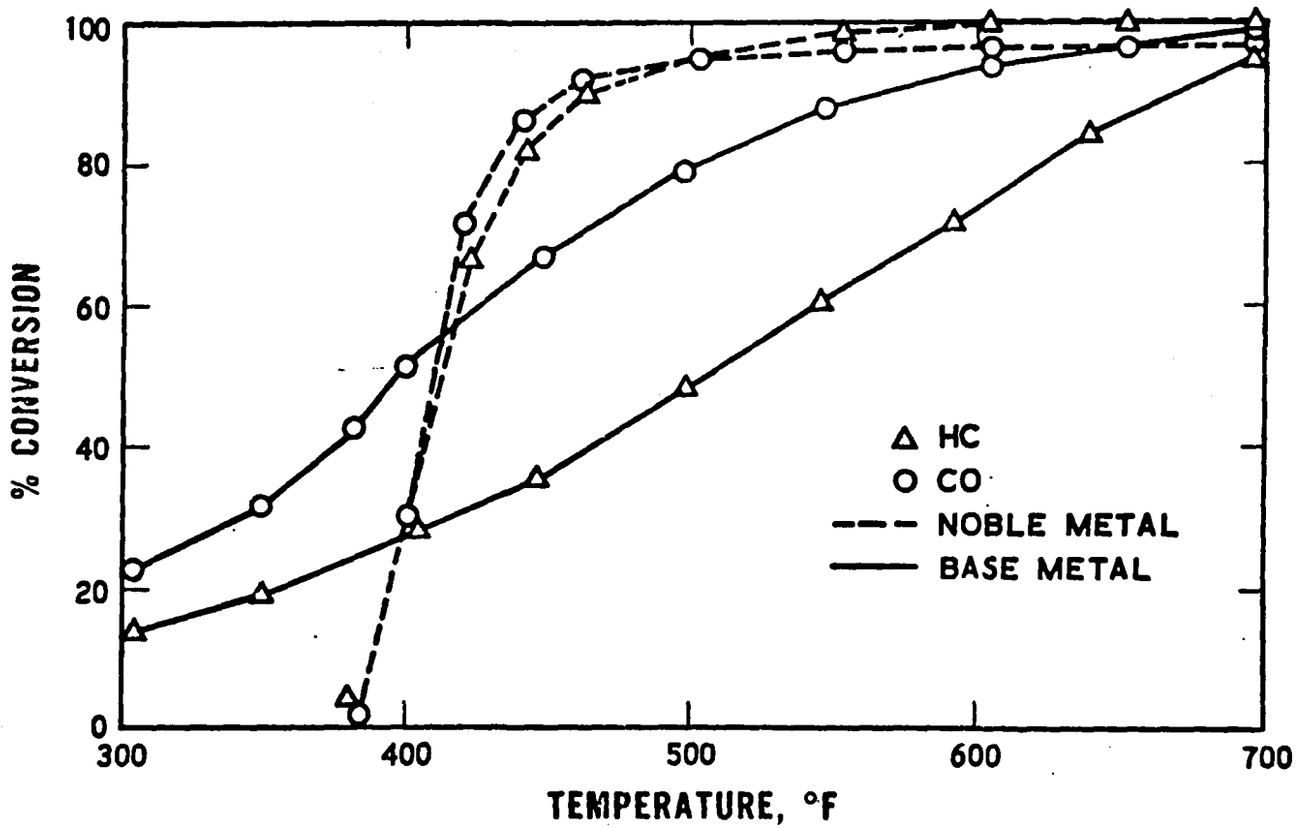
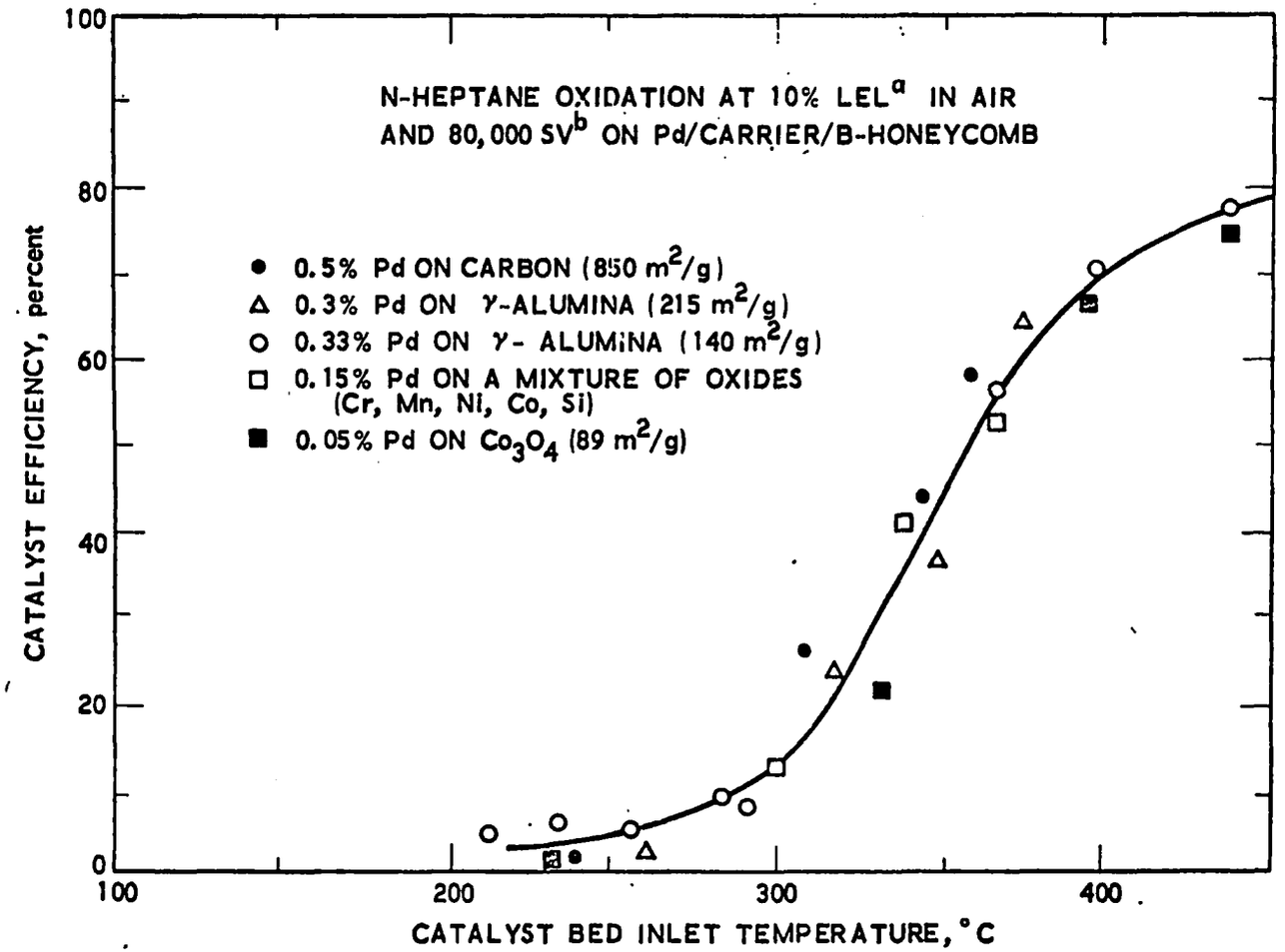


Figure 4-1. Conversion characteristics of base metal and noble metal catalysts (General Motors Bench Test Evaluation) (Reference 27).



[a] lean explosive limit

[b] space velocity

Figure 4-2. Palladium catalyst performance (Reference 28).

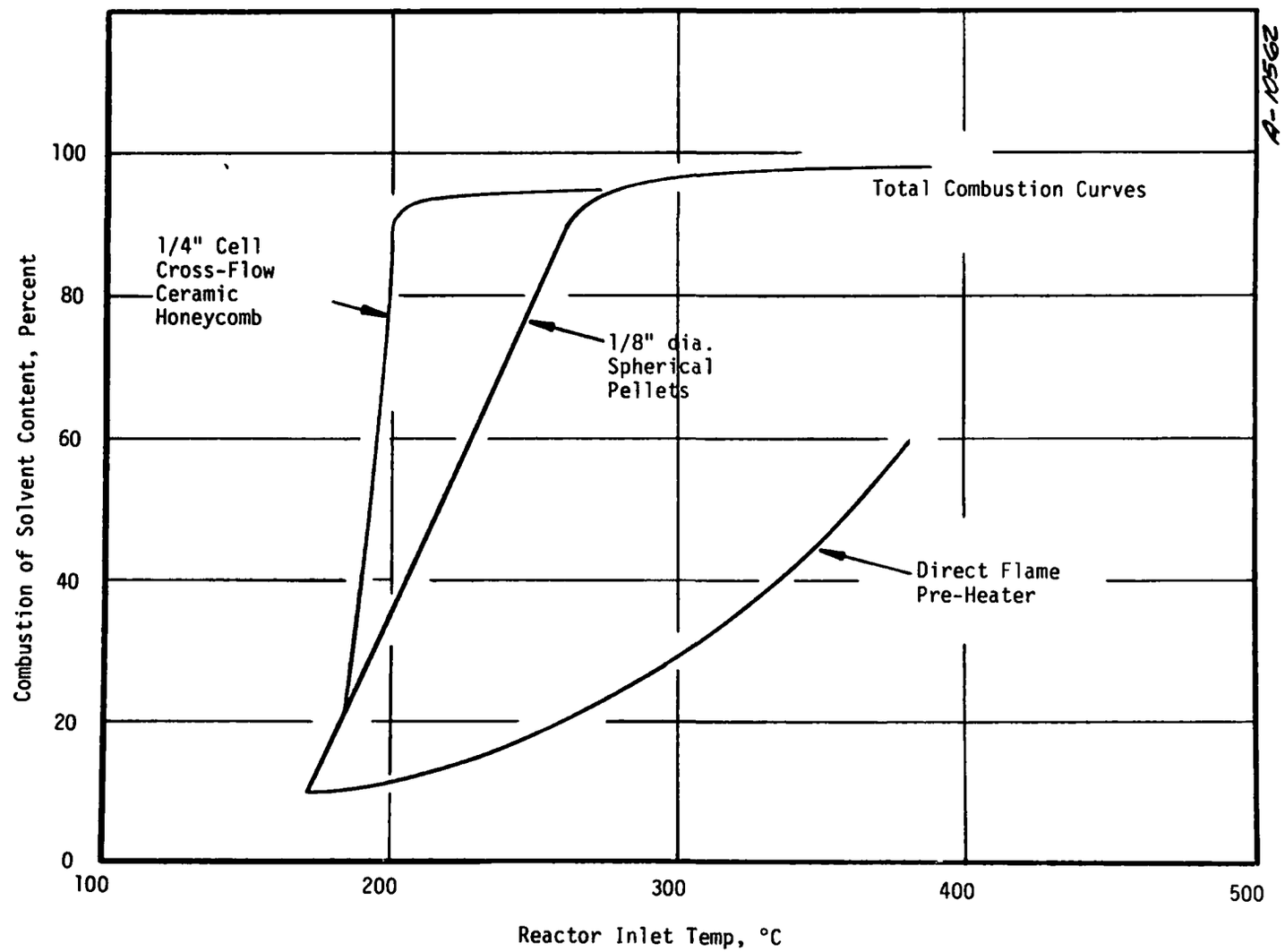
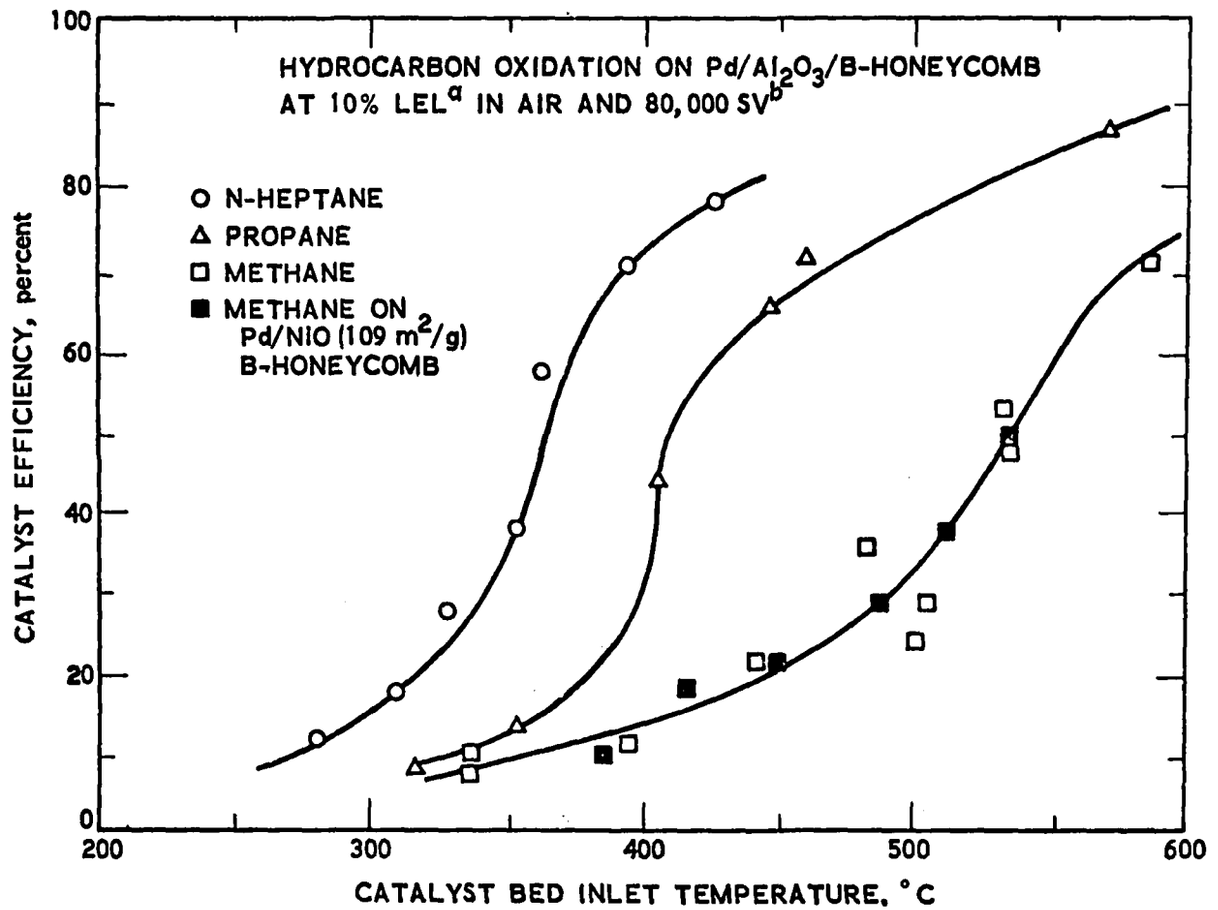


Figure 4-3. n-Heptane fume abatement effectiveness (115,000/hr space velocity) (Reference 29).



[a] lean explosive limit

[b] space velocity

Figure 4-4 . Lightoff characteristics--palladium catalyst (Reference 28).

Typical variations in light-off temperature due to space velocity are shown in Figure 4-5 (Reference 29). This shows light-off temperature increasing with space velocity for n-heptane combustion in a pellet bed catalyst.

4.1.2 Flashback Potential

Flashback refers to the propagation of a flame back to the fuel-air mixing chamber, with the resulting possibility of explosion and equipment damage. Flashback can be avoided by

- Keeping the temperature of the surfaces enclosing the mixing chamber below the ignition temperature
- Keeping the velocity of the mixture through the injection port higher than the normal flame velocity for that mixture
- Operating outside the flammability limits for the mixture.

The tendency of a catalyst/fuel combination to exhibit flashback can be evaluated by operating the catalyst at the maximum space velocity. From this point the fuel mixture supply can be decreased until either flashback or extinction occurs. If extinction does not occur, it is expected that flashback will occur when the flow velocity becomes smaller than the flame propagation velocity.

4.1.3 Lean and Rich Flammability Limits

A fuel-air mixture will fail to ignite when a large excess of either fuel or air prevents the temperature from rising to the ignition point in spite of the precombustion reactions that occur. One technique for the determination of the flammability limits for a particular catalyst-fuel combination in air is as follows: a lean equivalence ratio, ϕ_1, is selected and the fuel/air throughput increased until a rapid increase in unburned hydrocarbon emissions is noted. A second equivalance ratio, ϕ_2, and two rich equivalence ratios, ϕ_3 and ϕ_4, are then tested in the same fashion. From this data the flammability limits as a function of space velocity for a given catalyst-fuel combination can be determined. The data would appear as shown in Figure 4-6.

4.1.4 Maximum Specific Heat Release

The maximum specific heat release from the catalyst bed can be determined from

$$HR \quad \frac{\dot{m}_{fuel} HHV_{fuel}}{v_{system} p_{system}} \eta_{fuel}$$

where HR is the heat release rate in Btu/hr-ft^{3}atm, $\dot{m}_{fuel}$ is the mass flow rate of fuel in lbm/hr, HHV_{fuel} is the higher heating value of the fuel in Btu/lbm, v_{system} is the combustor volume in ft^3, p_{system} is the inlet pressure in atm, and η_{fuel} is

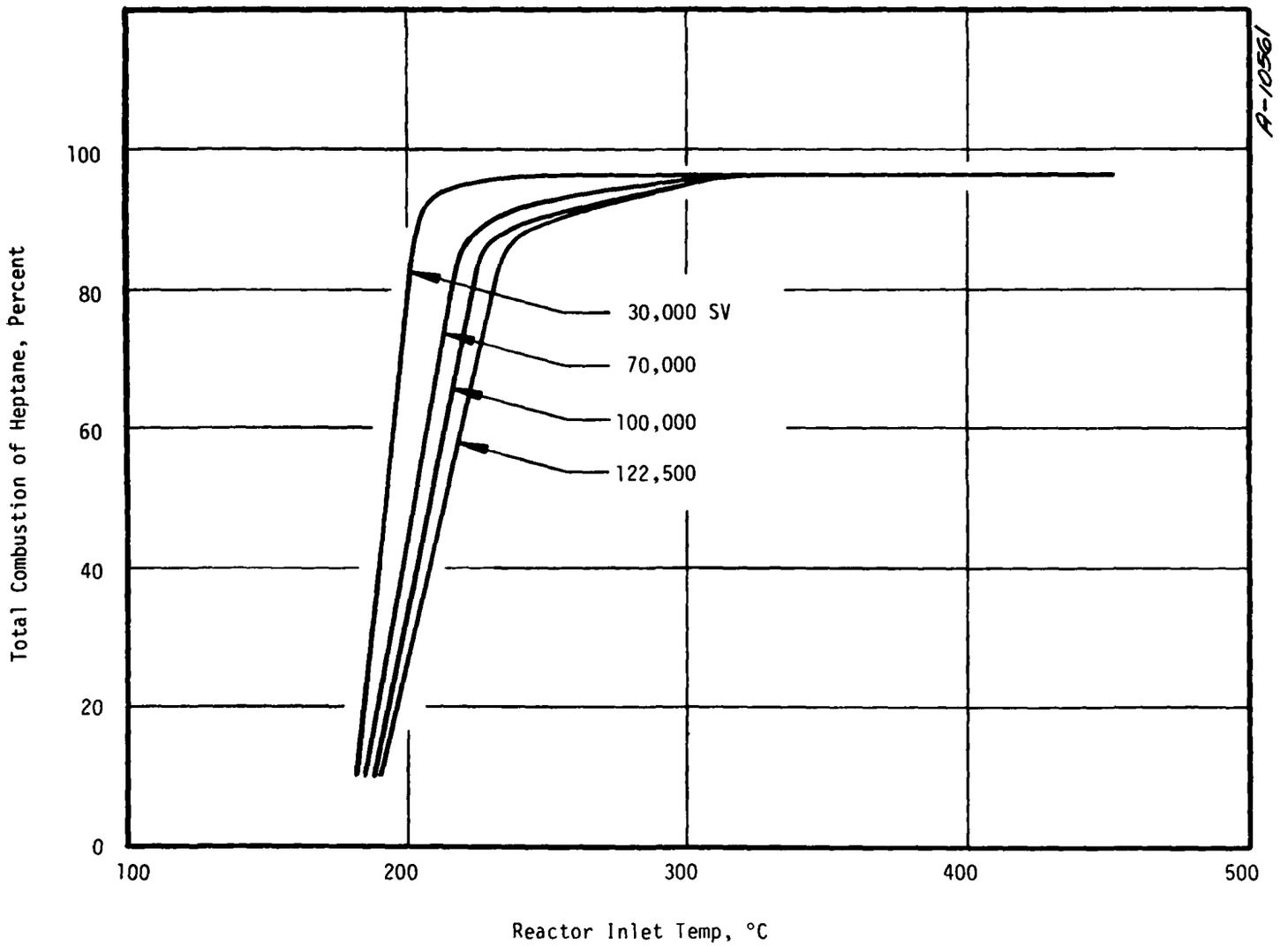


Figure 4-5. n-Heptane conversion efficiency vs temperature and space velocity — granular catalyst substrate (Reference 29).

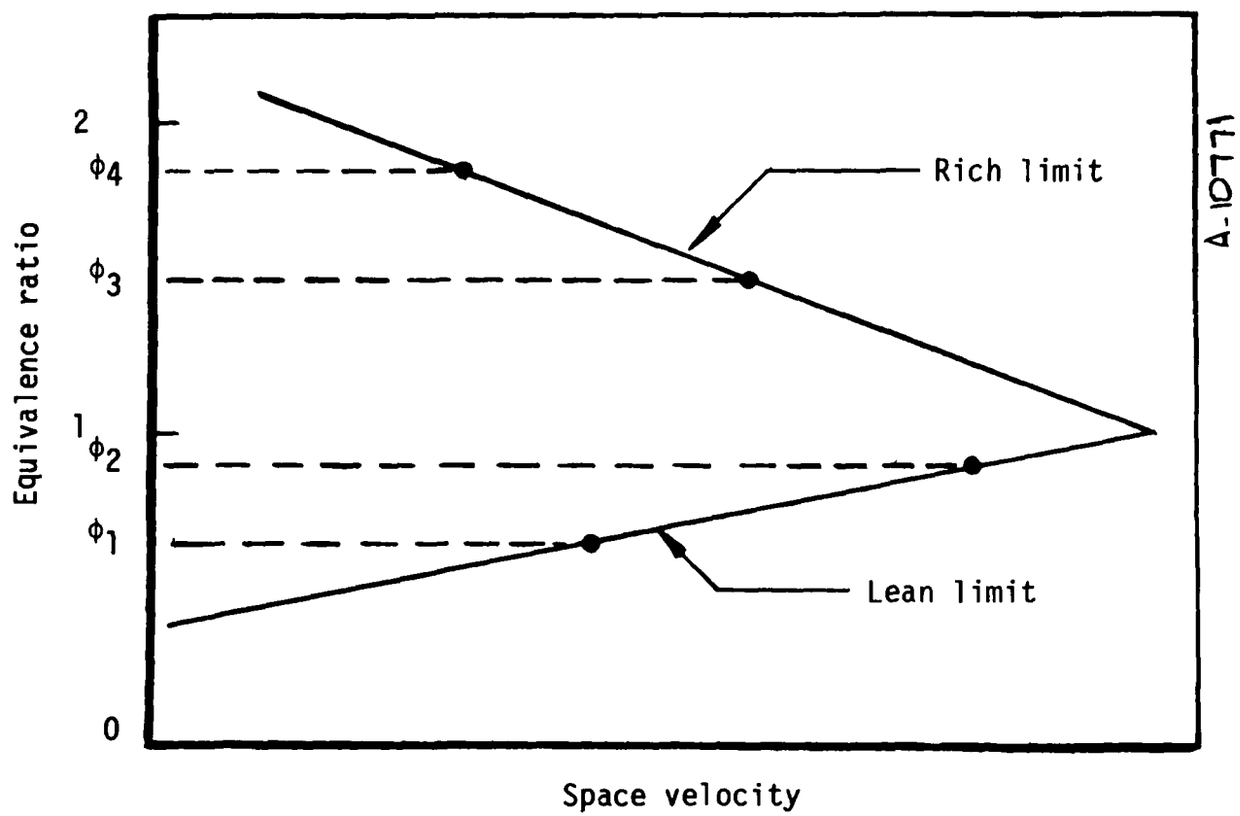


Figure 4-6. Example of flammability limit determination.

the conversion efficiency of the fuel. The maximum specific heat release will be obtained when the fuel mass flow rate is at its maximum value, the fuel conversion efficiency is nearly 100 percent (i.e., complete combustion), and stoichiometric fuel/air ratios are used. Since this would normally result in bed temperatures beyond the thermal stability limits of the bed, the maximum bed temperature is determined by varying the equivalence ratio and dilution, and the maximum specific heat release determined at that condition.

4.1.5 Heat Removal Mechanisms

Heat may be removed from the catalyst bed through conductive, convective, or radiative heat transfer. Depending on the bed geometry and overall system design, one of these mechanisms will usually be dominant. Section 5 discusses various bed heat removal techniques in detail as related to system concepts.

4.1.6 Combustion Efficiency

The combustion efficiency is another variable necessary to evaluate system performance. It can be calculated by the following formula

$$\eta_c = 1 - \frac{\left[\sum_i h_i m_i\right]_{\text{combustibles in emissions}}}{\left[\sum_i h_i m_i\right]_{\text{combustibles in inlet gas}}}$$

where h enthalpy

m mass flow rate

i species index

The energy of the combustibles ($\sum_i h_i m_i$) in the inlet gas is computed from the fuel flow rate measurements and the heat of combustion of the fuel. The energy of the combustibles in the emissions can be computed by knowing the total flow rate and the mass fractions of all combustible species (which includes CO) in the exhaust. These species concentrations are obtained by FIR, NDIR, and gas chromatograph instrumentation.

4.1.7 Pollutant Potential

Catalyst system performance can be evaluated in terms of unburned hydrocarbons, NO_x, particulates, and carbon monoxide. It must be recognized that pollutants once formed (or already present) in the bulk flow can be reduced by factors of approximately 100 by surface interactions but not by factors of 10^4 or greater. This comes about from the idealized requirement for 2.3 transfer units for each order of magnitude reduction of a gas phase pollutant by surface contact. For typical compact heat exchangers,

operating near optimum, each transfer unit involves a length of approximately 100 hydraulic radii. Typical optimum compact heat exchangers utilize about two transfer units (Reference 30). Thus, the occurrence of significant gas phase reactions is mandatory for reduction of UHC to ppm levels.

4.2 CHARACTERISTICS AND PROPERTIES OF CATALYST MATERIALS

A review of catalyst materials which are suitable for the oxidation of hydrocarbon and other fuels was conducted to obtain information on their characteristics and availability. The review included

- Support types and characteristics
- Substrate wash coat materials
- Catalyst coatings
- Temperature capability of the catalyst/support system
- Poisoning effects
- Characterization techniques

These items are discussed in detail below.

4.2.1 Support Material Types and Characteristics

The catalytic support serves three important functions in a catalyst system:

- It increases surface area of the active metal or metal oxide by providing a matrix that stabilizes the formation of very small particles.
- It increases thermal stability of these very small particles, thus preventing agglomeration and sintering with consequent loss of active surface.
- In certain cases, it provides catalytic activity due to special properties of the support.

These functions have found increasing use in catalytic applications, in particular in the petroleum and petrochemical areas. Most common support materials are Al_2O_3 and SiO_2, and they are prepared as pellets in a variety of shapes and sizes. In some cases, they are formulated in such a way that their surface has inherent catalytic activity without the addition of a transition metal or metal oxide. This is the case for a combination of SiO_2 and Al_2O_3 to give highly acidic surfaces active for hydrocarbon cracking reactions via the formation of carbonium ion intermediates. More commonly, however, they are impregnated with an active catalyst and special techniques have been developed to obtain uniform distribution of finely dispersed particles. These techniques are particularly important for the expensive noble

metals such as platinum. Dispersions of 100 percent (all the noble metal atoms are exposed to the surface) are often obtained, leading to complete utilization of the expensive active component of the catalyst system.

The application of these supports in catalytic combustion presents a number of problems that have to be considered:

- The large space velocities used in a catalytic combustion unit will result in severe pressure drops if the catalyst beds are packed with conventional pellets like those used in the petroleum and petrochemical industry.
- The high reaction rates of complete combustion usually present severe pore diffusion limitations for the effective operation of the system.
- The high temperatures and heat fluxes place special constraints on the thermal properties of the system.

Over the last decade, a number of new materials and new preparative techniques have been developed to overcome this problem. They are:

- Monolithic Supports
- Fibers and Fiber Pads
- Surface Impregnated Pellets

4.2.1.1 Monolithic Supports

Monolithic supports are composed of small parallel channels of a variety of shapes and diameters. These structures may be in the form of honeycombed ceramics extruded in one piece, oxidized aluminum alloys in rigid cellular configurations, or multilayered ceramic corrugations. The channels in honeycomb-like structures have tubular diameters of 1 to 3 mm. The overall diameter of the monolithic support may vary from 1 inch to 2 feet, and is limited, in the case of extrusion processes, by availability and operation of the metal die. Materials of fabrication are usually low surface area ceramics such as mullite ($3Al_2O_3 \cdot 2SiO_2$) or cordierite ($2MgO \cdot 5SiO_2 \cdot 2Al_2O_3$). The refractory monolith is produced with macro-pores (1μ 10μ) and may be coated with thin layers of catalytic materials, 5-20 wt% coatings being common.

The two major advantages of monolith supports for catalytic operations are:

- High superficial or geometrical surface area
- Low pressure drops during operation

A comparison of the properties of a monolith with a bed of spherical pellets shows these advantages dramatically. From Figure 4-7 it is clear that the pressure drop

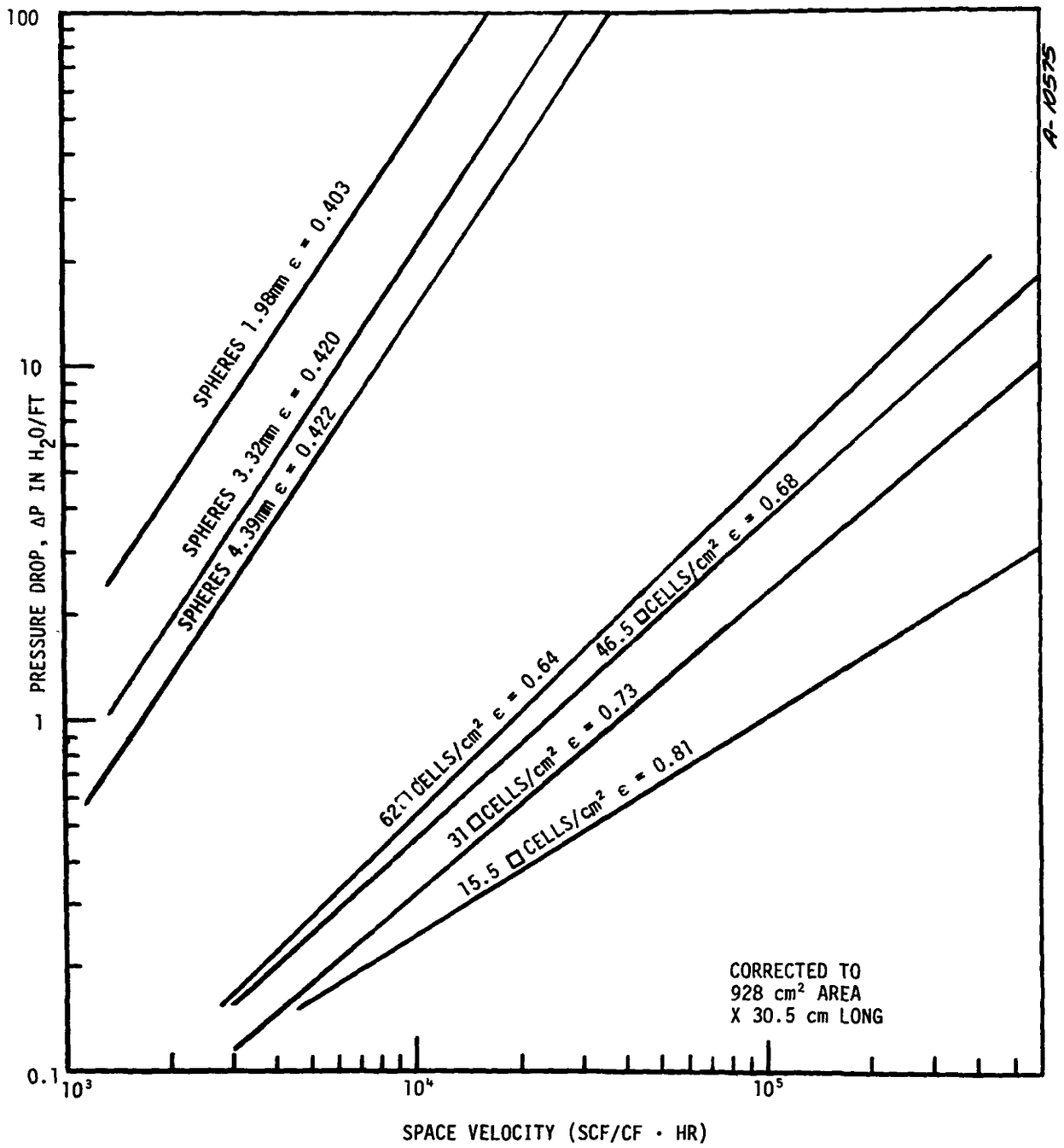


Figure 4-7. Comparison of pressure drops for monolith and pellet bed systems (Reference 31). ε = open area fraction.

is decreased by over one order of magnitude. This is achieved without loss in geometric surface area, as shown in Figure 4-8. In order to achieve comparable catalytic (total) surface areas, on the other hand, coating a material on the monolith is required. The nature of this coating will be discussed later.

Manufacturers of monolith supports include American Lava Corporation, Corning Glass Works, E. I. Dupont de Nemours & Company, General Refractories Company, and Norton Company. A variety of materials and configurations are available, and Table 4-1 presents some of the significant characteristics of the various monolith supports.

American Lava's Thermacomb corrugated ceramics are available in two ceramic compositions (alpha-alumina and cordierite), and in two structure types (honeycomb and split cell). Figure 4-9 shows examples of Thermacomb corrugated products, while Figure 4-10 shows the structural types available. The cross-flow, split cell structure shows potential for a cross-flow ceramic heat exchanger.

Corning Glass Works produces Celcor, a porous cordierite ceramic, in a honeycomb structure with square or triangular cells. Examples of Celcor monoliths are shown in Figure 4-11. Celcor has been used extensively as a catalyst support for controlling automobile emissions.

Dupont produces TORVEX ceramic honeycomb in two ceramic compositions, alumina and mullite. Three geometric configurations (straight honeycomb, slant cell honeycomb, and cross-flow honeycomb) are available, and examples of these configurations are shown in Figure 4-12.

Versagrid ceramic honeycomb is produced by the General Refractories Company. Versagrid is available in four cell shapes (round, square, triangular, and rectangular) and two compositions (cordierite and mullite). The maximum operating temperature of Versagrid is among the highest of the monolith supports listed in Table 4-1, and samples of Versagrid honeycomb are shown in Figure 4-13.

Norton Company produces SPECTRAMIC Honeycomb products in three compositions (silicon carbide, silicon nitride, and silicon oxynitride) and in either rectangular or circular cell shapes. The products can be supplied with the cell axis at any specified bias angle, and have very high maximum use temperatures. An example of SPECTRAMIC Honeycomb is shown in Figure 4-14.

4.2.1.2 Fibers and Fiber Pads

Fibrous substrates are used primarily in low-temperature combustors for domestic, agricultural, and industrial heaters (Reference 7). Recent U.S. patents, however, have proposed the use of fiber pads in high temperature combustors (References 32-24). In Reference 32, a pre-mixed combination of fuel and air is passed through a refractory fiber of alumina and silica such as Cerafelt, produced by Johns-Manville.

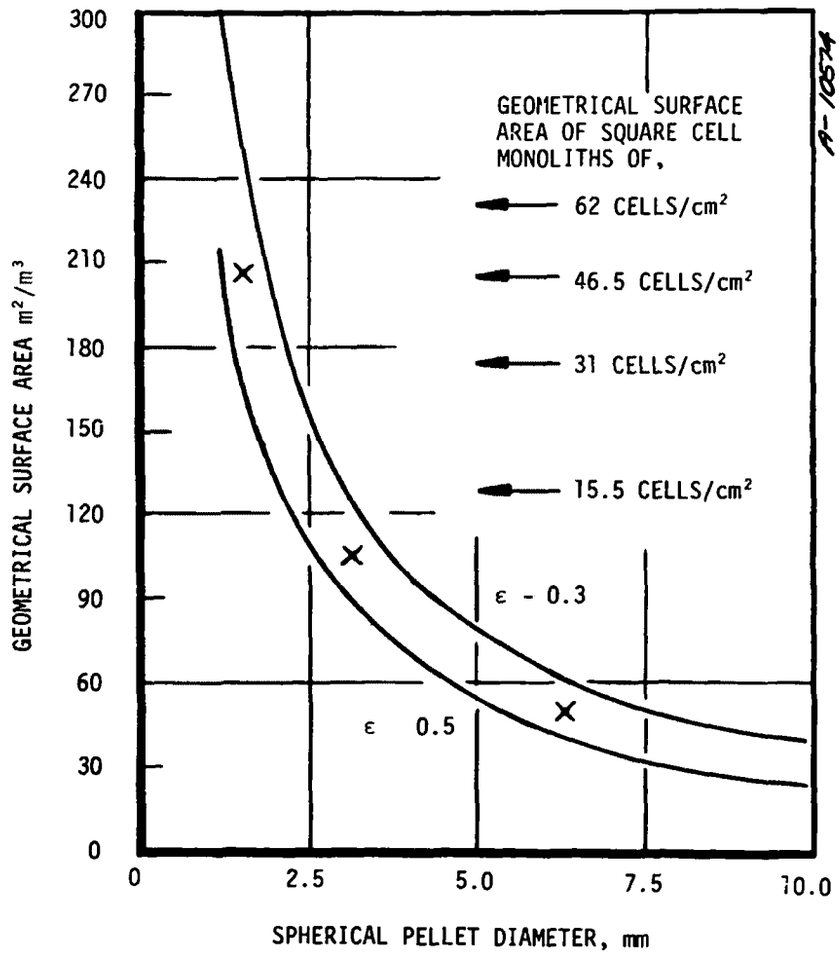


Figure 4-8. Surface area for various pellet sizes. ε = open area fraction.

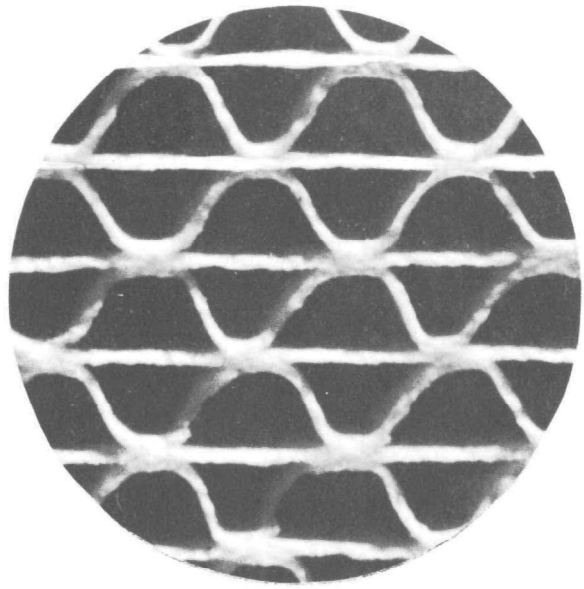
TABLE 4-1. MONOLITH SUPPORT DATA

Manufacturer	Product	Description	Temperature Limit (°F)	Specific Heat (Btu/lb-°F) @ 1000°F	Density lb/ft^3	Thermal Conductivity (Btu-in/ft^2-°F-hr) @ 1000°F
American Lava Corporation	Thermacomb AlSiMag 614	Dense 96% alpha-alumina	2800	0.21	N/A	119.0[a]
	Thermacomb AlSiMag 776	Porous 96% alpha-alumina	2192	0.21	N/A	85.0[a]
	Thermacomb AlSiMag 795	Cordierite	2192	0.19	16 - 40	10[a]
Corning Glass Works	Celcor 9475(EX-20)	Cordierite	2200	0.27	94.9 - 99.9	5.37
E. I. DuPont de Nemours & Company	TORVEX	Alumina	2732	N/A	10 - 34	6[b]
		Mullite	2462	N/A	20 - 35	6[b]
General Refractories Company	Versagrid	Cordierite	2550	N/A	35 - 40	N/A
		Mullite	3000	N/A	45 - 50	N/A
Norton Company	SPECTRAMIC honeycomb	Silicon carbide RX387	3000	0.15	25 - 31	110[c]
		Silicon nitride RX384	2800	0.15	25 - 37	22[c]
		Silicon oxynitride RX385	2800	0.22	19 - 25	29[c]

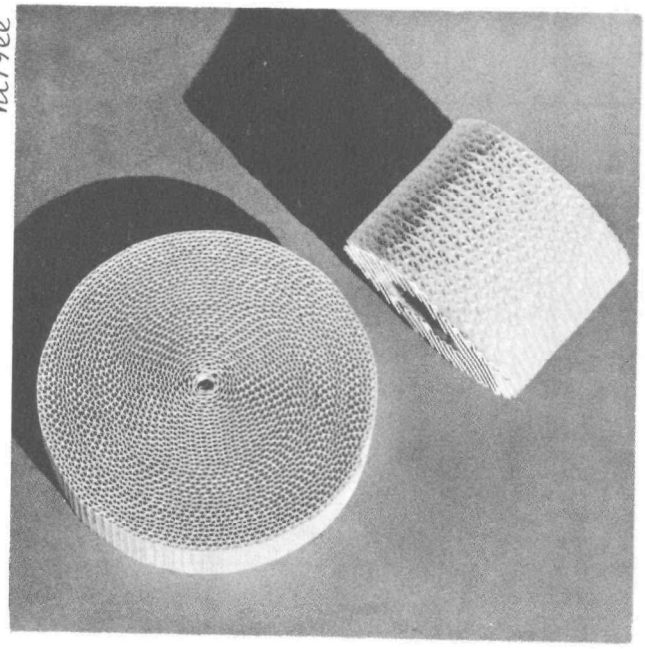
[a]Solid ceramic at 570°F

[b]At 1470°F

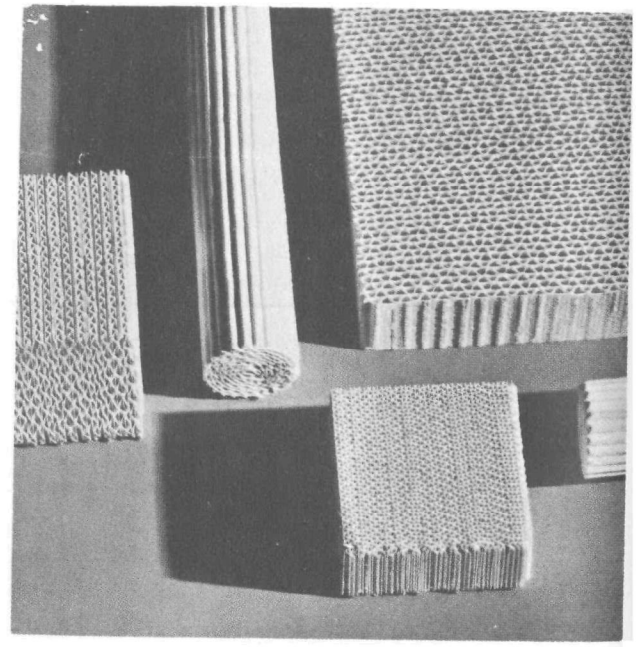
[c]At 2550°F



a. 8x enlargment



b. Rolled structures



c. Rolled and stacked structures

Figure 4-9. Examples of Thermacomb corrugated ceramics, produced by American Lava Corporation.

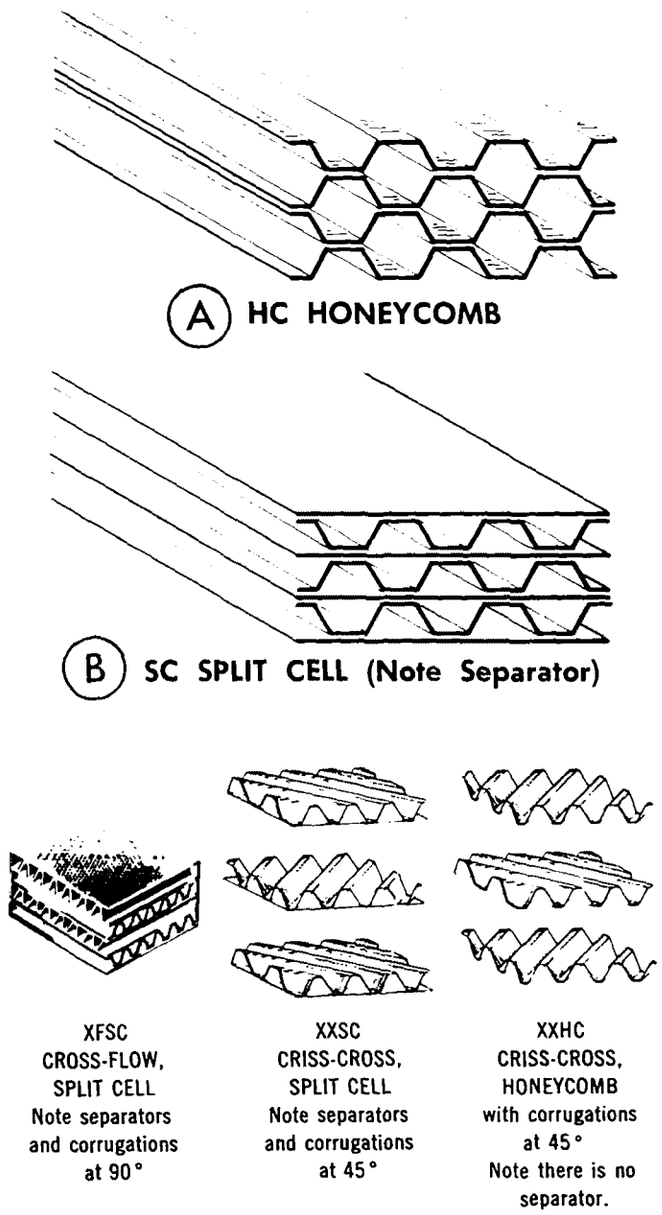


Figure 4-10. Structural types of Thermacomb corrugated ceramic monoliths.

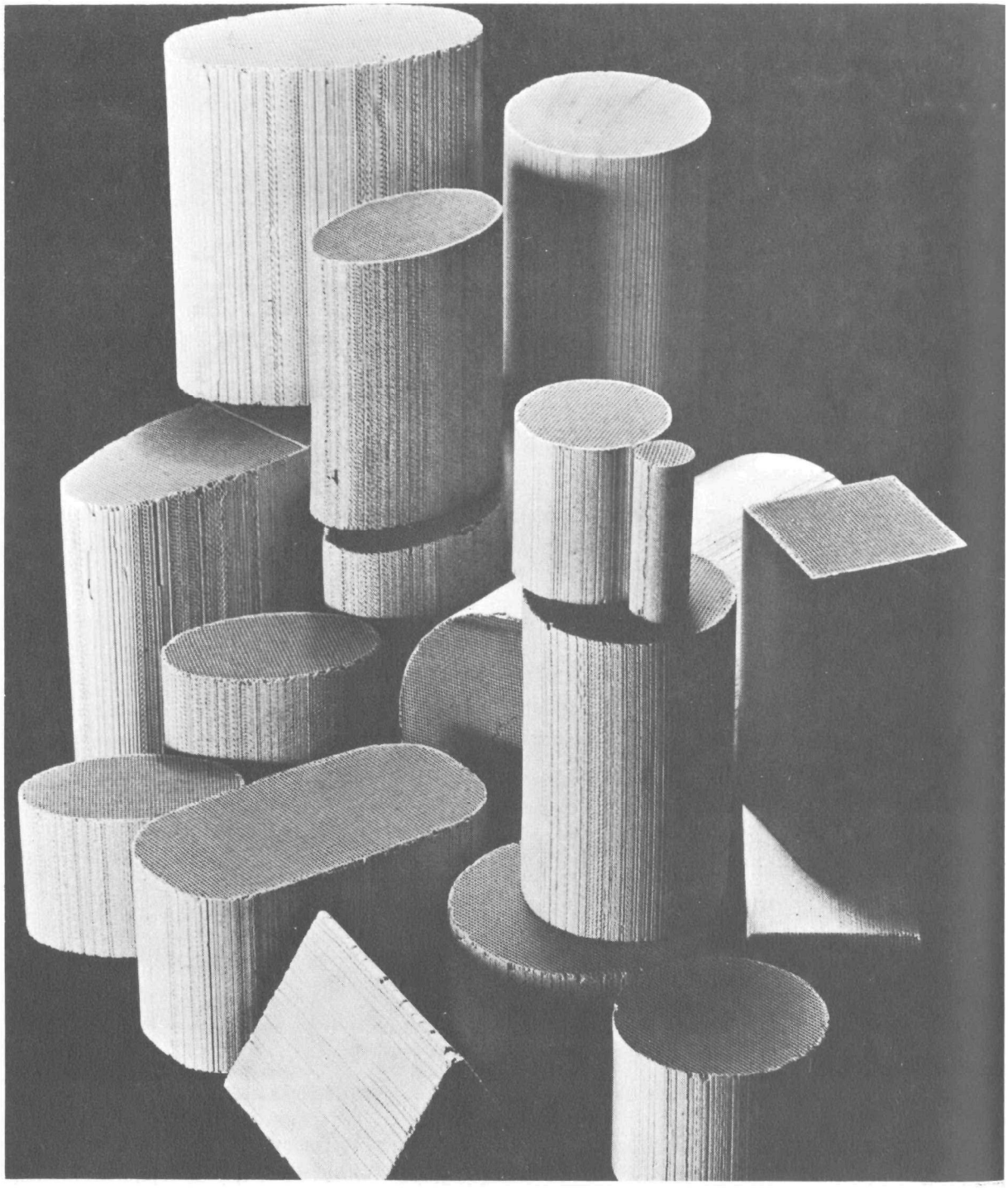
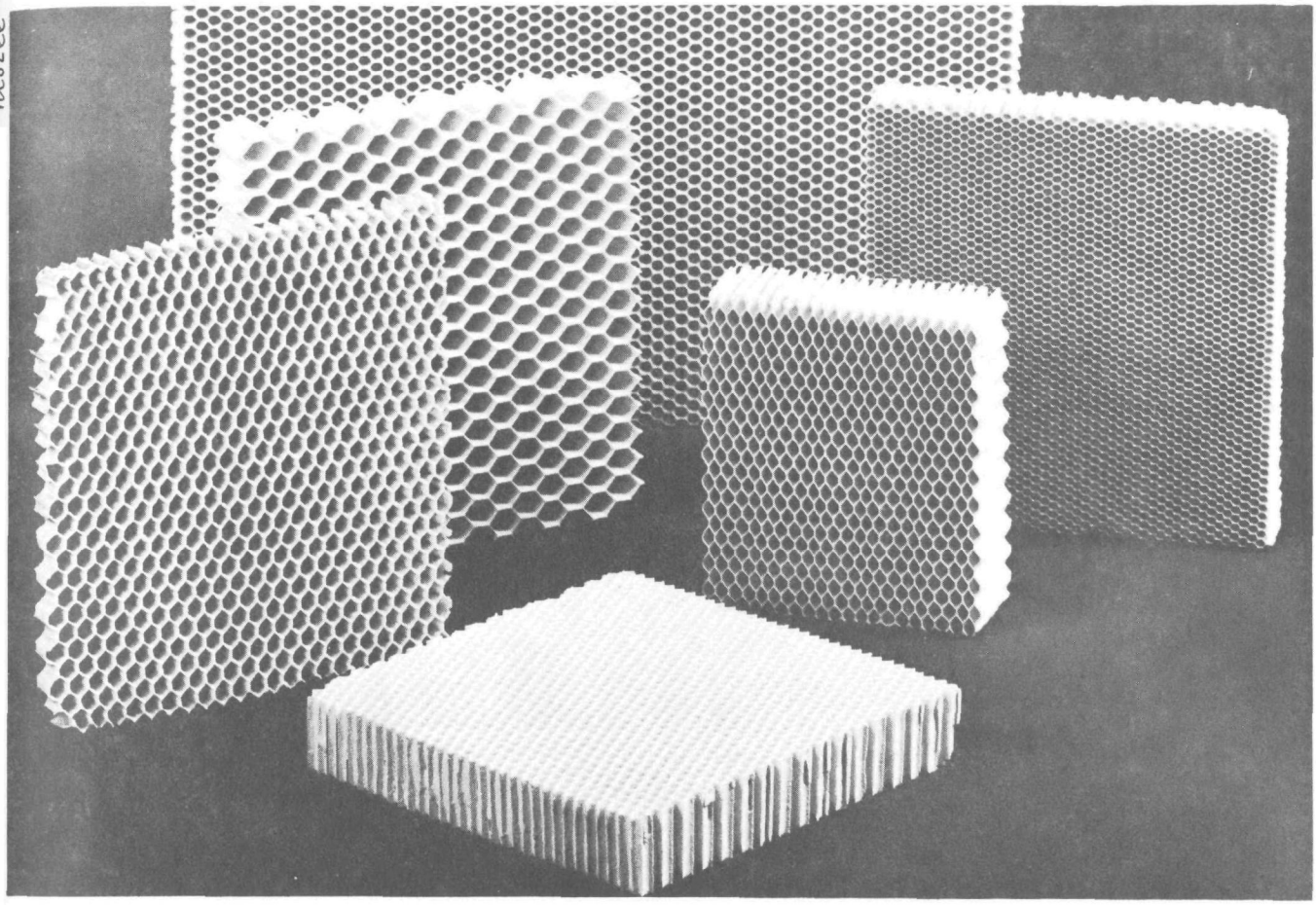
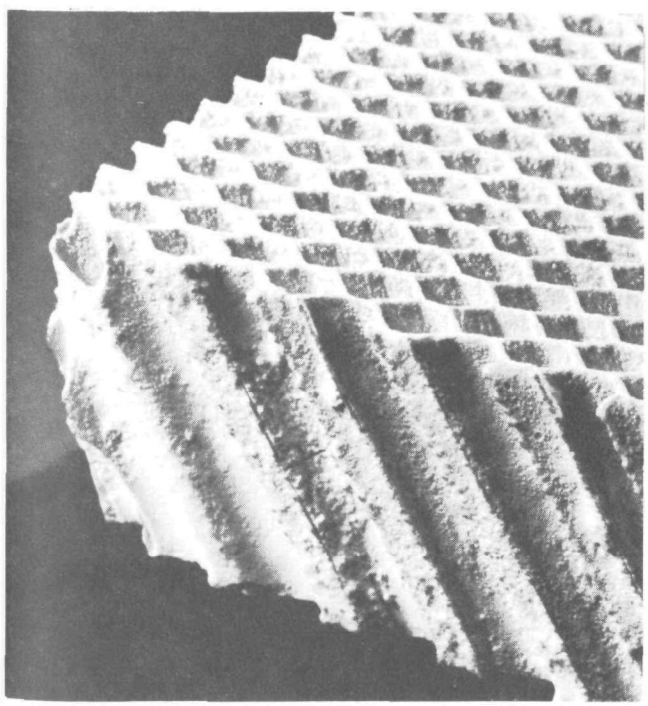


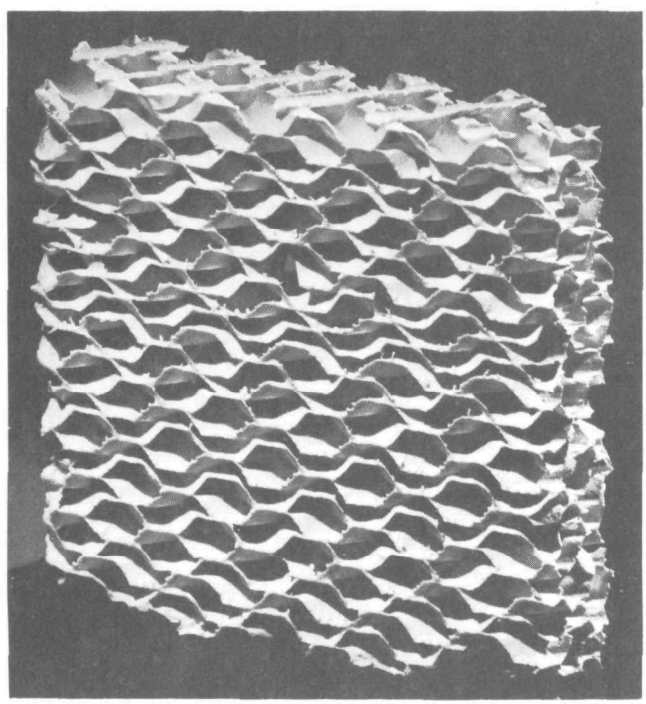
Figure 4-11. Examples of Celcor cordierite monoliths, produced by Corning Glass Works.



a. Straight honeycomb



b. Slant cell honeycomb



c. Crossflow honeycomb

Figure 4-12. Examples of DuPont's TORVEX ceramic honeycomb.

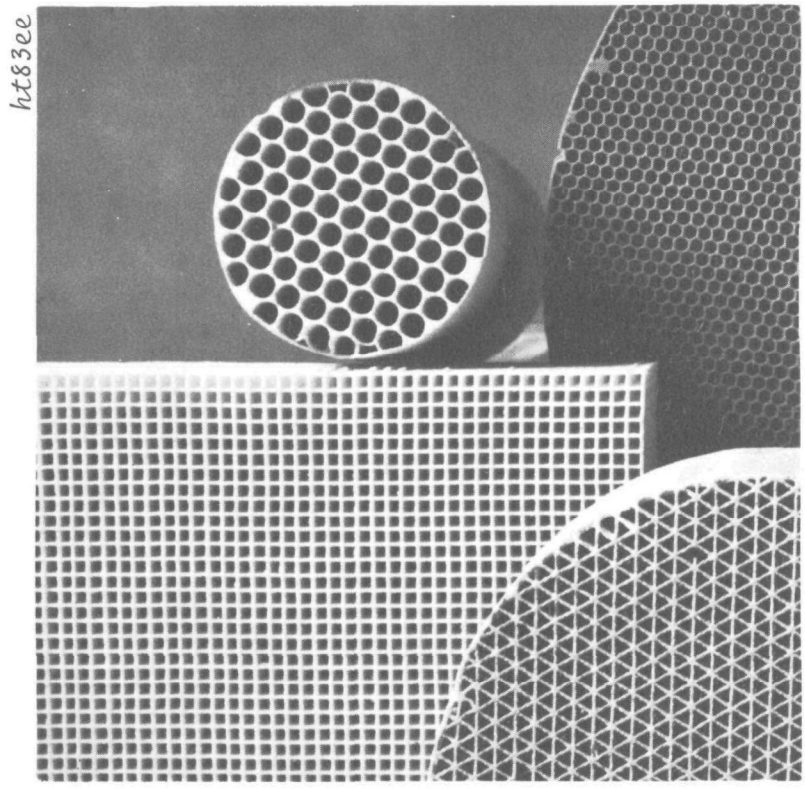


Figure 4-13. Examples of General Refractories Company's Versagrid ceramic honeycomb.

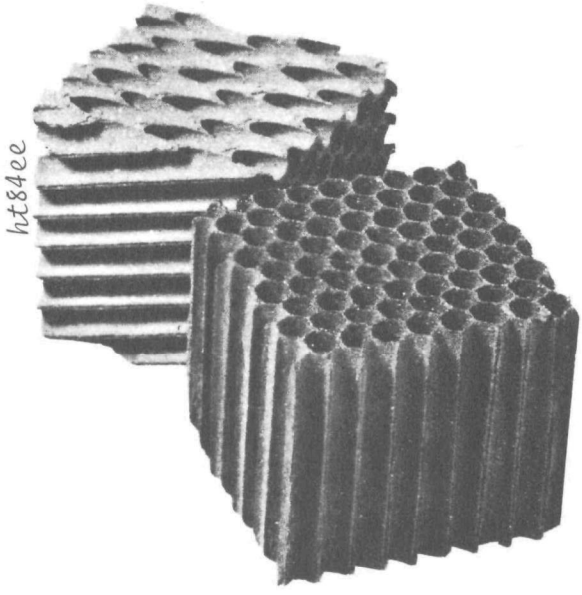


Figure 4-14. Norton Company's SPECTRAMIC honeycomb material.

Upon ignition, the Cerafelt supports the combustion on the surface, but has no tendency to flash back. Porous heat-insulating fibers such as asbestos, silica, or basaltic fiber are proposed for use in catalytic heaters in Reference 33, and Reference 34 describes the use of Johns-Manville's Fibrechrome refractory felt as a burner face material.

While asbestos is suitable for low-temperature applications, high-temperature requirements call for fibers of silica or alumina. For example, Johns-Manville's Fibrechrome is formed from an alumina-silica-chromia composition and has a maximum use temperature of 2700°F. This material is shown in Figure 4-15. Imperial Chemical Industries United States Incorporated markets both alumina and zirconia fiber materials, under the trade name SAFFIL, with Figure 4-16 showing their alumina fiber. Table 4-2 lists some important properties of these fiber materials; one advantage of all fiber pads is their low thermal conductivity, thus preventing flashback since the plenum side of the pad remains well below ignition temperature.

4.2.1.3 Surface Impregnated Pellets

One advantage of monolithic supports is the presence of a large geometric surface area and the possibility of depositing the catalytic materials on this surface. This increases the availability of the active catalyst to the main stream of the combustion mixture, a property that increases performance in these fast reaction systems. The presence of the catalyst as close to the geometric surface of the support as possible is important to minimize diffusion limitations of the reactants into pores. This property can be achieved with highly porous pelleted catalysts as well. It requires the application of a special technique of catalyst preparation called surface impregnation. The pellets, or catalyst carriers, come in a variety of material composition, including alumina and silica. Formed by a variety of methods, such as extrusion, the catalyst carriers come in different shapes and forms. Both Norton, Chemical Process Products Division and Houdry Division, Air Products and Chemicals offer catalyst carriers that have a wide range of surface areas and pore size distributions. Typical shapes and forms of Norton catalyst carriers are shown in Figure 4-17.

4.2.2 Substrate Wash Coat Materials

As mentioned earlier, the low surface area of the monolith structure requires the application of a thin coat of oxide such as Al_2O_3. This wash coat, which strongly adheres to the ceramic or refractory support, provides a uniform high surface area while still insuring that the catalytic material which is subsequently impregnated on the wash coat is close to the main flow of reactants. The thickness of the wash coat is usually between 10×10^{-6} and 20×10^{-6} m (10-20 microns).

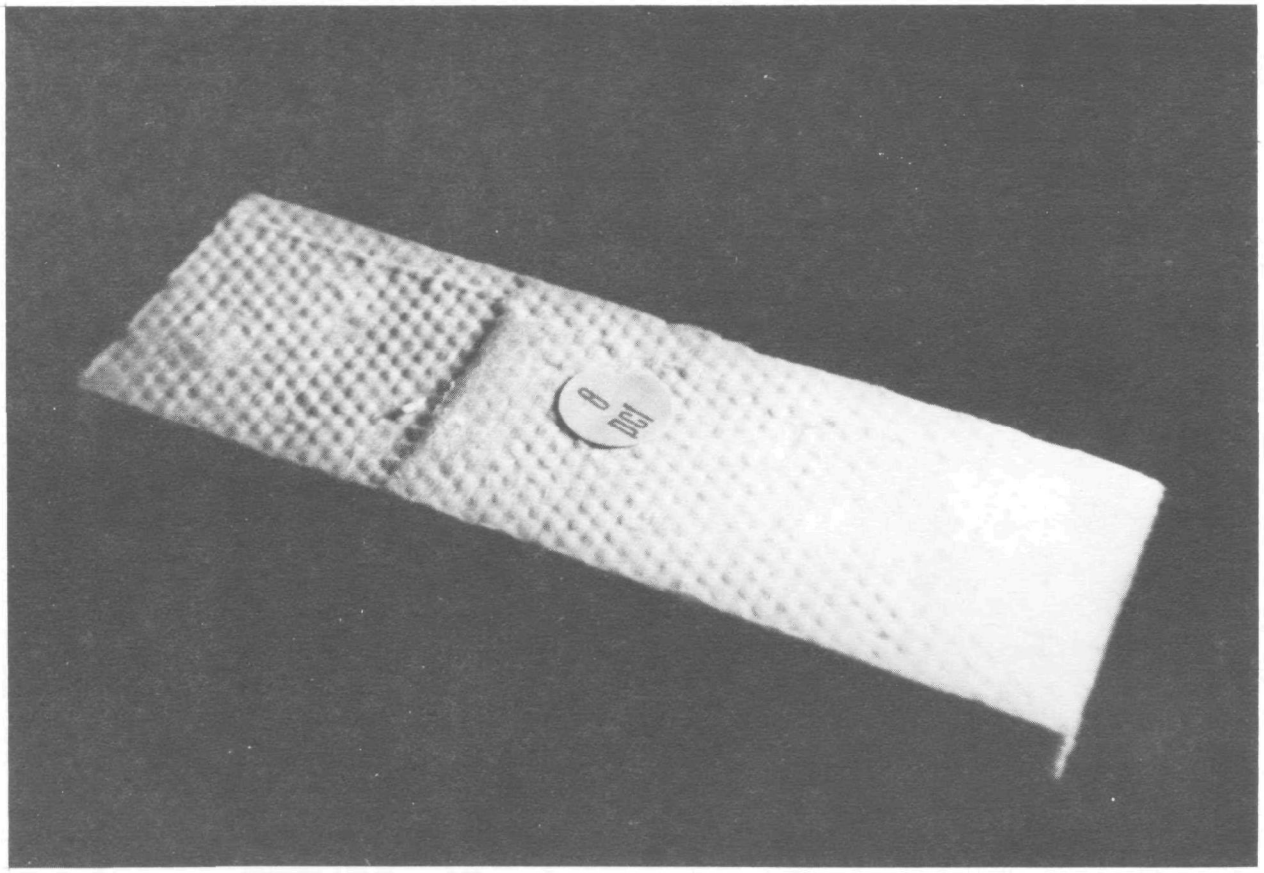


Figure 4-15. Johns-Manville's Fibrechrome - a fiber pad.

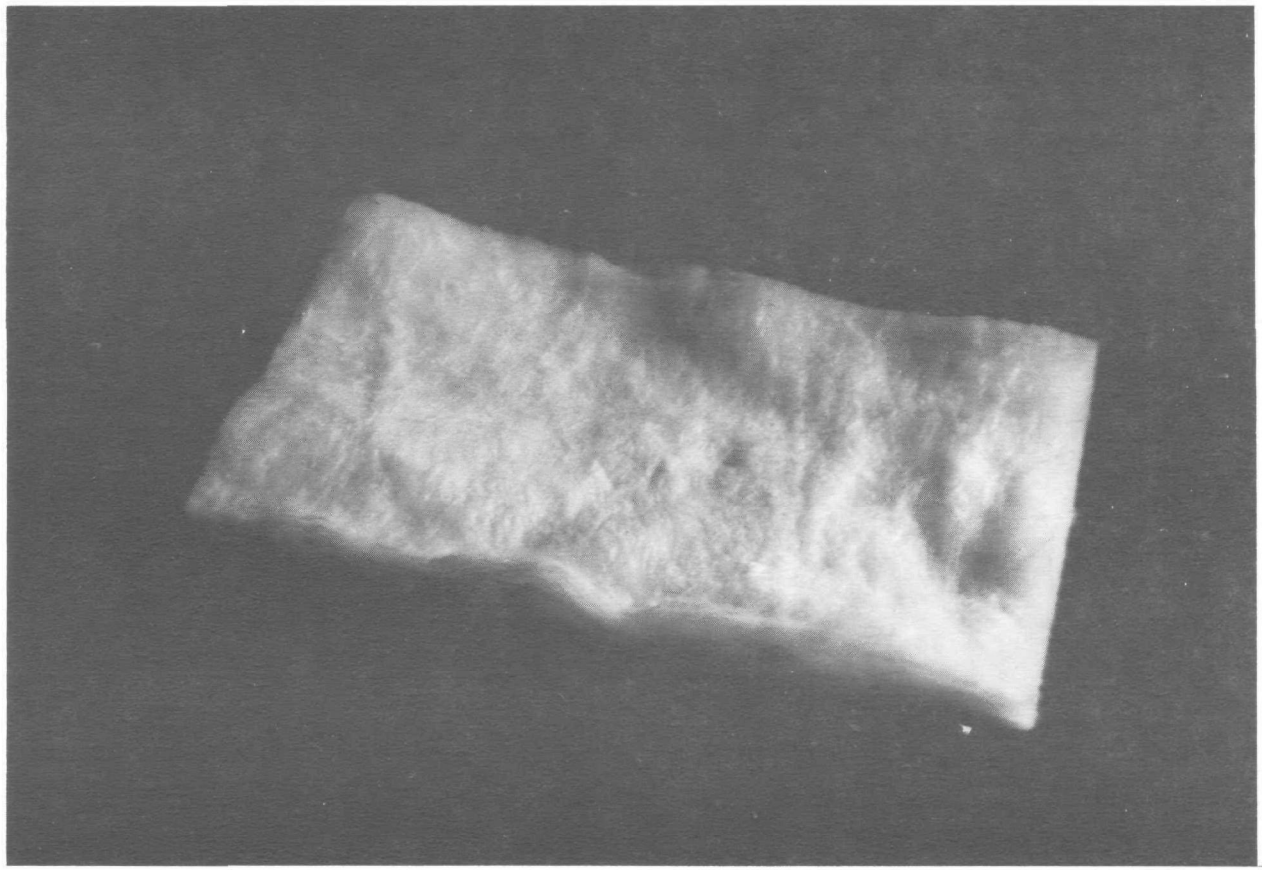


Figure 4-16. ICI United States' SAFFIL — an alumnia fiber.

TABLE 4-2. FIBER PAD DATA

Manufacturer	Product	Description	Temperature Limit (°F)	Specific Heat (Btu/lb-°F) @ 1000°F	Fiber Density (gm/cm^3)	Thermal Conductivity ($Btu\text{-}in/hr\text{-}ft^2\text{-}°F$) @ 1000°F
ICI United States Inc.	SAFFIL (Standard Alumina)	Inorganic alumina fiber	1850	0.25	3.0	0.95
	SAFFIL (High Temperature Alumina)	Inorganic alumina fiber	2750	0.25	3.5	N/A
	SAFFIL (Standard Zirconia)	Inorganic zirconia fiber	2000	0.14	5.0	0.90
	SAFFIL (High Temperature Zirconia)	Inorganic zirconia fiber	2900	0.14	5.5	N/A
Johns-Manville	Cerafelt	Silica-alumina fiber	2300	0.25	N/A	0.7[a]
	Fibrechrome	Silica-alumina-chromia fiber	2700	0.25	N/A	0.75[a]

[a]Density 10 lb/ft^3

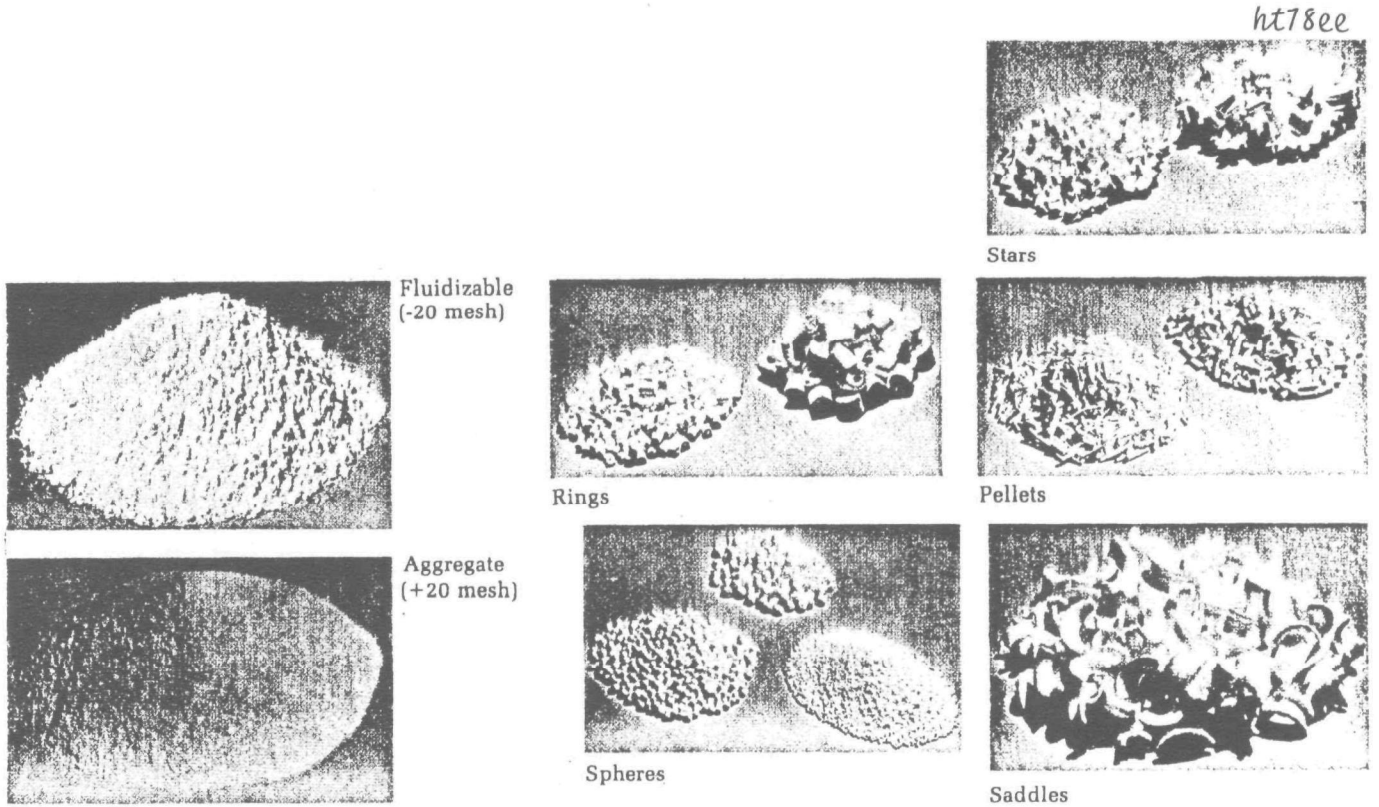


Figure 4-17. Examples of Norton Company's catalyst carriers.

Many different materials can be used as wash coats. ZrO_2, for example, has been used in test runs for the catalytic combustion of hydrocarbons in automotive exhaust. Variation in the type of wash coat can have important consequences in the stability and life of the catalyst system.

4.2.3 Catalyst Coatings

Although the field of catalysis has progressed substantially over the past decade, its theoretical aspects are not yet at the degree of sophistication which would enable one, a priori, to choose or design an active oxidation catalyst with a given set of catalytic properties. However, a vast amount of data exists which permits the development of correlations useful for choosing promising candidates based on excellent catalytic activity and catalyst stability. Over the last decade there has been a rapid development of the art, science and technology necessary to synthesize, test and manufacture ultrastable oxidation catalysts for the abatement of automotive emissions. These catalysts operate under the most stringent conditions, and sometimes at temperatures close to 2000°F. The expertise developed in this area will be useful in the development of a stable catalytic combustion system.

Two broad classes of catalytic coating materials are available: metals and oxides. These are discussed separately in the following sections.

4.2.3.1 Metals

The metals of catalytic interest, which are readily synthesized in the zero valent state at reasonable conditions, are listed in Table 4-3. Of these metals, the only ones which have a possibility of remaining in the metallic state in a high-temperature, oxidizing environment are the noble metals. The others readily form oxides, and will be discussed in Section 4.2.3.2. Of the noble metals, a large volume of data and correlations are available for Pt and Pd because of their use as automotive oxidation catalysts. They are among the most active catalysts for the oxidation of a number of fuels, e.g., methane (Reference 35), methanol (Reference 36) and hydrogen (Reference 37). The high activity of these metals is related to their ability to activate H_2, O_2, and carbon-hydrogen and oxygen-hydrogen bonds. Palladium and platinum are readily prepared in a highly dispersed form on a number of support materials. Because of the high activity of these metals per unit area of metal surface (specific activity) and the ability to attain high dispersions, only small amounts are necessary for catalytic combustion (0.1 - 0.5 wt%). Ruthenium metal is another possible candidate for catalytic combustion; however, under oxidizing conditions it forms a volatile oxide (RuO_4), which is rapidly removed from conventional catalyst supports. This problem has been recently solved by researchers interested in the NO_x reduction properties of Ru. One approach has been to anchor Ru to a support by forming a relatively stable perovskite structure with certain

TABLE 4-3. METALS OF CATALYTIC INTEREST FOR CATALYTIC COMBUSTION

GROUP VIII*			GROUP IB*
Fe	Co	Ni	Cu
Ru	Rh	Pd	Ag
Os	Ir	Pt	Au

*Enclosed metals are considered noble.

oxides such as La_2O_3 (Reference 38). Osmium is even more volatile and poisonous than ruthenium in an oxidizing environment. Also, as with iridium and rhodium, it is very costly, and available in limited supply. The use of the latter two metals, if at all, would be restricted to small quantities in multimetallic systems. Silver, while quite active at low temperatures for the activation of O_2, melts at low temperatures and therefore sinters to a significant degree at the high temperatures of catalytic combustion. However, it could find use as an additive in a multimetallic catalyst. Gold is very inactive for oxidation, and would therefore only be considered as a structural or electronic modifier for multimetallic catalysts.

Based on the above considerations, those metals which show the greatest promise for use in a single-active-element catalyst system are:

- Pt
- Pd
- Ru (stabilized)

Highly active and stable catalyst systems can be produced through the use of multimetallic systems and the addition of structural and electronic promoters. For example, Pd/Pt bimetallic clusters, which have been extensively studied as automotive oxidation catalysts, combine the high catalytic activity of platinum with the relatively low cost of palladium. Similarly, extensive studies with metals have shown that the rate of catalytic oxidation of hydrocarbons parallels the catalytic activity for O_2 isotope exchange:

$$O_2^{16} + O_2^{18} \rightarrow 2O^{18}O^{16}$$

Thus, exchange is thought to be sensitive to the electronic properties of the metal. These properties are readily changed by alloying or forming supported multimetallic clusters. Therefore, Groups VIII and VIII-IB combinations appear promising. Bimetallic combinations can have high structural and thermal stability, especially if one of the metals is high melting.

4.2.3.2 Metal Oxides

The catalytic properties of metal oxides have been extensively studies by a number of research groups (Reference 39). Some of the simple oxides, e.g., Co_3O_4, have oxidation activity comparable to the very active noble metals like Pt and Pd. A primary difference between these metals and the oxides is the so-called "light-off" temperature. This relates the ability of a catalyst to reach a significant conversion level at low temperatures and in short periods of time. This is more of a problem for automotive oxidation systems where a significant amount of emissions occurs after a cold start. Therefore, it is imperative that the oxidation catalyst

bed reach operation temperature as quickly as possible. This could also be a problem for catalytic combustion installations, although for some units a precombustor might be built into the system for startup. Other alternatives include doping a high light-off temperature catalyst with small amounts of noble metals to initiate low temperature combustion, or using a multi-bed catalyst where the first small bed is a noble metal catalyst.

There has been a significant amount of work with oxides in the area of catalytic oxidation. The specific catalytic activity, i.e., per unit surface area, can be varied over very wide limits. It has been found, as for the case of metals, that the activity for hydrocarbon oxidation parallels the ability of the catalyst to catalyze the homomolecular exchange of oxygen. Figure 4-18 illustrates the extensive range of activities one can achieve for this exchange reaction. It also shows the parallel behavior of various oxidation reactions. One will note that the oxides of transition metals containing ions with partially filled d-orbitals have the greatest activity. It also has been found that the rate of hetero-exchange,

$$O_2^{18} + O^{16}{}_{surf} \rightarrow O^{18}O^{16} + O^{18}{}_{surf}$$

over oxides which contain an equilibrium amount of oxygen in the surface layer is equal to that for homomolecular exchange (Reference 40). The coincidence of rates of homomolecular and hetero-exchange suggests that on oxides with an equilibrium oxygen content, simple isotopic exchange of molecular oxygen takes place with participation of oxidic lattice oxygen. Since this exchange parallels oxidation rate (Figure 4-18) one can deduce that the strength of the oxygen bond in the oxide plays a significant role in determining activity. This point is further amplified by the data of Figure 4-19, which shows the correlation between activation energies for methane oxidation and oxygen bond strength for a number of oxide catalysts. An analysis of these data suggests that the rate limiting step for methane oxidation involves the breaking of an oxygen-catalyst bond (Reference 40). The oxygen lattice energy in many cases can be controlled by the addition of certain dopants. Thus, Figure 4-20 shows that one can control this parameter and therefore the rate of exchange and the catalyst's oxidation activity.

The above considerations have indicated that the most active simple oxides are:

$$Co_3O_4,\ MnO_2,\ NiO,\ CuO,\ Co_2O_3,\ Fe_2O_3,\ V_2O_5.$$

Other simple oxides such as TiO_2 and ZnO have very low activity, and would therefore be of interest only in the consideration of complex oxides and multicomponent systems.

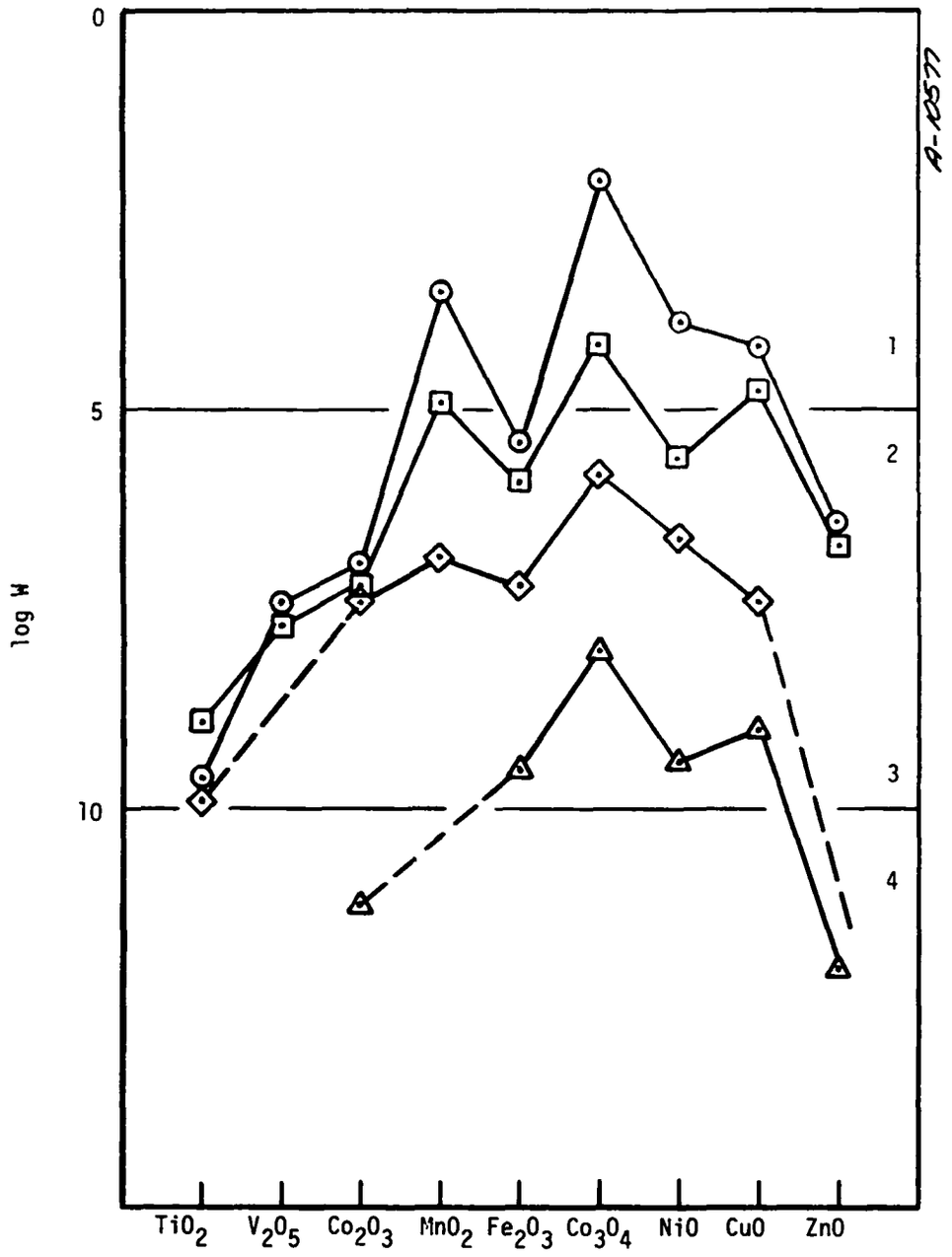


Figure 4-18 . The catalytic activity of oxides of the elements of the fourth period in the homomolecular exchange of oxygen (1), oxidation of hydrogen (2), oxidation of methane (3) and nitrogen oxide decomposition (4) at 300°C.

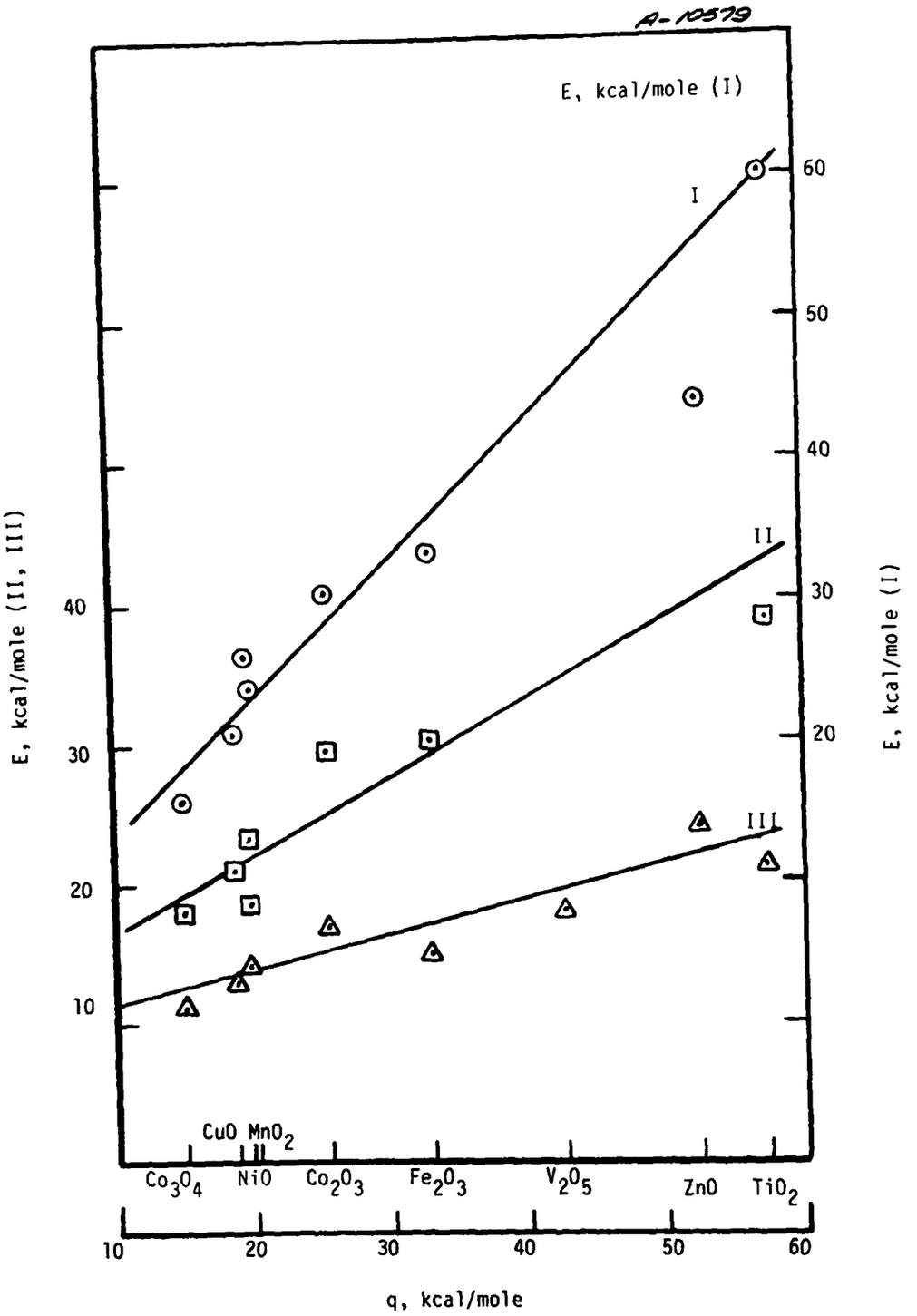


Figure 4-19. Activation energies of homomolecular oxygen exchange reaction (I), methane oxidation (II), as a function of oxygen bond energy, for oxides of elements of the fourth period (Reference 40).

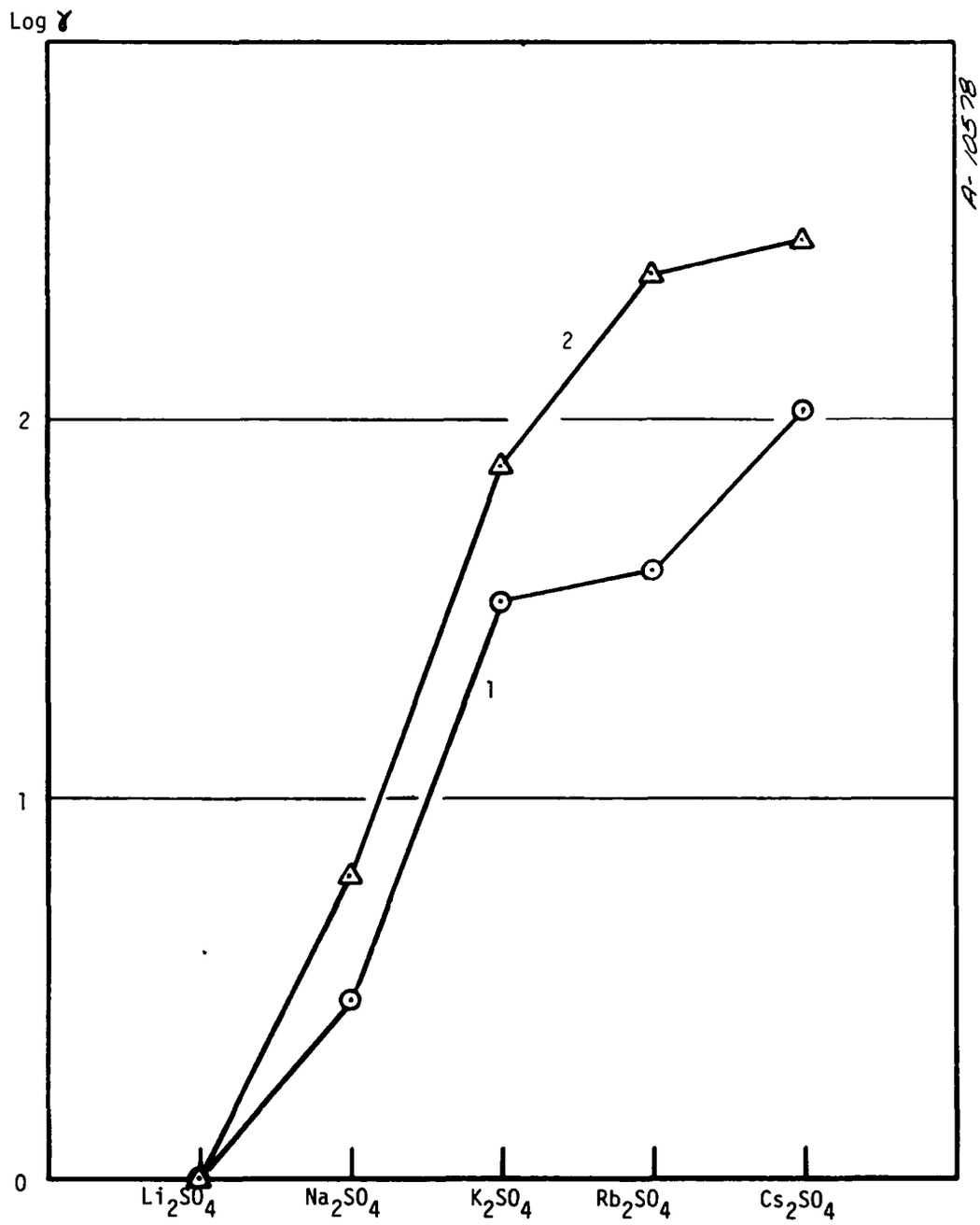


Figure 4-20. Catalytic activity of vanadium pentoxide promoted with sulfates of various alkali metals. Curve 1 – reaction of exchange of molecular oxygen; curve 2 – reaction of oxidation of sulfur dioxide (Reference 40)

As with the metal, multi-component catalysts may provide increased activity and stability. Materials of interest include stable spinel structures such as Co_3O_4/CuO, Cr_2O_3/CuO and La_2O/Co_3O_4. These materials are likely to be very active and show good thermal stability. Doping, using alkali, alkaline-earth metals and rare-earth metals, may also show increased activity and thermal stabilization.

4.2.4 Temperature Capability of Catalyst/Support System

The choice of an optimum catalyst/support combination requires a consideration of the temperature capability of a given combination. The low temperature limit is dictated by the so-called "light-off" temperature. This limitation has been discussed in Section 4.2.3.2. Solutions to this problem are not complex for most catalytic combustion systems, and some of the possible solutions have been discussed in that section. The major thermal limitation for catalytic combustion is the high temperature of operation. The phenomena which lead to catalyst deactivation at high temperatures are:

- Sintering of the catalytic species
- Changes in catalyst stoichiometry
- Sintering of the wash coat
- Thermal degradation of the ceramic support material
- Mechanical failures

Sintering of the catalytic species will lead to a concomitant loss in surface area and therefore a loss in catalyst activity per unit mass of catalyst. The temperature at which sintering occurs is a function of the catalytic material. Thus, Ag will sinter at much lower temperatues than Pt or Rh. In an oversimplified manner this sintering or crystallite growth is a function of the melting point for metals. Thus, Ag melts at much lower temperatures than Pt or Rh, and therefore Ag atoms will have greater mobility at a given temperature than Pt or Rh atoms. Such mobility is required for crystallite growth. A number of techniques have been developed to minimize or prevent sintering. For example, multimetallic systems can be prepared which are more stable than the constituent metals. A number of structural promoters are known. For example, Al_2O_3 is used to stabilize high surface area Fe, which is active for NH_3 synthesis, and ThO_2 is similarly used to stabilize Fe for Fischer-Tropsch syntheses.

Stoichiometry changes for oxides can lead to a catalyst with dramatically different catalytic properties. As previously discussed, loss of lattice oxygen can cause an increase in the energy required to activate O_2 and thereby decrease combustion activity. As indicated in Section 4.2.3.2, one method for overcoming this

problem is to dope the lattice with a material which causes a decrease in the energy necessary to activate oxygen and also stabilizes the stoichiometry of the lattice.

A third mechanism of thermal deactivation is wash coat sintering. At temperatures above 1650°F high surface area η- or γ-Al_2O_3 undergoes a phase change to α-Al_2O_3 with concomitant sintering. The change may be from a surface area of 300 m^2/g to about 5 m^2/g. This sintering results in pore closure and a "burying" of active catalytic sites in the Al_2O_3. To minimize this problem, it is possible to work with catalysts for which the catalytic phase has been deposited on a presintered Al_2O_3. Alternatively, other materials which are thermally more resistant may be investigated as wash coats. These might include ZrO_2, ThO_2 and UO_2.

At very high temperatures, the ceramic support, be it spheres or monolithic honeycomb structures, begins to degrade. Typical substrate fail temperatures have been given in Tables 4-1 and 4-2. Although catalytic combustion units are not expected to operate continuously at the temperatures listed, the possibility of local hot spots occurring due to uneven air/fuel mixing and local catalyst bed nonuniformities must be considered.

Thermal expansion and contraction may also occur at high temperatures. Both pellet and monolithic substrates have thermal expansion coefficients different than their mounting hardware. Considerable catalyst mechanical attrition can occur if the catalyst becomes loose, thus causing a decrease in catalytic performance.

4.2.5 Poisoning Effects

Two types of adsorptive poisoning can be distinguished; (a) homogeneous adsorption of the poisoning molecule, and (b) selective adsorption. In homogeneous adsorption, the poison is uniformly distributed over the catalyst surface and throughout the pores. This usually occurs when the poison is weakly adsorbed on the surface and usually with a strength comparable to that of the reactants. An example of this type of poisoning is the effect of small amounts of sulfur in a dehydrogenation reaction over a Pt catalyst. In this case the sulfur will be removed in the presence of hydrogen at reaction conditions and activity can be recovered. Selective poisoning occurs when the poison is so strongly adsorbed that the pore mouth in the catalyst becomes almost completely poisoned before the pore interior is affected. For this type of poisoning, one can measure the progressive poisoning across the cross-section of the catalyst pellet, provided the concentration of poison is low in the reactant stream. This type of poisoning is usually irreversible and leads to a stoichiometric reaction with the catalytic phase. A typical example is the sulfur poisoning of a nickel catalyst, where the interaction results in a compound formation of nickel sulfide.

Particulate poisoning is also possible and occurs when the catalyst bed acts as a filter and removes particulate material such as carbonaceous particles from the combustion products. This coats the catalyst surface and acts as a physical barrier to the diffusion of reactant species to the catalyst. Deposits of poisons such as lead and inorganic materials are very harmful, as shown by previous work with automotive catalysts.

In general, lead, sulfur and phosphorous are considered strong poisons for metal catalysts because of the possibility of particulate poisoning (lead) or selective adsorption (sulfur and phosphorous). This is confirmed by studies performed in the automotive industry. Other potential poisons are zinc, barium, halides and other trace elements. Restricting consideration to natural gas and light distillate oils, many of these poisons are not expected. Possibly phosphorous, sulfur and certain halides would be the major poisons encountered.

4.2.6 Characterization Techniques

A common basis of comparison is crucial for the effective evaluation of a series of different catalysts. Since catalytic action occurs on the surface of the solid, surface area is the basis that has to be used. Therefore, the only meaningful activity comparison for catalysts is to express the rate on a surface area basis, e.g., moles/sec/cm^2. If this is not done, a catalyst coating of normally very high activity may appear to be less active than one which is normally of lower activity because the former is poorly dispersed and the latter is highly dispersed. A knowledge of the surface characterization of the catalyst is needed to determine the light-off characteristics of the catalyst and the area available for the diffusion of reactant species to active catalyst sites. Ideally, only the surface area of the active catalyst component should be included on this basis. By selective adsorption of either H_2 or CO, one can determine the amount of catalyst exposed at the surface. The titration technique pioneered by Benson and Boudart (Reference 41) can be used to determine the surface area of the noble metal catalysts. No such technique is available for oxides. Total surface area, e.g., by the BET technique (which includes the support), is used for the evaluation of these catalysts.

The correlation of catalytic behavior with the physical properties of a catalyst is crucial in understanding the reasons for catalyst performance. Measurement of the physical properties before and after reaction is particularly important in assessing the thermal stability of a catalyst. Sintering of the catalyst will lead to a loss in surface area and thus a loss in catalyst activity per unit mass of catalyst. Wash coat sintering results in pore closure and the burying of active catalyst sites, again leading to a loss in surface area and a lessening of catalyst activity. The properties that should be determined for the catalysts tested would be:

- Total surface area by the Brunauer, Emmett, Teller method (BET)
- Selective surface area of metallic catalysts by titration, H_2 or CO adsorption

- Pore volume and pore size distribution by physical adsorption or Hg porosimetry
- Structure and particle size by x-ray crystallography
- Metal or oxide distribution within the catalyst pellets by scanning microprobe analysis.

In cases where catalyst agglomeration cannot be measured by selective chemisorption, x-ray diffraction can be used to determine an average particle size. This technique, however, is limited to particles greater than 40 Å in size and crystalline in structure. In the case of oxides, x-ray crystallography is also helpful to determine the phase of the oxide and any changes in stoichiometry that may occur due to the high temperatures of the reaction.

4.3 EXISTING APPLICATIONS OF CATALYTIC OXIDATION CONCEPTS*

The existing applications of catalytic oxidation concepts in industry are largely in the low-temperature area at this time. Several current research programs are concerned with high-temperature catalytic combustion applications, and these will be discussed in Section 4.4. In this section the use of catalytic combustion for the following applications will be discussed:

- Nitric acid plant tail gas cleanup
- Industrial odor control
- Small catalytic heaters
- Automotive oxidation catalyst systems.

4.3.1 Nitric Acid Plant Tail Gas Cleanup

Nitric acid is produced commercially by reacting ammonia with air to produce nitrogen oxides, which are then absorbed in water to yield nitric acid. The basic steps in the production of nitric acid from ammonia are:

- Reaction of ammonia with air over a catalyst at high temperature to produce nitric oxide
- Oxidation of the nitric oxide by oxygen remaining in the gas stream to produce nitrogen dioxide
- Absorption of the nitrogen dioxide in water to produce nitric acid, with additional nitric oxide being released which must be reoxidized.

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*This discussion will deal only with catalytic combustion, as defined in Section 2, rather than with high-temperature refractory surface combustion; Reference 7 reviewed applications in this second category in detail.

Large amounts of unabsorbed nitrogen oxides in the tail gas from the absorption tower pose a pollution problem, which has been solved in some cases by the catalytic processing of this tail gas over platinum-group metals to yield useful energy in the form of steam and/or power (References 42-26). The basic reactions for the catalytic treatment of nitric acid tail gas over platinum, palladium, or rhodium for methane reducing fuel are:

- $CH_4 + 4NO_2 \rightarrow 4NO + CO_2 + 2H_2O$ (decolorization)
- $CH_4 + O_2 \rightarrow CO_2 + 2H_2O$ (combustion)
- $CH_4 + 4NO \rightarrow CO_2 + 2H_2O + 2N_2$ (abatement)

The tail gas reactor outlet temperature is usually between 1250°F and 1380°F. Support materials for the catalyst have included nichrome wire, alumina pellets, and alumina honeycomb materials

4.3.2 Industrial Odor Control

The elimination of organic fumes is desirable from both air pollution and fire safety points of view. The platinum metals have been used for several years as catalysts for the oxidation of carbon monoxide and a wide range of organic molecules in the presence of air or oxygen. Most odors are caused by the emission of low concentrations of organic molecules to the air, with these organic molecules always containing carbon and hydrogen and generally sulphur, nitrogen, and oxygen as well. Since most industrial odor problems are caused by organic compound concentrations well below the level required for spontaneous combustion in air, it is necessary to raise the contaminated air stream temperature to a level at which combustion can occur The use of catalysts lowers the temperature needed to achieve odor removal, and also lowers the necessary residence time at the combustion temperature. A typical catalytic incinerator using a platinized ceramic honeycomb catalyst is shown in Figure 4-21.

Various catalyst systems presently in use for industrial odor control are discussed in References 48-54. In Reference 49, heat removal from the catalyst bed is achieved through the use of pipe coils embedded in the catalyst layers. This technique is very effective in limiting the catalyst temperatures.

4.3.3 Low-Temperature Catalytic Heaters

Low-temperature catalytic heaters are characterized by the small portable radiant heaters that operate at temperatures below 800°F. Operating characteristics include heat release rates of approximately 75 Btu/in^2 and lifetimes of several thousand hours. A typical low-temperature catalytic heater is shown in Figure 4-22. Gaseous fuel enters the metal disk through an orifice. The disk is designed to

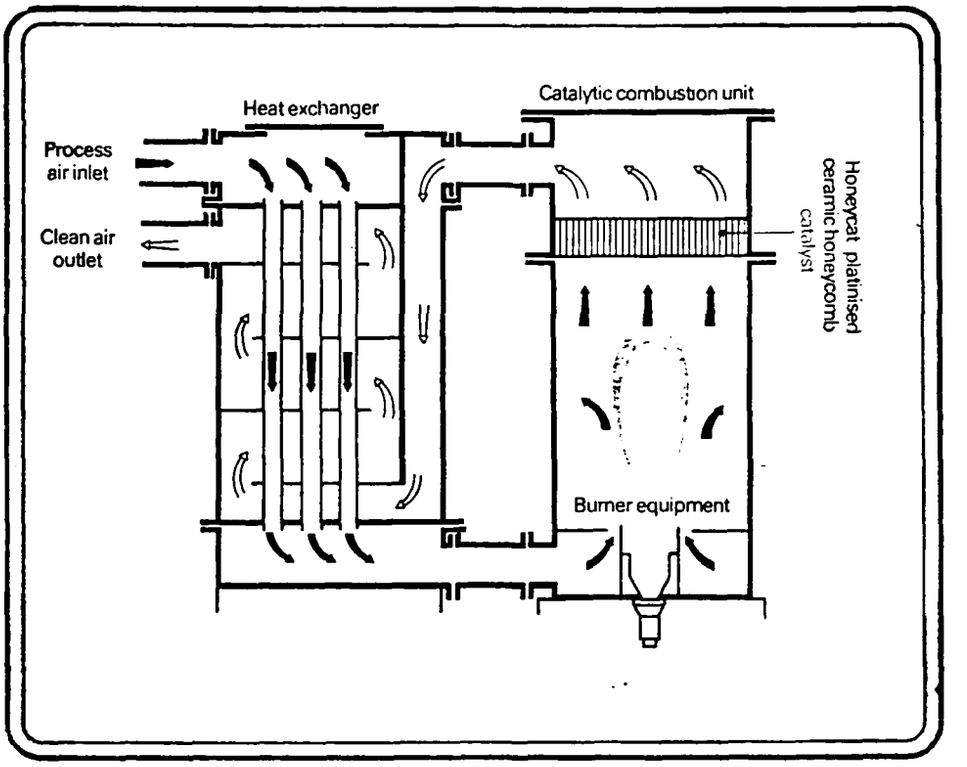


Figure 4-21. Flow diagram of a typical catalytic incinerator using a honeycomb catalyst (Reference 11).

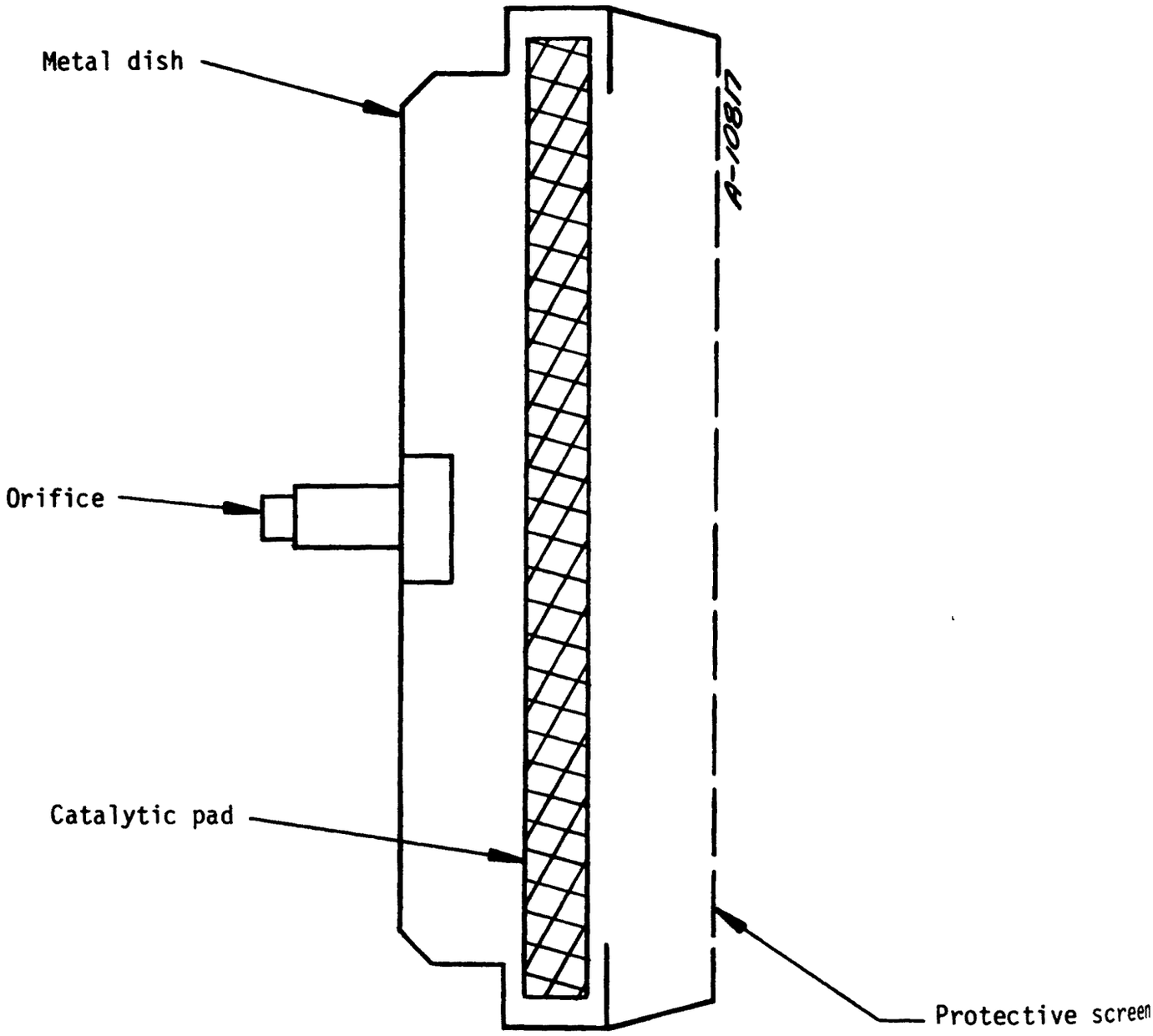


Figure 4-22. Schematic diagram - low temperature catalytic heater.

evenly distribute the gas to all parts of the catalytic pad, and combustion takes place on the surface of the fibers of the pad. A metal screen protects the front face of the pad. A variety of applications for low temperature catalytic heaters is given in Reference 55.

The Control Systems Laboratory of the EPA has conducted an extensive emissions testing program on a number of catalytic heaters, as reported in Reference 56. No correlation between emissions and specific heat release rates was found, and CO and UHC levels were generally quite high.

4.3.4 Automotive Exhaust Catalysts

Since platinum metal catalysts were selected for emission control on conventional automotive internal combustion engines for the 1975 model year, a great deal of development work went into these emission control systems. In general, NO_x emissions are controlled by a reduction mechanism, and CO and UHC emissions are removed by catalytic oxidation with secondary air added to the exhaust stream to ensure complete oxidation.

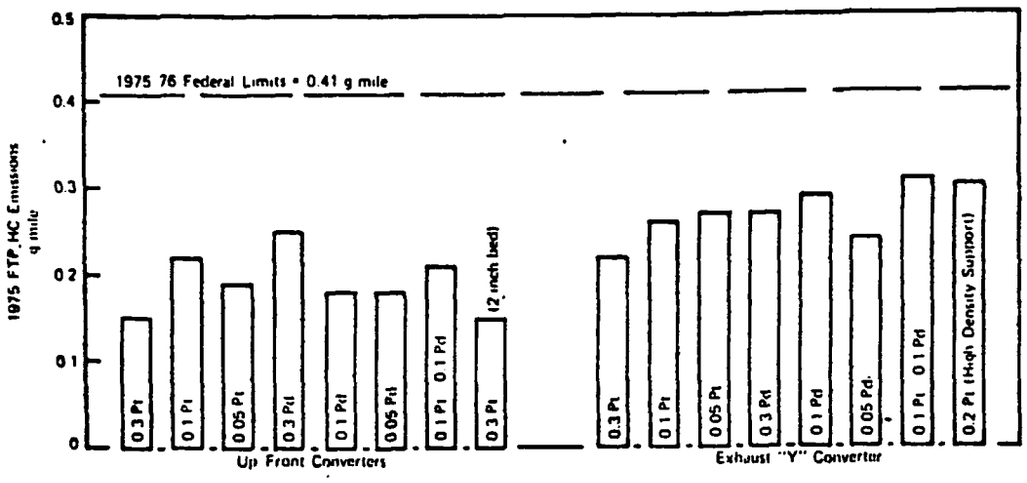
A reactor for catalytic exhaust emission control has three essential design features:

- A ceramic support on which the catalyst is deposited in a manner that prevents attrition
- Rapid warm-up of the catalyst unit, and hence rapid light-off
- Nearly complete conversion efficiency.

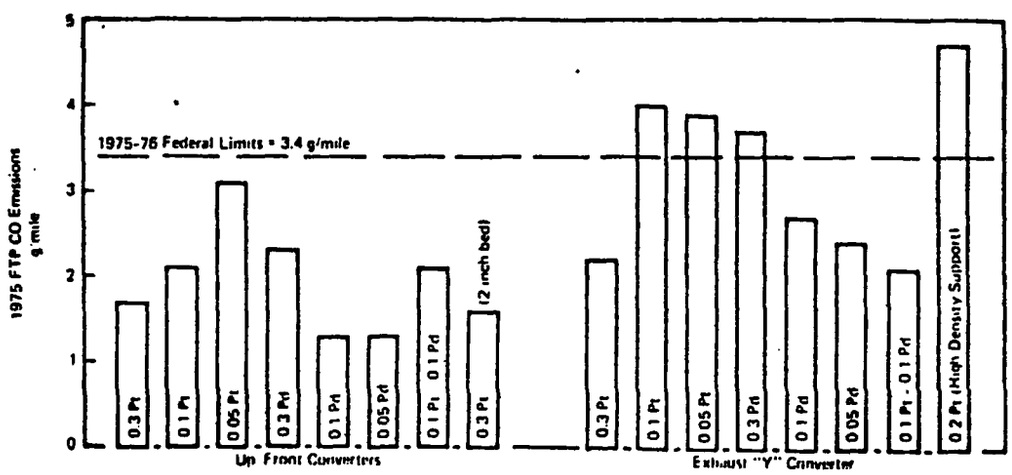
The essential features of a satisfactory CO/UHC oxidation catalyst for automotive emission control are (Reference 57):

- A light-off temperature in the region of 250°C
- Conversion efficiencies in excess of 90 percent for both CO and UHC at space velocities up to 150,000/hr
- High temperature stability of the support and platinic crystallite system at temperatures to 950°C
- Poison resistance to compounds containing lead, phosphorous, and sulfur.

Platinum-palladium catalysts have been extensively tested in full-scale vehicle tests (Reference 58). Two different locations were tested: at the exhaust manifold outlet flange (up-front), and at the exhaust system "Y", where the exhaust streams merge. Figure 4-23 shows the effect of catalyst composition on CO and UHC emissions. As seen here, the differences between Pt and Pd catalyst performances were quite small.



a. UHC emissions



b. CO emissions

Figure 4-23. Effect of catalyst composition on 1975 FTP emissions (Reference 58).

Reference 59 discusses possible substitute catalysts for platinum in automobile emission control. In this study it was concluded that base metal catalysts generally are not as effective as platinum/palladium catalysts for automobile emission control, especially for hydrocarbon and carbon monoxide oxidation. For NO_x reduction, certain base metal catalysts initially are more active and selective than are noble metal catalysts; however, most suffer from rapid deactivation.

4.4 CURRENT RESEARCH PROGRAMS IN CATALYTIC COMBUSTION

Since catalytic combustors have excellent potential for low NO_x emissions, a number of research programs investigating their use in automotive, gas turbine, domestic appliance, and home furnace applications are currently going on. Much of this work is being conducted under proprietary secrecy agreements, making it impossible to gather information on the catalyst material and method of preparation.

This section describes on-going research programs in catalytic combustion. It cannot provide an all-inclusive compilation of catalytic combustion research, due to the proprietary nature of the subject.

4.4.1 Air Force Aero Propulsion Laboratory

The AFAPL has conducted an in-house program to study the feasibility of using solid catalytic beds in the reaction zone of aircraft gas turbine combustors, and reported this work in Reference 60. The catalytic unit used in this program was supplied by Engelhard Industries at no charge under a secrecy agreement as to the nature of the combustor. The bed was of the monolith type, with pressure drops of approximately 1 percent at 40 fps inlet velocity and 4 percent at 80 fps inlet velocity. No igniter was needed as preheated air at 800°F was used to get the bed to operating temperature.

All tests were run at low equivalence ratios (fuel-lean operation) on JP-4 fuel. Flashback and pre-ignition were observed during the tests, causing the Air Force to do considerable work in developing an acceptable fuels introduction system.

At all operating conditions tested, NO_x concentration was below 2 ppm. Virtually 100 percent combustion efficiency was obtained at combustor inlet temperatures above 700°F and fuel-air ratios above 0.02, and specific heat release rates of 3.5×10^6 Btu/atm-hr-ft^3 were achieved. A diagram of the AFAPL catalytic combustor system assembly is shown in Figure 4-24, with CO and hydrocarbon emission data shown in Figure 4-25, and combustion efficiency in Figure 4-26. Figure 4-25 indicates that emissions were sharply reduced when the fuel-air ratio was above 0.0212. These data were then translated into the combustion efficiency curve of Figure 4-26, where combustion efficiencies of nearly 100 percent are noted for fuel-air ratios above 0.0195.

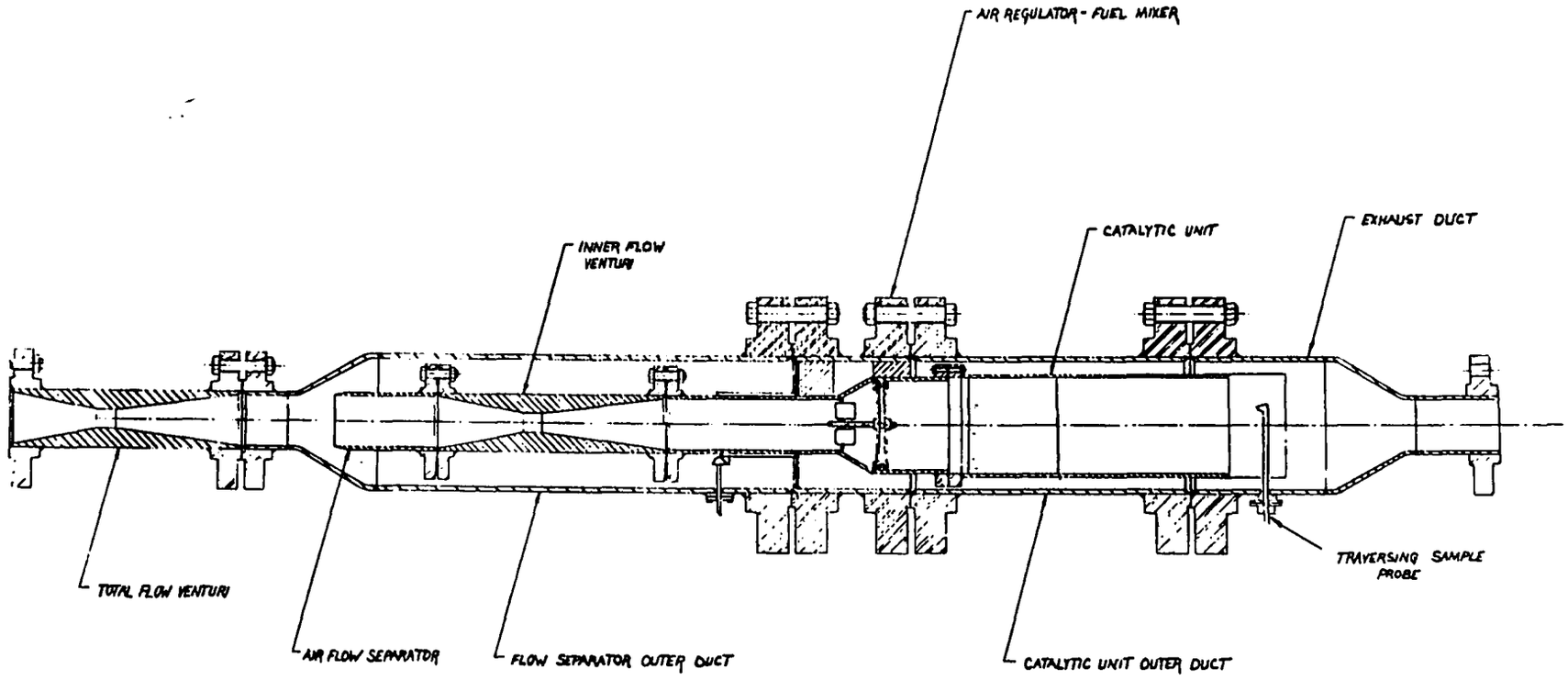


Figure 4-24. AFAPL's catalytic combustor system assembly.

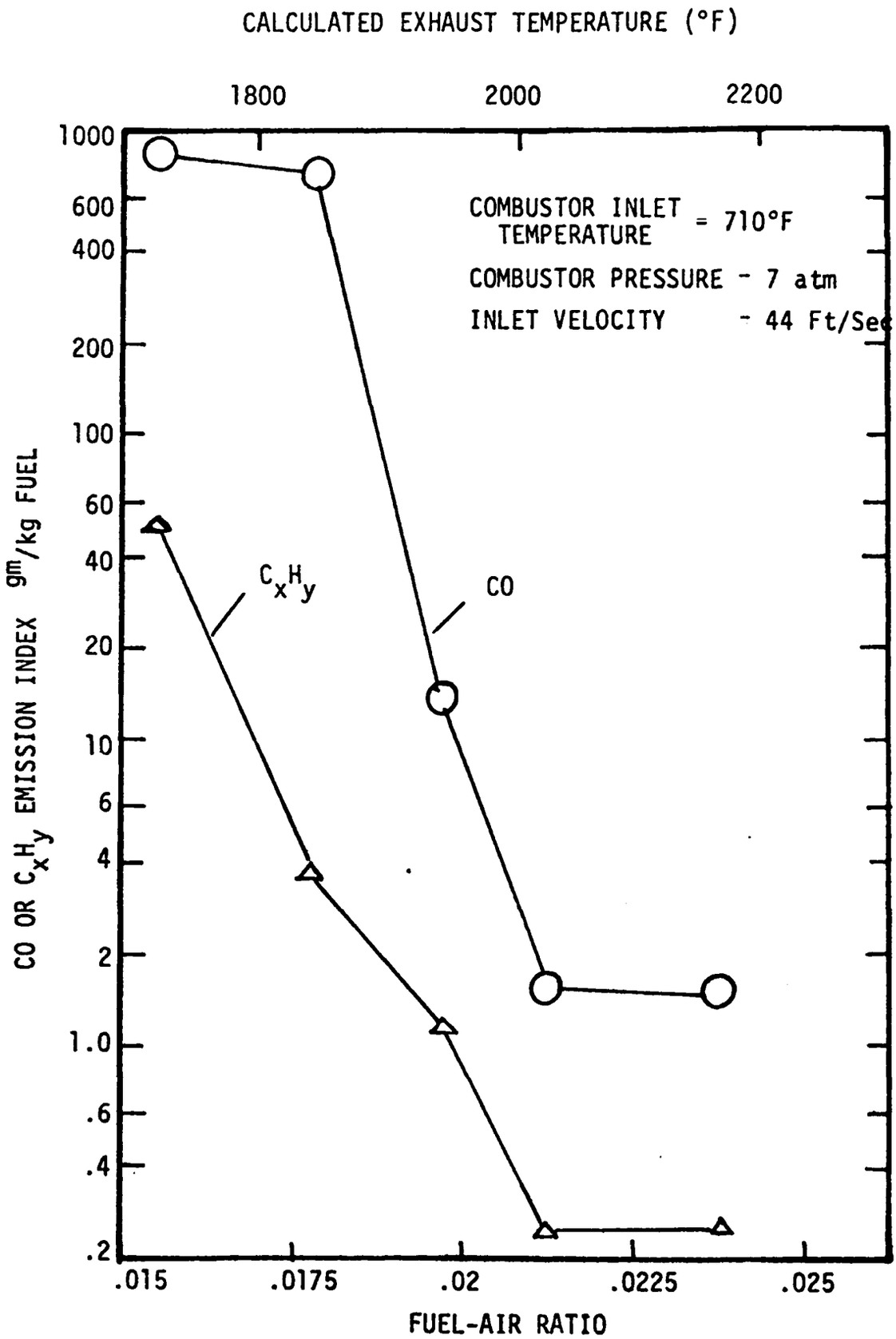


Figure 4-25. CO and C_xH_y emission index variation with fuel air ratio (Reference 60).

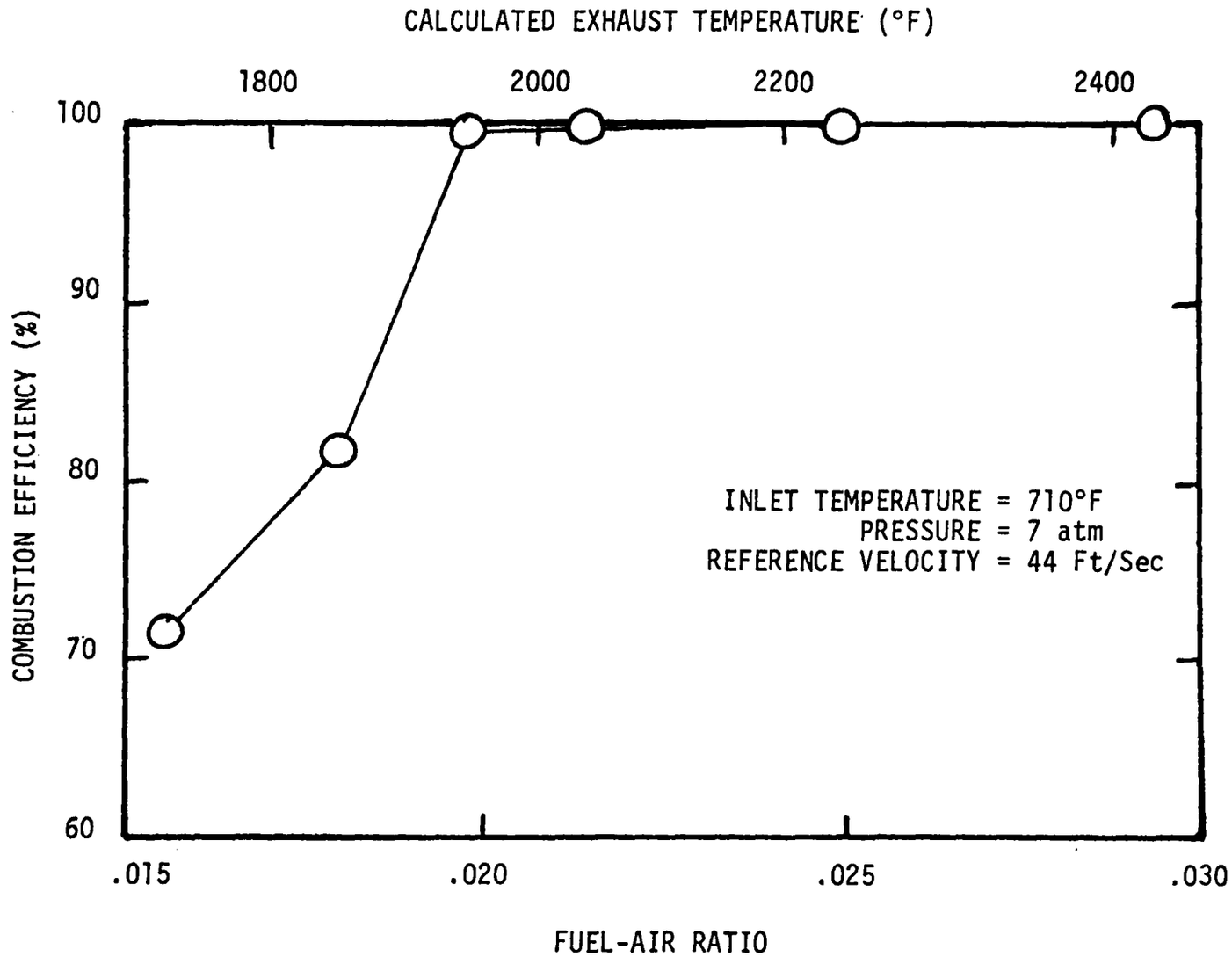


Figure 4-26. Combustion efficiency variation with fuel-air ratio (Reference 60).

The combustor tested in this program was designed for high-power application, and the AFAPL is presently involved in selecting a contractor to begin work on a low-power catalytic combustor. Work on the low-power phase should begin by June 1, 1976.

4.4.2 Bratko Corporation

Rudolph Bratko, owner of the Bratko Corporation, is engaged in industrial process heating work, and is also active in the use of fiber pads as combustors in radiant-furnace applications. Mr. Bratko holds patents for the application of Johns-Manville fiber pads to surface or catalytic combustion applications (References 32, 34), and is presently working on a home furnace concept in which the fiber pad is built in the shape of a top hat. Using natural gas or propane as the fuel, Bratko passes a premixed air-fuel stream through the fiber pad and ignites the mixture on the pad surface. The extremely low thermal conductivity of the pad prevents flash-back, and Bratko claims 100,000 Btu/ft^2 heat release, with combustor surface temperatures of approximately 1700°F. The top hat combustor has been placed in a conventional home furnace by Bratko, with excellent results.

4.4.3 Detroit Diesel Allison Division, General Motors Corporation

Detroit Diesel Allison has conducted a test program in which three different catalysts, consisting of Pt-catalyst coated ceramic monoliths having different catalyst surface concentrations, were used to investigate the combustion of propane-air mixtures at inlet temperatures of 700°K as a function of fuel-air ratio. No details are available on the composition of the catalysts. These tests, reported in Reference 61, are intended as screening tests for gas turbine applications. A typical set of data for one of the catalysts is shown in Table 4-4, and shows that at a fuel-air ratio of 0.0152, excellent NO_x, HC, and CO emission levels are attained.

4.4.4 Engelhard Industries

Engelhard has done a great deal of work on gas turbine catalytic combustors, both in-house and in liaison arrangements with other investigators. Because of Engelhard's proprietary concerns, however, they are able to make very little of their information public. Their efforts in catalytic combustion include the following areas:

- Catalyst screening
- Catalyst evaluation/performance studies (fuel-air ratio, inlet temperature, etc.)
- Liaison area-working with others (AFAPL, NASA-Lewis, industries)
- Interfacing of catalyst with product.

TABLE 4-4. COMBUSTION PARAMETERS FOR CATALYST C, DETROIT DIESEL ALLISON TESTS, 7.6 CM LENGTH x 8.9 CM DIAMETER[a]

Run No.	Air (kg/hr)	(Mass/Mass) C_3H_8/Air	°K		% CO_2	g/kg C_3H_8			% η_b
			Inlet	Outlet		NO_x	HC	CO	
B.G.	41.8	0	708	653	0.08	--	--	--	0
1	41.8	0.00586	711	686	0.30	0	712	0.164	26.3761
2	41.8	0.00895	711	739	0.70	0	542	1.08	41.6383
3	41.8	0.0106	714	789	1.17	0	465	1.91	53.8397
4	41.8	0.0121	714	869	1.77	0.013	376	54.2	65.2915
5	41.8	0.0143	719	1000	2.83	0.022	244	82.3	78.9164
6	41.8	0.0152	719	1144	4.95	0.042	0	0.222	99.9998

[a]B.G. denotes background readings obtained prior to run.

From data generated internally on small test rigs, Engelhard's present operating range for the catalyst bed is:

- Inlet temperature: 400°F 1000°F
- Operating temperature: 2000°F 2600°F
- Pressure: 1-10 atm
- Heat release rate: 100,000 20,000,000 Btu/hr-ft^{3}atm
- Fuel — Gaseous, lead-free distillate (almost all fuels have been tested)
- Combustion efficiency: 99.99 percent
- NO_x emissions: 1 ppm.

Engelhard has done some studies on catalyst life, and found good performance after 1000 hours of operation for some combinations. They have also tested both pellet bed and honeycomb monoliths, but prefer the honeycomb because of its low pressure drop.

Engelhard is now actively engaged in conducting full-scale tests of catalytic combustors for gas turbine application. Some of their test results to date include:

- Size: 5- to 7-inch diameter, 0.5- to 2-foot length
- Fuels: Gasoline, JP-4, diesel, propane
- Operating range: Catalyst inlet temperature 600°F 1000°F
  Catalyst exit temperature: 2000°F 2800°F
  Pressure: 3-10 atm
- Emissions: HC = 0.01 g/kg fuel
  CO = 0.1 g/kg fuel
  NO_x 0.1 g/kg fuel.

The goal now is to interface the catalyst with the engine and develop a burner that is not simply a laboratory device. Their in-house work is actively pursuing this goal.

4.4.5 Institute of Gas Technology

IGT has been involved in the development of catalytic combustors since the early 1950's. Their main investigations have involved the use of methane and propane for fuels in catalytic combustion devices. Currently, IGT has three programs going on in the catalytic combustion area:

- Subcontractor to Engelhard on an EPA contract on cracked ammonia
- Contractor on a Southern California Gas Company contract for ventless home appliances
- Contractor on a joint EPA-SCG range-top burner development for hydrogen catalytic combustion

- Contractor on methane and propane catalytic combustion units for various commercial sponsors.

Since there are different temperature requirements for various appliances, IGT feels that more than one burner design will be necessary for the variety of home appliances. They have investigated the complete combustion and emissions aspects of ventless home appliances, using reformed natural gas as the fuel. The gas produced by steam reforming of methane is approximately 80 percent hydrogen, 20 percent carbon dioxide, and a trace of carbon monoxide. Using this fuel, a variety of appliances have been developed (Reference 62). These burners use a noble metal catalyst placed on a permeable support plate, and are self-igniting at room temperature (Reference 63). Emissions data have been reported for these ventless appliances (Reference 64), and show very small amounts of NO_x and CO (typical values are 1.1×10^{-4} lb/10^6 Btu for NO_x, 4×10^{-2} lb/10^6 Btu for CO).

In summary, IGT's work on ventless home appliances shows the following advantages and disadvantages:

- Advantages

  Produce minimal quantities of pollutants

  - Ventless appliances reduce building construction costs

  Can humidify homes concurrently with heating

  High efficiency from catalytic combustion

  Lower operating temperatures reduce fire hazard

  Self-igniting catalytic appliances eliminate pilots or ignition systems

- Disadvantages

  Hydrogen not currently available as fuel

  Catalyst life may be limited

  Odorant required for safety which must not poison catalyst

  Safety hazard from extreme combustibility of hydrogen

  Excessive humidification of homes may result

4.4.6 Jet Propulsion Laboratory

JPL has been conducting tests over the past 18 months on a compact onboard hydrogen generator for use with a hydrogen-enriched gasoline internal combustion engine. This modified fuel system, called partial hydrogen injection, substantially lowers NO_x emissions and also increases engine efficiency considerably. Details of the system are discussed in References 65 and 66.

The hydrogen generator uses gasoline and air in a partial oxidation reactor to produce a gaseous product consisting of hydrogen, carbon monoxide, minor amounts of methane, carbon dioxide and water, and nitrogen. It was found that a nickel catalyst speeds up the partial oxidation reaction, and commercially available nickel catalysts known as steam reforming catalysts were used. A sketch of JPL's catalytic reactor is shown in Figure 4-27, and an exploded view of the reactor is seen in Figure 4-28. Alumina pellets have usually been used as the support, but monolith structures are also being tested.

Typical catalytic generator operating conditions and output are given in Table 4-5. Air preheat of 450°F is utilized to prevent any condensation of the vaporized gasoline. The air-fuel ratio of 5.15 is the theoretical optimum operating point, where a hydrogen/fuel mass ratio of 0.136 can be obtained under soot-free conditions. Note that the hydrogen/fuel mass ratio actually obtained in this test was 0.12.

4.4.7 NASA-Lewis Research Center

The NASA-Lewis program in gas turbine catalytic combustor development began when Engelhard provided a test unit to Lewis on a no-cost basis and under a secrecy agreement. This unit had very low CO, UHC, and NO_x emissions, and encouraged Lewis to continue working with Engelhard on catalytic combustor development for gas turbines.

In addition to contractual work with Engelhard, NASA-Lewis is currently pursuing two in-house programs on catalytic combustion. Both programs are just being initiated at this time. One program will consider the screening of a large number of catalyst-support combinations, determining such parameters as ignition temperature, maximum temperature, and poisons. The goal is to select several good candidate catalyst-support combinations for further development work.

The second in-house program is concerned with the fuel-air preparation systems for introduction of the premixed fluid to the catalyst bed. Fuel distribution and start-up properties of the catalyst system will be studied, with an effective carburetion system as the goal.

4.4.8 Oxy-Catalyst, Incorporated

Oxy-Catalyst, long active in fume abatement by catalytic oxidation, has been assigned a patent on a dual-catalytic bed device for the oxidation of internal combustion engine exhaust gases (Reference 67). In this device, shown in Figure 4-29, a catalytic hot resistance element of small mass and surface area is placed upstream of a catalyst bed of large mass and surface area. The hot resistance element quickly reaches catalytically effective temperature, and its heat plus the heat of catalytic

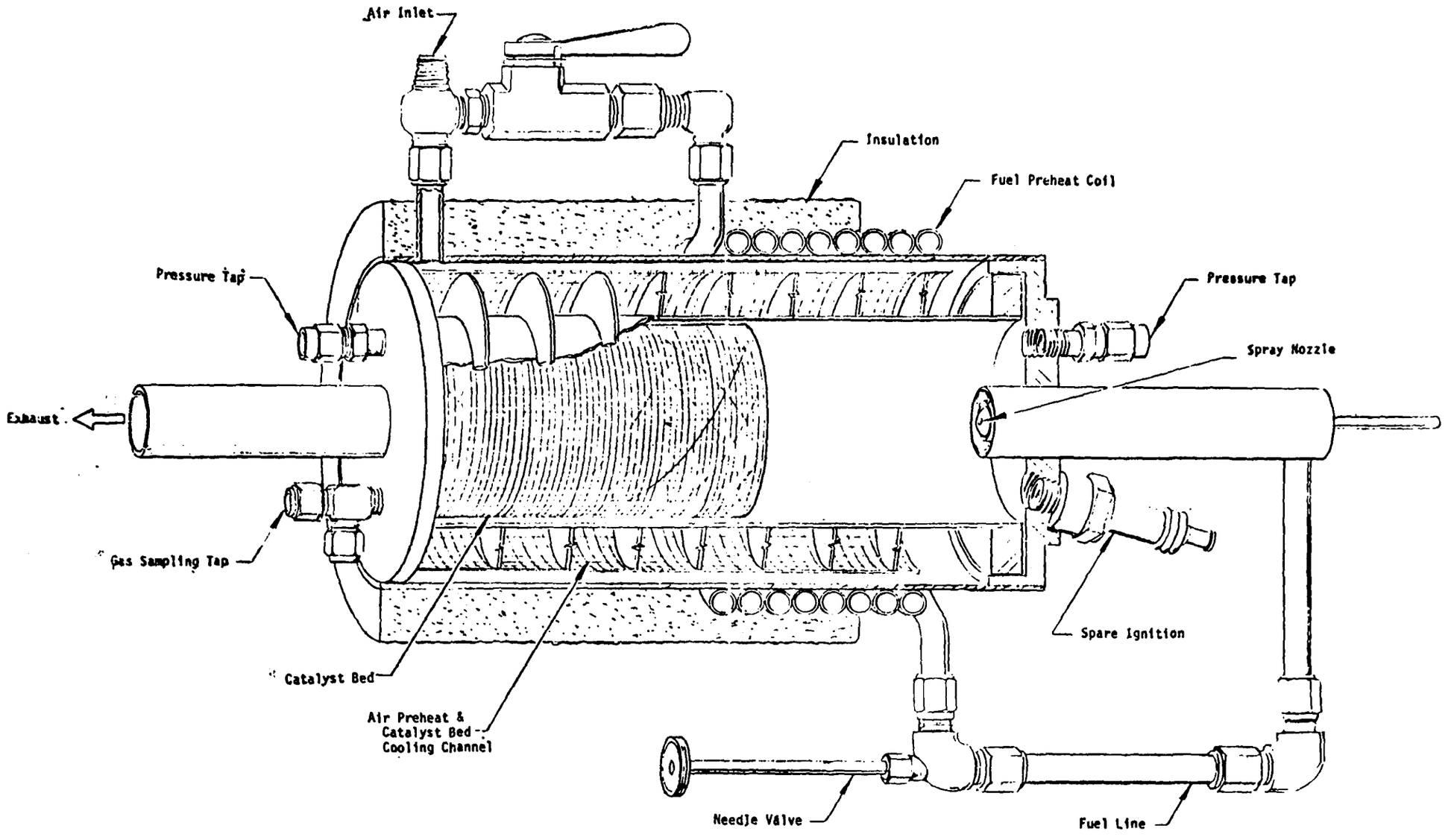


Figure 4-27. JPL Small Scale Catalytic Combustor System.

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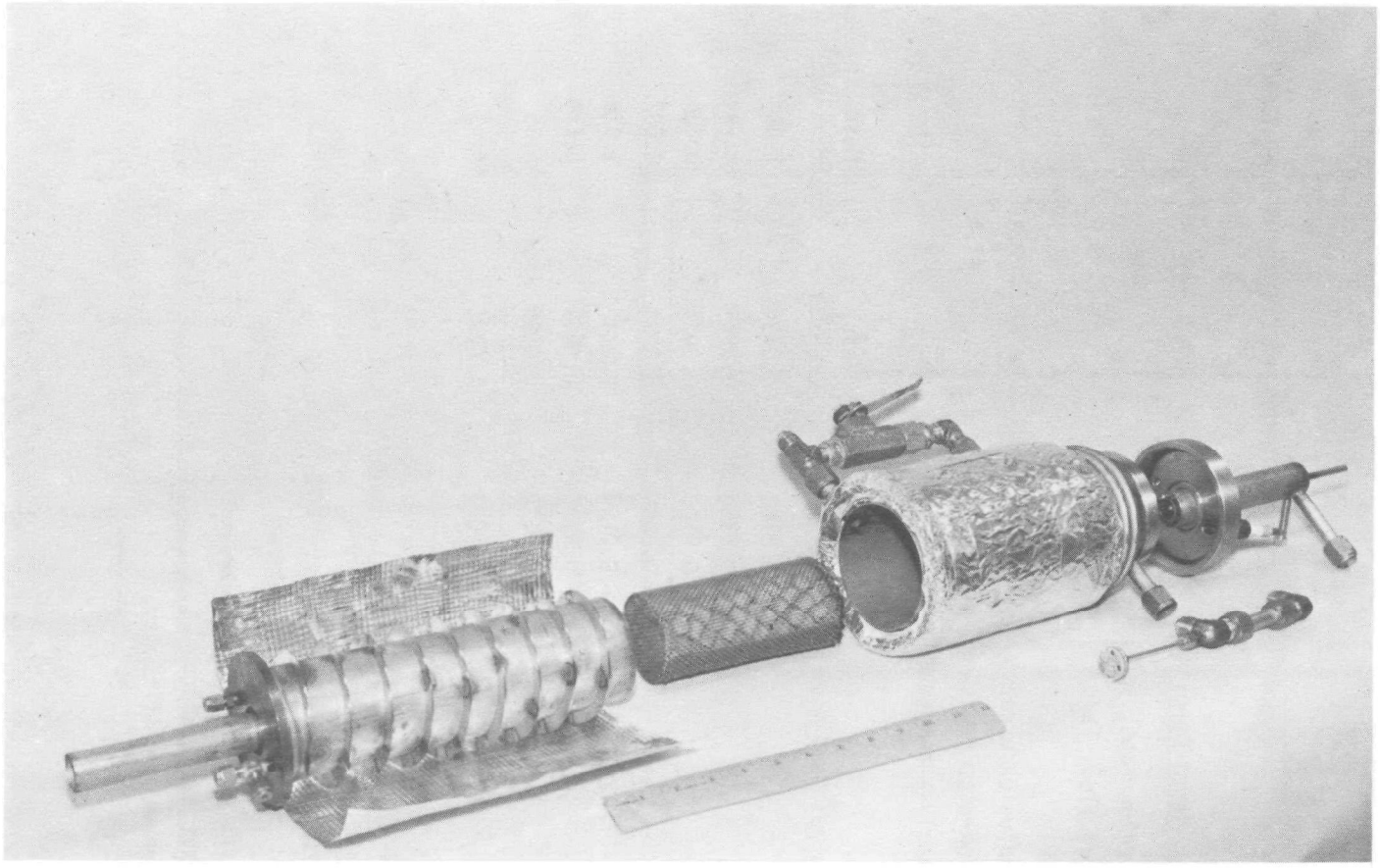


Figure 4-28. Exploded view of catalytic compact reactor containing cold-start burner, air pre-heat heat exchanger, and catalyst bed containing 1.5 pounds of catalyst pellets.

TABLE 4-5. TYPICAL JPL CATALYTIC GENERATOR OPERATING CONDITIONS

Input Condition	Value
Airflow rate, lb/h	45.6
Fuel flow, lb/h	8.9
A/F	5.15
Equivalence ratio	2.83
Generator pressure, psig	1.4
Catalyst temperature, °F	1774

Output Condition	Mole Fraction	Mass Fraction	Mass Output, lb/h
H_2	0.2160	0.0194	1.06
CO	0.2360	0.296	16.19
CH_4	0.0103	0.0074	0.404
C_2H_4	0.0009	0.0011	0.062
CO_2	0.0123	0.024	1.326
H_2O	0.0120	0.0097	0.529
N_2	0.5125	0.6420	35.15
	1.0000	1.000	54.72

Mean molecular weight	22.33
H_2/hydrocarbon mass ratio	0.12
H/C atomic ratio	1.925
Exit pressure, psig	1.0
Exit temperature, °F	1527.0
Generator efficiency	0.785

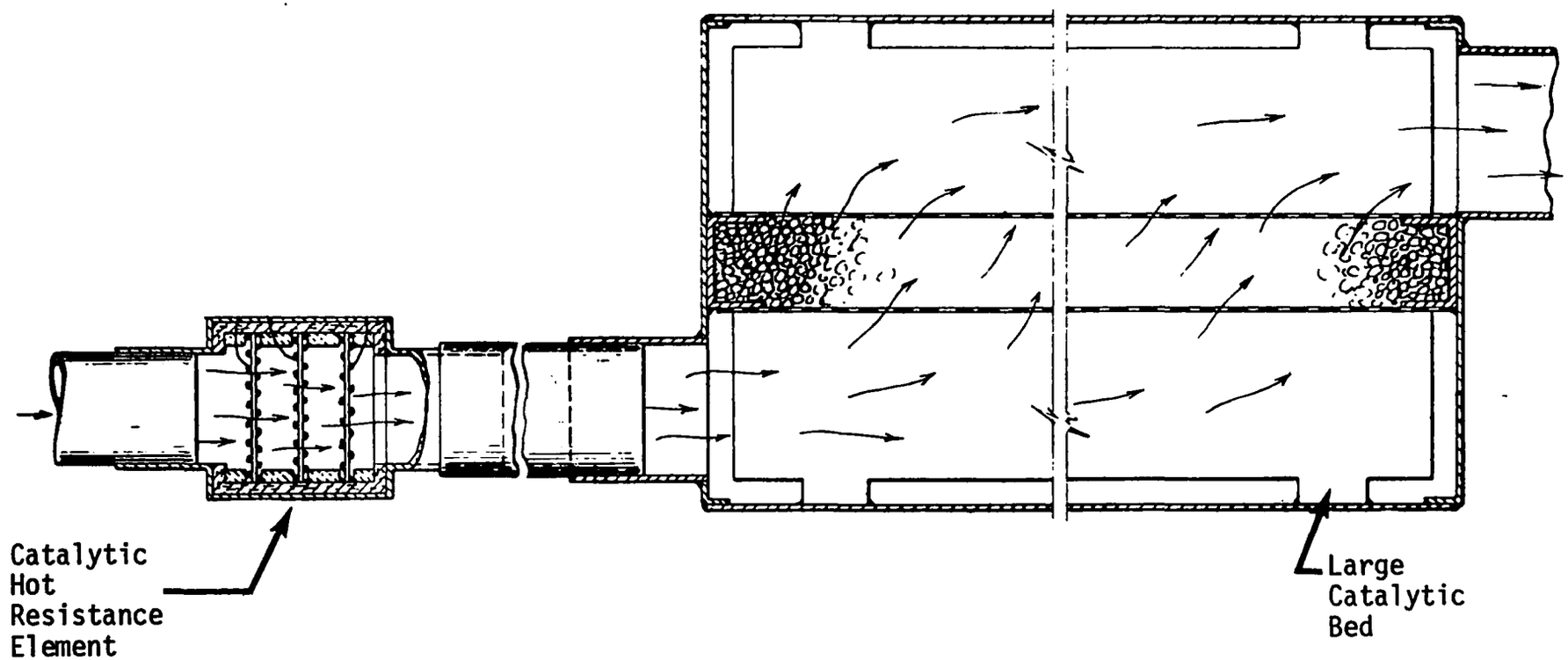


Figure 4-29. Oxy-catalyst's dual-catalytic bed oxidation apparatus (Reference 67).

oxidation serve to accelerate the heating of the second, large catalyst bed. The device thus serves as an aid in overcoming the problems of cold starting, wherein the catalytic bed is ineffective until considerable time has passed.

4.4.9 Tokyo Gas Company, LTD

In order to reduce NO_x emissions, the Tokyo Gas Company has developed a technique for two-stage combustion wherein partial combustion at high fuel-air ratios is carried out in the first stage, secondary air is added, and the combustion is completed in the second stage. Nitrogen compounds such as HCN, NH_3 and NO are formed in the first stage and are converted to NO_x in the second stage. These nitrogen compounds can be reduced by carrying out the primary combustion with the aid of a catalytic bed. Reference 68 discusses the work done in detail; a schematic diagram of the experimental facility is shown in Figure 4-30.

The amount of nitrogen compounds NO, HCN, and NH_3 formed in the fuel-rich conditions of the first stage is closely related to the type of primary combustion. Figure 4-31 shows the variation in nitrogen compounds as a function of primary combustion chamber equivalence ratio. The use of catalysts to promote the partial combustion and thus suppress the formation of these nitrogen compounds is shown in Figure 4-32. As the nitrogen compounds decrease in the primary combustion, NO_x in the exhaust gas is also reduced.

4.5 CONCLUSIONS

Based upon the review of the catalytic combustion process, the available catalyst materials and their properties, the existing applications of catalytic combustion, and the current research programs in catalytic combustion, the following conclusions have been made:

- The overall success of a catalytic combustion system in reducing CO and UHC to low levels is a function of both heterogeneous and gas-phase reactions; surface reactions alone cannot achieve the desired low values.
- New high-temperature catalyst support materials that are capable of maintaining their structural and thermal integrity at temperatures up to 3000°F are necessary for high system efficiency unless methods for cooling the catalyst bed are used. These materials come in pellet, monolith, and fiber pad geometries. However, the catalyst coating is limited to much lower temperatures (i.e., 1800°F) than the support.
- The most promising catalyst materials are the noble metals, such as platnum and palladium, because of their high activity and relatively low activation temperature.

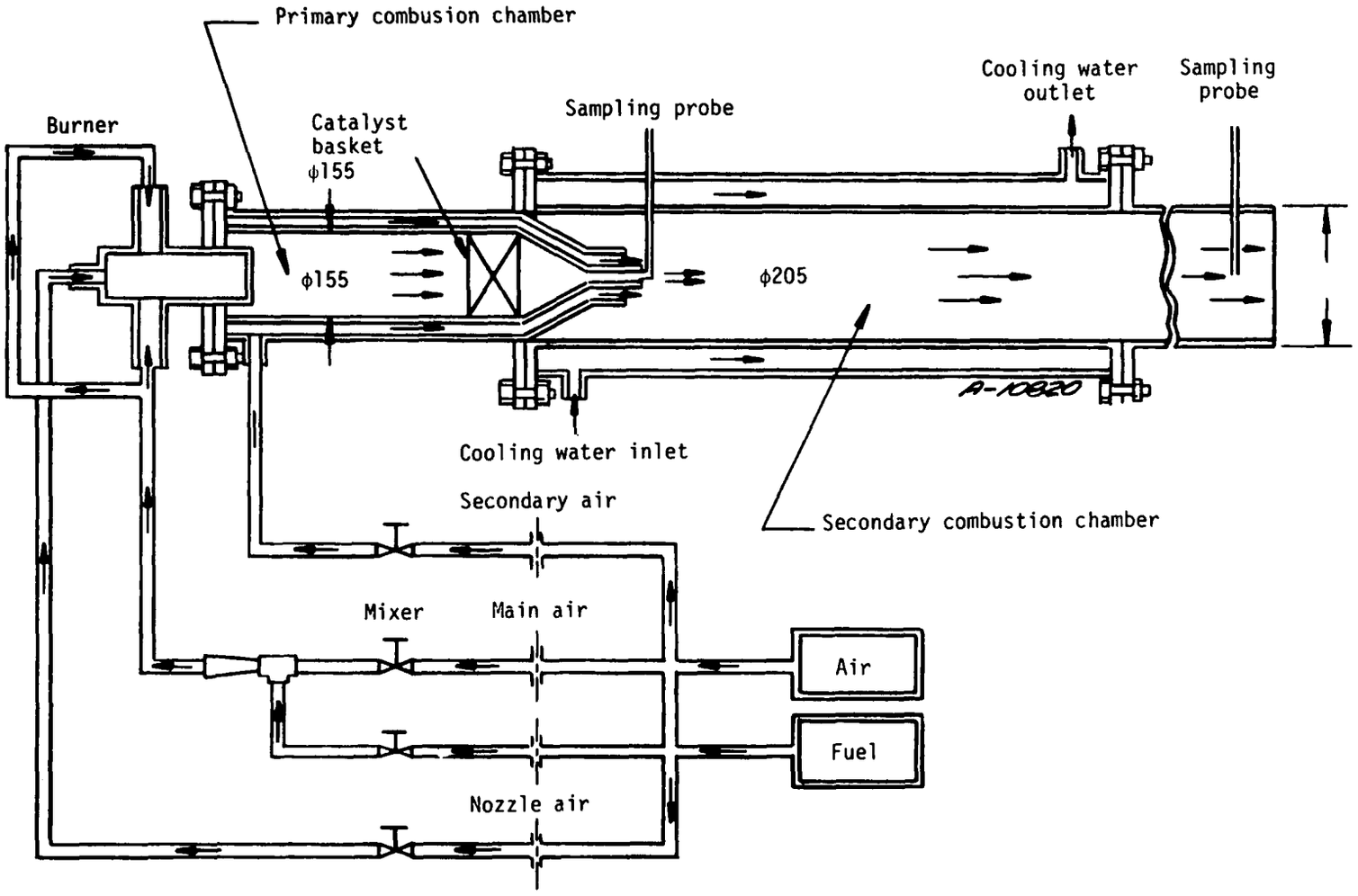


Figure 4-30. Schematic diagram — Tokyo Gas Company's two-stage combustion method for NO_x reduction (Reference 68).

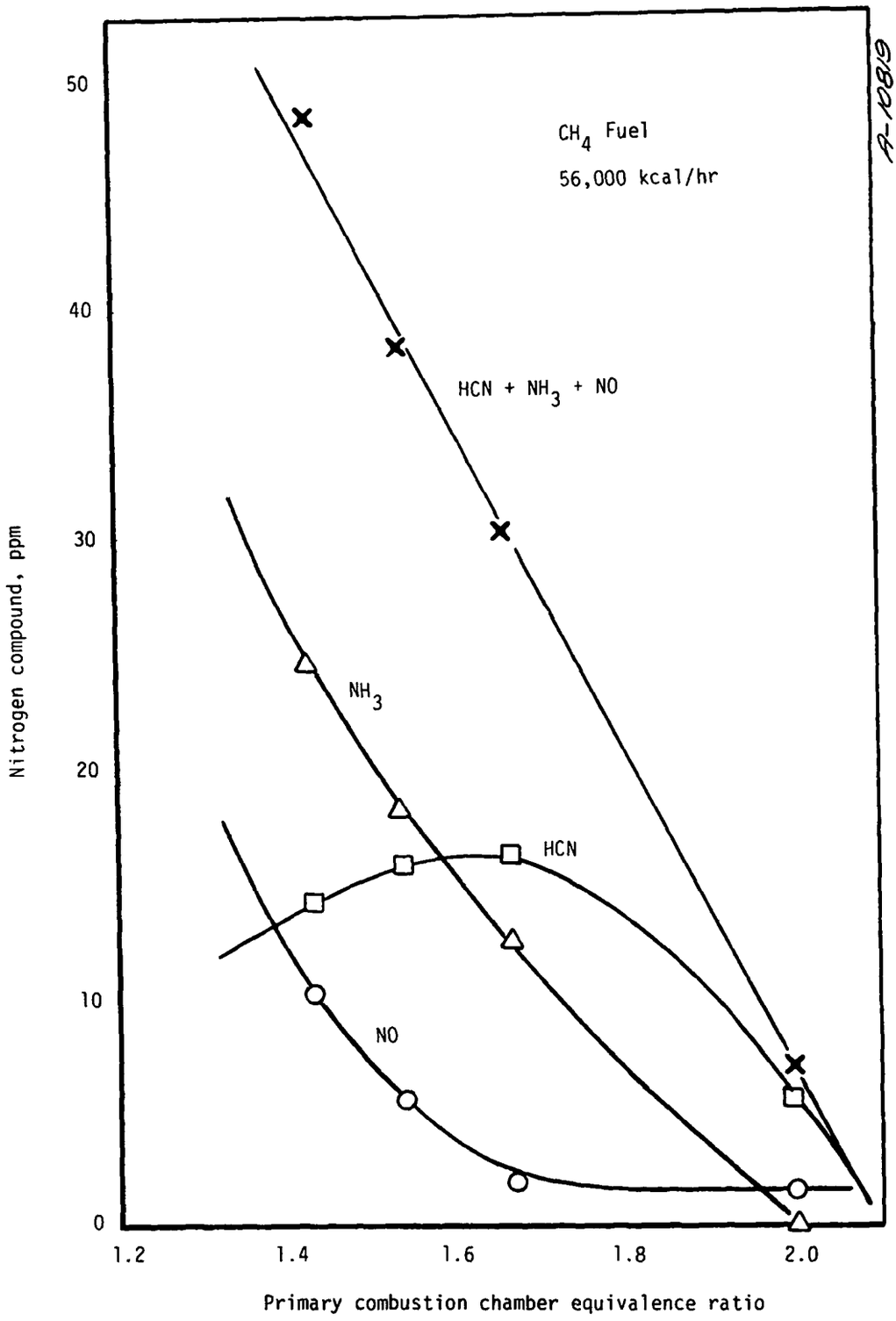


Figure 4-31. Variation in nitrogen compounds as a function of primary combustion chamber equivalence ratio (Reference 68).

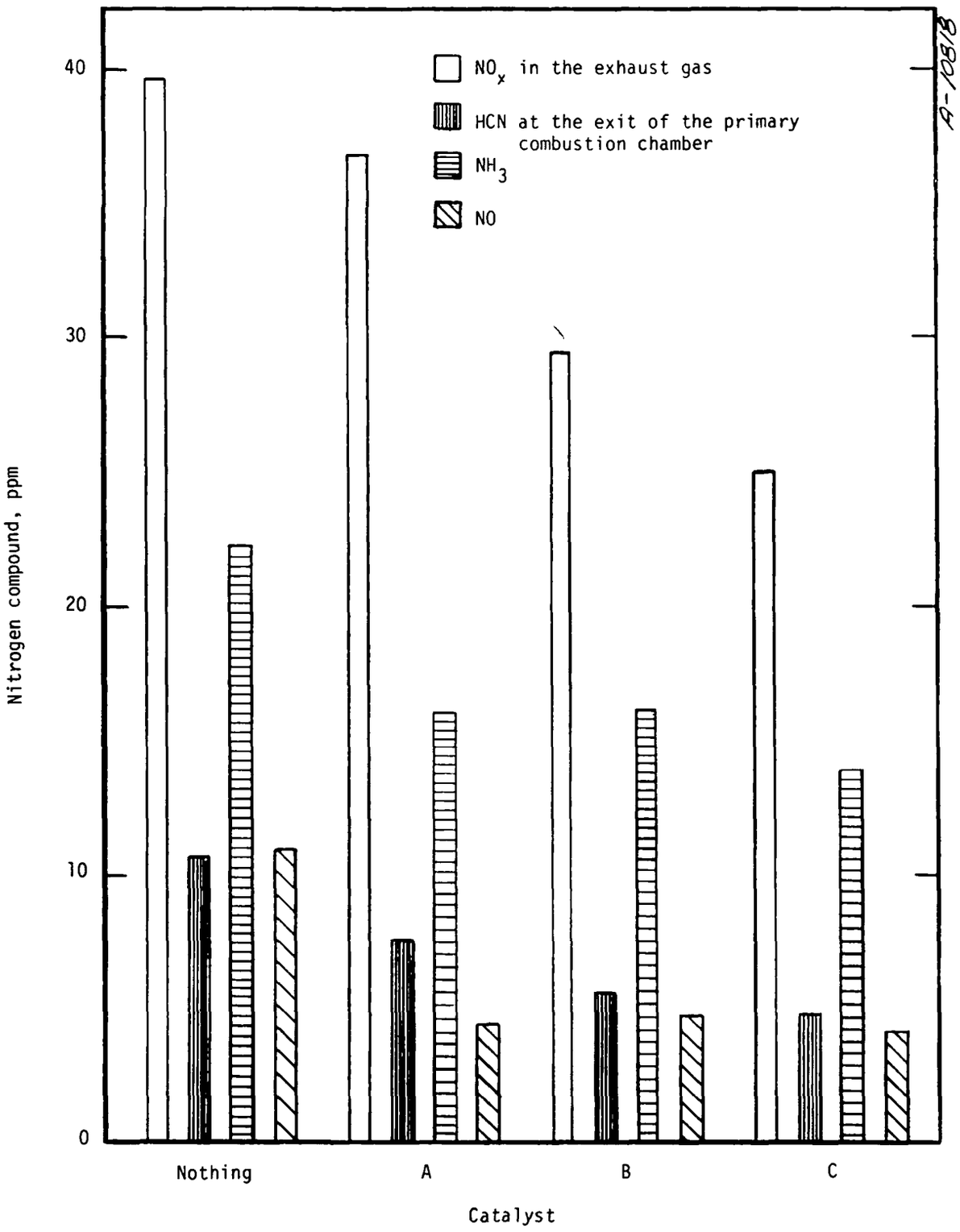


Figure 4-32. Effect of various catalysts on the formation of nitrogen compounds (Reference 68).

- Metal oxides have activities which approach those of the noble metals, but have significantly higher light-off temperatures, probably limiting their use to spinel structures.
- The principal catalyst poisons for natural gas and light distillate oils will probably be phosphorous, sulfur, and certain halides. Their effect on a variety of catalysts is not known.
- The existing applications of catalytic oxidation concepts in industry, such as in nitric acid plant tail gas cleanup, industrial odor control, small catalytic heaters, and automotive oxidation catalyst systems, are generally in the low-temperature range of applicability. The applicability of this technology to high-temperature catalytic combustion is therefore quite limited, since the problems of catalyst sintering and thermal degradation of the support are avoided at low temperatures (i.e., <1400°F).
- Research is presently being conducted in the area of high-temperature catalytic combustion for application to gas turbine engines. This research is done with extremely fuel-lean conditions, making it difficult to relate directly to domestic, commercial, and industrial space heaters, where near stoichiometric conditions are desirable.
- Two-stage combustion, wherein the first stage is run fuel-rich and secondary air is added in a catalytic second stage to complete the combustion, is effective in controlling emissions of NO_x. CO and UHC emissions can be controlled at the same time by proper design, keeping the system fuel-air ratio near stoichiometric. Staging should be examined carefully for application to catalytic combustor technology.
- Because of the necessity of avoiding local "hot spots" in the catalyst bed, premixed fuel-air systems are needed for catalytic combustors. To prevent blockage of the passages in a catalyst bed, liquid fuels must be pre-vaporized. The problems associated with fuels introduction to the catalyst bed are formidable ones that require careful attention.
- At the present time, it is assumed the catalyst bed temperature must be held below 2800°F to minimize the formation of NO_x. Further research work should be undertaken to determine this temperature.
- The current research programs have all been conducted at catalyst bed temperatures well below 2800°F (i.e., 2400°F), and have all demonstrated a successful minimization of NO_x formation.
- Because much of the research concerning catalytic oxidation is proprietary information and therefore not available to the general research community, an experimental program which examines catalyst-support performance and addresses the application of these catalysts in various combustor-heat exchanger systems is needed. Information on the proper methodology to follow in selecting a catalyst is also unavailable from catalyst manufacturers.

SECTION 5

APPLICABILITY OF CATALYTIC FUELS OXIDATION CONCEPTS TO AREA SOURCES

The usefulness of the information presented in the previous sections will be proven through the development of a complete combustion system. This study has been limited to assessing the applicability of the information generated to three area sources: home heating systems, commercial boilers and industrial boilers. The following section includes a discussion of the options and problems associated with the applicability of catalytic combustion to these areas. The ultimate test of the concept through actual hardware development must await a further study.

This section attempts to discuss the factors which must be considered when assessing the applicability of catalytic combustion to this equipment. Following this, some conceptual designs are presented and the advantages and disadvantages discussed.

This section begins with a discussion on the potential matrix of possibilities that confronts the designer.

5.1 POTENTIAL DESIGN MATRIX

The potential design matrix may be considered by reference to the "design tree" illustrated in Figure 5-1. Six levels of design choices, consisting of New/Retrofit, Applications, Catalyst Support Arrangement, Cooling, Staging, and Flue Gas Recirculation (FGR), are shown on the tree. The complete tree, of course, is not shown. Whenever there is a branch ending with "same" and an arrow pointing to the next level, this indicates that the identical set of branches is below <u>each</u> of those boxes. Even this extensive tree does not represent the full choice of options available to the designer, since within the catalyst support structure category there are different monolith styles (materials, open area, shape, wall thickness), packed beds (shape, size, material), or fiber pads that could be considered. The objective is to prune this tree; to either eliminate whole application areas (if only because another area appears more promising) or to narrow the choices for a given area. It

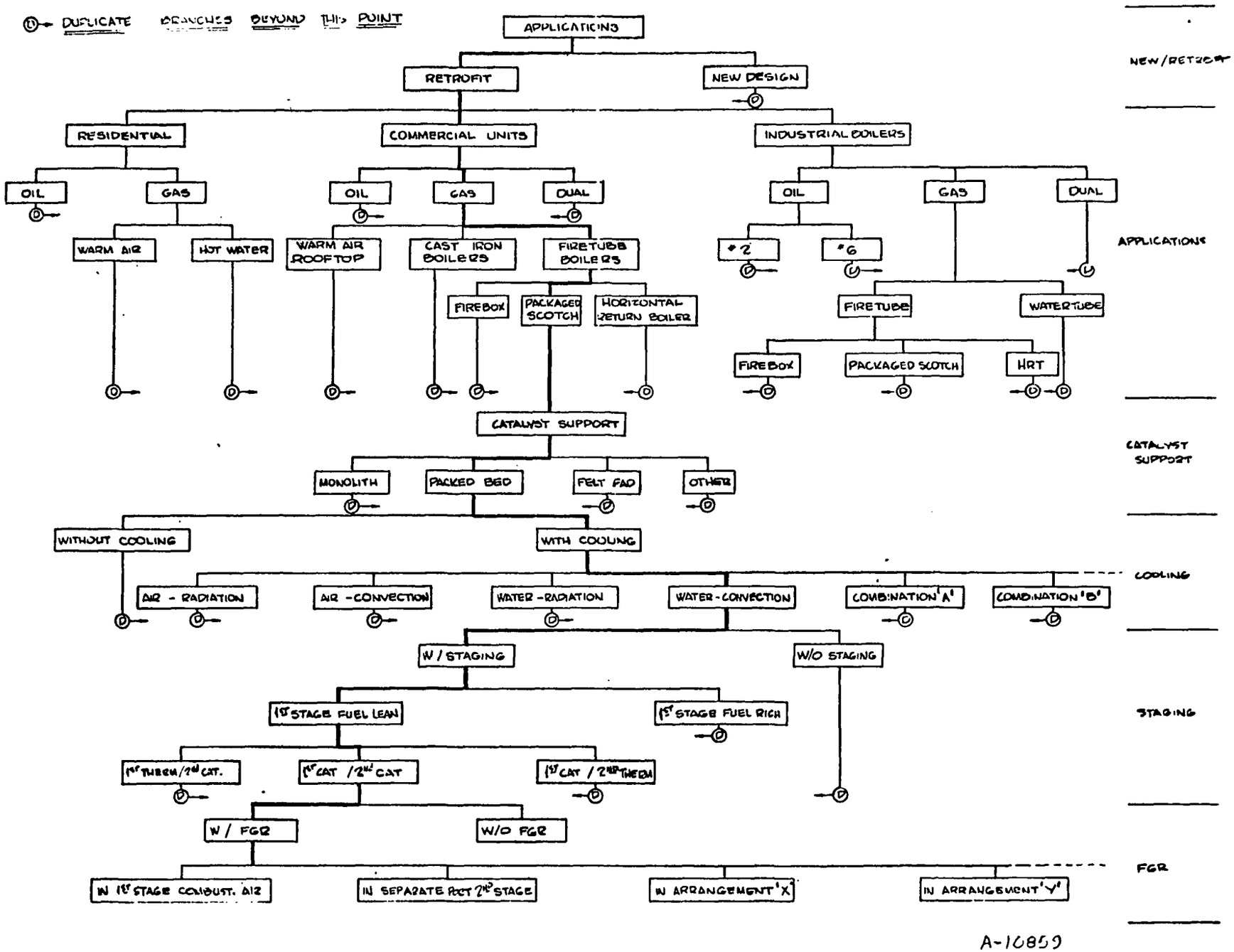


Figure 5-1. Potential design matrix.

may be necessary to make some arbitrary choices when there is no rational reason for one option over another, but clearly these options must be reduced in some logical manner to limit the choices to a practical number. A brief review and discussion of each of these areas is given below.

5.1.1 New Versus Retrofit

A new design requires a totally different design approach than a retrofit design. In a new design one can arrange the heat transfer area as required to take advantage of the unique characteristics of catalytic combustion particularly where radiation is required. The design will also not necessarily be restricted to design for minimum pressure drop. It also may be easier in a new design to reduce the overall volume and thus cost using catalytic combustion. Finally, in a new design there are many more options available to the designer. This is good in the sense that he is not as restricted but unfortunately it makes it more difficult to select the best approach.

In a retrofit design there will always be certain dimensional as well as process constraints. Pressure drop and particularly heat transfer problems have to be overcome using existing equipment. But, perhaps most importantly, cost will be a much more significant factor in a retrofit design.

At this point it seems possible to come up with designs for both the new and retrofit application areas.

5.1.2 Applications

Section 3 discussed the important features of the potential application areas in some detail, and indicated that the design requirements for each of the three application areas vary considerably. Here the relationship of each of the applications to the other design variables as shown in Figure 5-1 is discussed.

5.1.2.1 Residential Furnaces

As can be seen in Figure 5-1 there are basically two furnace types that are of interest: warm air furnaces and hot water boilers (either gas or oil fired). Gas fired warm air furnaces will be discussed first, followed by oil fired warm air furnaces, gas fired hot water and oil fired hot water boilers.

Warm air furnaces, under present design practices, are quite pressure-drop limited on both the flue gas and process side (when the process fluid is air). There is no inherent reason, however, other than cost of blowers and perhaps noise, why the pressure drop should be so limited in new designs. To retrofit, however, care must be given to these pressure levels and if higher pressure drops are required it may

necessitate replacing or adding a combustion air blower or induced draft fan. In addition, higher velocities may be required on the process side to increase heat transfer rates. Whatever is done that might influence cost, it should be remembered that home owners and developers operate on a lowest first cost basis rather than total operating cost; this will significantly influence the maximum permissible system cost. In addition, no flue gases may be allowed to leak to the process side and the ratio of process stream/flue gas is on the order of 100 to 1. Home furnaces have a heat release rate of 10,000 to 300,000 Btu/hr and operate at nominally atmospheric pressure.

Also of prime concern for the home heating application is the cyclic nature of the equipment as discussed in Section 3.2. Where thermal masses may be significantly higher in a catalytic system it may be advisable to try to modulate the firing rate to match the load. Either way presents problems with flame stability and off-design heat transfer and special problems for liquid fuels, as will be discussed in a later section. Also of importance here is the ratio of warm-up time to cycle-on time because most any catalytic system will require a thermal combustion warm-up period. If the thermal mass of the unit can be kept low then the period of higher pollutant formation will be kept low.

For the gas fired warm air furnace, then, the felt pad may be a good choice for a catalyst support material. However, both the monolith and packed bed approach are also feasible. The monolith is a better choice from a pressure drop view point. Gas fired units typically operate with uncontrolled secondary air. Thus, some form of closure will be required if the fuel/air ratio is to be controlled. Staging, cooling and flue gas recirculation will be discussed in a later section.

Most any of the design options look feasible for new designs, although with warm air furnaces an auxiliary fluid may be required to achieve significant radiation heat transfer from a bed.

The oil fired warm air furnace typically uses a relatively large refractory or refractory felt-lined combustion chamber with a separate heat exchanger. This volume should allow sufficient room to incorporate most any design configuration which involves staging, internal bed cooling, various catalyst supports and an oil vaporizer. One drawback is that little heat transfer surface or local heat sink will be available to assist in cooling the bed. Problems associated with all oil systems will be discussed in a section on fuels.

The oil fired hot water furnace (or cast iron boiler) also utilizes a similar large combustion volume. One advantage in this case is that oftentimes the combustion

volume is backed by a flooded water surface. This surface may be able to be utilized as a heat sink to aid in cooling the bed.

Gas fired hot water furnaces come in a variety of designs. Some look almost identical to the oil fired cast iron boilers except the combustion volume is foreshortened. Usually the same "gas logs" are used as with the warm air furnace and the combustion volume is open for secondary air addition. Therefore, the same comments apply as with the warm air furnace except that the combustion volume is considerably larger which may allow greater latitude in design concepts.

5.1.2.2 Commercial Units

Commercial heating systems can be broken down into basically three categories – warm air roof top, cast iron boilers and firetube boilers. Any of these may be gas fired, oil fired and dual fuel fired. The gas fired warm air system utilizes a forced combustion system with a Maxon type burner even though the heat release rates are not much different than residential furnaces. Considerable excess air is still used, however, to keep the hot flue gas temperature down. Units employ a variety of flue gas to air heat exchange surfaces but most have higher heat transfer rates than the home furnace. This may allow sufficient radiation cooling of the catalyst bed. The cast iron commercial boilers are not unlike the residential units and offer considerable combustion volume to work with. Dual fuel units present the problem of trying to design a complete oil fired system with all the associated ramifications and cost penalties as well. Firetube designs also offer considerable volume to work with and have the added advantage of a water wall for heat transfer purposes.

With regard to a preference for any of the design parameters at this time no one design branch seems to have an advantage over another. These systems may allow greater pressure drop and a more sophisticated design due to greater capital cost of this size of equipment. This may allow use of the packed bed approach with its greater pressure drop. Since most commercial heating systems utilize water it will easily be available as a heat transfer medium. If two stage catalytic combustion is eventually shown to be one of the optimum routes to pursue there surely will be ample volume to incorporate that approach. It may even be possible to introduce the second stage air at the first return manifold in a multipass firetube configuration and to use the smaller tubes as a catalyst holder in the second stage.

Cycling will also be a factor but will not be as severe as in the residential application. Many manufacturers are now advertising using several small units to achieve modulation by bringing them on line only as needed. The same approach could be taken using catalytic combustion.

5.1.2.3 Industrial Boilers

In the lower heat release range the units are predominately firetube whereas in the larger sizes they are almost exclusively watertube, either package or field erected. Essentially the same comments apply with the firetube boilers in the industrial size range as with the commerical boilers. The only additional criteria governing the design will be that again greater capital costs will be involved and the loads will be more uniform.

Watertube boilers are generally of the waterwall design with single or multiple burners in front wall, horizontally opposed or tangentially fired configurations. Although there certainly will be sufficient volume to accommodate most any catalytic replacement burner design by extending into the combustion volume it may be rather difficult to accomplish for a retrofit design. The water walls will usually provide only a minimum opening or access for the burner into the combustion space. If the catalytic burner cannot be accommodated into this open area it will either require extending the burner into the firebox or to the backside. If it extends into the firebox this will present many materials and structural problems. If it extends to the backside some auxiliary internal cooling will be required. Again at this point any of the catalyst support materials are candidates as well as any of the other NO_x control schemes. Flue gas recirculation may be a strong candidate due to the simplicity, especially for the retrofit application. Testing will be required to determine the performance of catalytic combustion with FGR. New designs for industrial boilers will probably arrange to facilitate radiation heat transfer from the bed. To do this in the very large heat release rates of large industrial boilers may require a very different design approach. For example, the burner may become a large radiative slab in the center of the boiler. Water walls could be incorporated into the structure of this burner to help support it and perhaps provide some internal bed cooling as well.

A very large packed bed with internal cooling may be an alternate approach for the industrial boiler. The bed itself would provide the initial heating of the water-steam circuit. The bed would be followed by conventional convective sections. Perhaps the chief problem with this approach is accessibility for maintenance to the water or steam tubes buried within the bed. The dual fuel capability must also be built into this equipment.

5.1.3 Catalysts

Section 4.2 indicates many possible candidate catalysts. Taking the above applications into account as well as start-up problems, catalyst support, cooling, staging, and fuel, different catalysts may be appropriate for different applications. From an applications viewpoint, cost will also be a significant factor.

5.1.4 Catalyst Support Arrangement

The choice of the catalyst support arrangement will be a strong function of the proposed design. Different supports can be formed into a variety of shapes to give different pressure drop characteristics and activity area per unit volume. Table 5-1 lists some of the characteristics of the various support arrangements from an application point of view, along with the respective advantages and disadvantages. As we shall see later in this section, a significant feature of the monolith (honeycomb) structure is the ability for this material to be fabricated into a crossflow heat exchanger (either metal or ceramic). From an applications standpoint, at this time we feel the monolith, pellet bed, and felt pad to be the primary catalyst support materials. A wire mesh is limited by temperature but is suitable for lower temperature application. The fluidized bed will probably suffer from attrition of the catalyst surface although this problem should be further explored. Combinations of various support arrangements may also be feasible. For example, monolith slabs may be used to containerize a packed bed.

5.1.5 Low NO_x Techniques

There are a great variety of potential arrangements involving catalytic combustion which could be used to aid in lowering NO_x emissions, while maintaining load and keeping CO and UHC emissions low. These possibilities include:

- Catalytic combustion with cooling
- Staged combustion
- Flue gas recirculation
- Catalytic combustion with variable catalyst loading to control heat release
- Combinations of any or all of the above.

Table 5-2 delineates the unique features of each of these schemes, together with the advantages and disadvantages. Table 5-2 also shows the various combinations within each NO_x reduction scheme. For example, nine different techniques of cooling the different types of beds are illustrated. An attempt has been made to rank these schemes from an applications point of view. Further analysis and testing will be required to verify this ranking. Some addition general comments appropriate to these various low NO_x techniques are in order.

5.1.5.1 Cooling Schemes

Some form of cooling the bed will be required either through active cooling, by staging with intercooling or by flue gas recirculation, to keep the catalytic bed within the materials structural temperature limits and to keep the thermal NO_x levels low.

TABLE 5-1. CATALYST BED TYPES FROM AN APPLICATION POINT OF VIEW

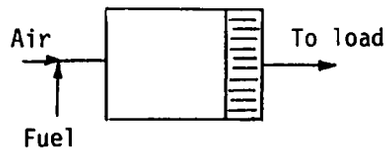
Bed Types	Description	Advantages	Disadvantages
A. Monolith	• Honeycomb ceramic • Square or round • Can be made into cross flow heat exchanger • Most any size, thickness, and pore size	• Can be formed in cross flow heat exchanger • Not as subject to abrasion as others • High temperature capability (2200°F - 2800°F)	• Subject to cracking and breakage; thermal shock • Heat exchanger configuration may be expensive to manifold
B. Packed Bed	• Any size or shape • Particle size any size or shape • Must containerize incompatible material • Coated pellets, solid catalyst, sintered balls	• Can be "filled" to any size and shape • High temperature capability • Can imbed cooling coils in any position or orientation • Easy Replacement	• Subject to abrasion • Must containerize (temperature considerations)
C. Coated Tubes	• Coat the inside surfaces of conventional firetube boiler	• No special "catalyst basket" required	• Low surface area • Low temperature capability
D. Felt Pad of Catalyst Fibers	• Felt blanket material derived from insulating material • May be all catalytic fibers or impregnated with a few fibers • Can be surface combustion or reactor bed provided temperature low enough	• Simple to form in most any size or shape • Cheap	• Life unknown • Limited to 2600°F • Unsupported life questionable

TABLE 5-1. CONCLUDED

Bed Types	Description	Advantages	Disadvantages
E. Wire Mesh	• Stainless, high alloy steel or other metal coated with catalyst or mesh made of catalytic material	• Can be formed into almost any size or shape	• Temperature limited • May be difficult to coat surfaces with catalyst
F. Fluidized Bed	• Catalytic bed in fluidized form (small particles) • Velocities kept below blow-off velocity of smallest particle	• High surface area • Good heat transfer characteristics • Most any size or shape • High temperature capability • Ability to transport and replenish (replace) catalyst material	• Attrition of particles (erosion of catalyst at surface) • Must containerize incompatible material
G. Combinations	• May want to combine one or more of the above into a given design	• May be able to select more than one type more suitable to a given support	• Any of the above

TABLE 5-2. POTENTIAL LOW NO_x CATALYTIC CONCEPTS

(a) Thermal Combustion/Catalytic Afterburning

Combustor Concept	Description	Advantages	Disadvantages
	• High temperature thermal combustion followed by reduction of NO_x by high temperature catalysis	• Can achieve good flame stability by firing with minimum of excess air • Good cyclic operation • Does not require prevaporized fuels	• May not work • High temperature catalysis support materials required

(b) Thermal Combustion With Cooling Followed by Catalytic Afterburning

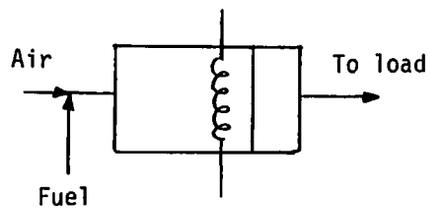
Combustor Concept	Description	Advantages	Disadvantages
	• Lower temperature thermal combustion followed by catalytic oxidation of CO and H/C.	• Lower catalyst bed temperatures • Achieve low NO_x • Possibly good cyclic operation • Does not require prevaporized fuels	• May have flame stability problems if cooled too much

TABLE 5-2. CONTINUED

(c) Catalytic Combustion With Cooling

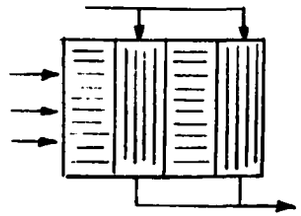
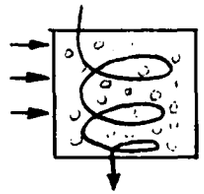
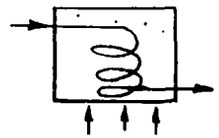
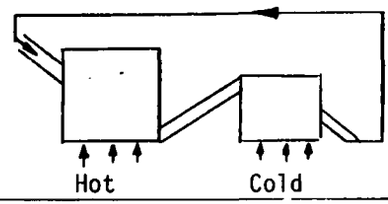
Combustor Concept	Description	Advantages	Disadvantages
1. Monolith Sandwich 	• Monolith could be heat exchanger • Sandwich material could be same support structure as catalytic surface or other • Cooling could be in tubes – Process fluid; gas or liquid – Combustion air – Flue gas – Intermediary fluid	• Compact • Amenable to many design configurations • Any cooling medium may be utilized	• Cooling rates have to be carefully controlled • May not be practical to use water cooling • Manifolding cold side may not be simple • Thermal stress problems
2. Packed Bed-Cooling Coil 	• Cooling coil imbedded in bed • Cooling fluid – Process fluid gas or liquid – Combustion air – Flue gas – Intermediary fluid	• Cooling can be distributed anywhere in bed • Cooling can be crossflow, counterflow, or parallel flow	• Must watch temperature of metal cooling tubes • Cooling uniformly across the bed could be difficult
3. Fluidized Bed-Cooling Coil 	• Same as above	• Same as above • Excellent heat transfer characteristics	• Metal cooling coils temperature limited
4. Fluidized Bed-Moving Bed 	• Fluidized catalytic bed is continuously or on a batch basis moved from the hot bed to a cold bed where it exchanges heat • Bed will achieve some steady state lower temperature than otherwise	• Can replenish catalyst • Can clean catalyst • Good heat transfer characteristics • May be solution to poison (S)	• Probably expensive • Carryover of residues and other unburned hydrocarbons, etc., to cold side • Transfer of catalyst back to hot bed not simple

TABLE 5-2. CONTINUED

(c) (Continued)

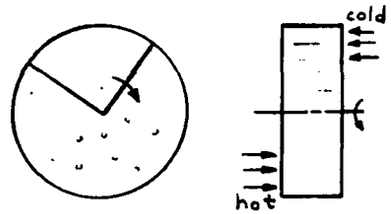
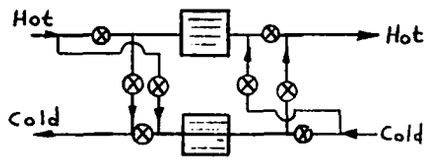
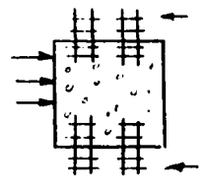
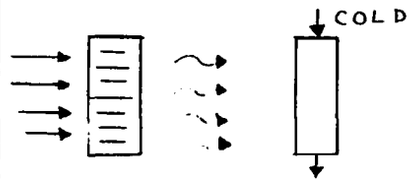
Combustor Concept	Description	Advantages	Disadvantages
5. Rotary Bed 	• Monolith, packed bed, wire mesh, tube bundle or other can make up the bed • Alternately exchanges heat with cold fluid in transient mode	• Uniform average temperature of catalyst • No metal cooling tubes to worry about	• Carryover of exhaust gases and even unburned hydrocarbons • Heat transfer fluid must be combustion air • Sealing problems • May be expensive to drive the wheel
6. Valved Beds 	• Hot and cold streams alternately flow through two beds by appropriately valving • Bed may be of any type described in Table 2-11 • Beds always operate in the transient mode	• Thermal stress and high temperature material problems minimized	• Carryover of partial products of combustion • Thermal cycling could cause problems • Valving may cause pulsations in combustion • Cold fluid must be combustion air
7. Heat Pipe Immersed in Bed 	• Multiple heat pipes immersed in bed or between monolith sandwich and transferring heat to a cold stream	• May be attractive from a construction standpoint for same designs • Manifolding and sealing problems between hot and cold streams may be minimized • Some thermal stress problems may be minimized	• Nonuniform bed and sandwich cooling • Heat pipe compatible with temperature may be excessive (liquid Na) • Bed design must be compatible with heat pipe configuration; i.e., the vapor "end" is relatively short
8. Radiation to Cold Surface 	• Any type catalytic bed transferring heat principally by radiation (IR)	• Amenable to many design configurations • May be combined with convective cooling schemes (sandwich concept above #1) • Can achieve large ratios of hot to cold side heat flux	• Bed must be kept relatively thin • If cooling fluid is air, metal temperatures must be carefully designed

TABLE 5-2. CONTINUED
(c) (Concluded)

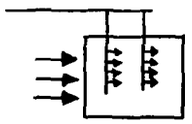
Combustor Concept	Description	Advantages	Disadvantages
9. Direct Injection of Water 	• Introduce water in the middle of a packed bed • Could be "slow leak" in combustion with cooling	• Becomes steam/methane reformer	• Thermal shock • Generation of steam • Consumes water

TABLE 5-2. CONTINUED

(d) Staged Combustion

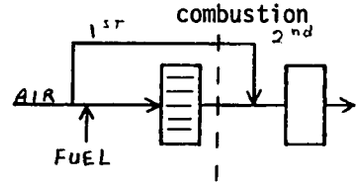
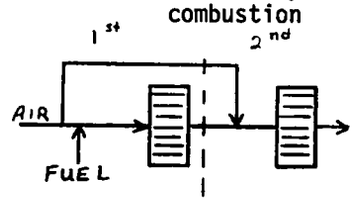
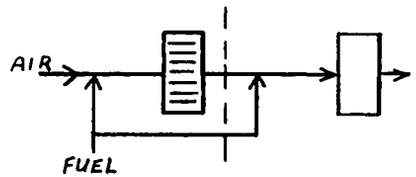
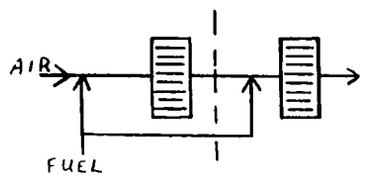
Combustor Concept	Description	Advantages	Disadvantages
1. 1st Stage: Fuel rich/ catalytic 2nd Stage: Remaining excess air/conventional combustion 	• First stage could be premixed or mixed in the chamber rapidly or slowly • Any of the catalyst configurations • Second stage air mixed rapidly or slowly • Air preheat or not	• Relatively simple to design such a concept for many of the applications • Controlled heat release between stages	• Depending on fuel (e.g., H_2) even first stage may produce excessive peak temperatures • Flame stability problems (this may be helped by catalyst) • Second stage temperatures may become too high without intercooling
2. 1st Stage: Fuel rich/ catalytic 2nd Stage: Remainder excess air/catalytic combustion 	• Same as above	• Same as (1)	• Same as (1)
3. 1st Stage: Fuel lean/ catalytic 2nd Stage: Remainder fuel/ conventional 	• First stage could be premixed or mixed in the chamber • Any of the catalyst configurations could be used • Additional fuel in second stage mixed rapidly or slowly • Air preheated or not	• Same as (1)	• Flame stability problems (this may be helped by catalyst) • Second stage temperatures may become too high without intercooling
4. 1st Stage: Fuel lean/ catalytic 2nd Stage: Remainder fuel/ catalytic 	• Same as (3)	• Same as (1)	• Same as (3)

TABLE 5-2. CONTINUED
(d) (Concluded)

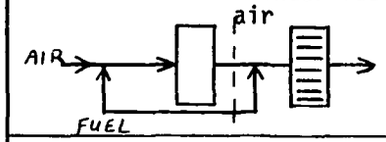
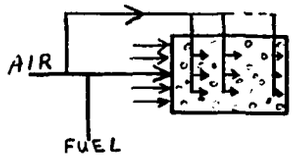
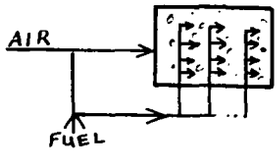
Combustor Concept	Description	Advantages	Disadvantages
5. 1st Stage: Thermal; fuel lean or rich 2nd Stage: Catalytic, remainder fuel or air 	• Normal thermal combustion operated in fuel lean or rich to achieve low NO_x • Remaining air or fuel added assisted by catalytic oxidation of unburned H/C and CO.	• Good cyclic operation • Possible retrofit	• Possible flame stability and light-off problem in first stage • Second stage temperatures may become too high without intercooling
6. Multiple Stage/All Catalytic/Air 	• Catalytic bed could be monolith sandwich or packed bed • Air injection in controlled fashion (perhaps transpiration type surface) • Air injection could be coolant as well	• Controlled rate of reaction and hopefully temperature	• Lots of manifolds and metering • Lots of experimenting to achieve proper configuration
7. Multiple Stage/All Catalytic/Fuel 	• Catalytic bed could be monolith sandwich or packed bed • Fuel injection in controlled fashion (perhaps transpiration type surface) • Fuel injection could be coolant as well	• Controlled rate of reaction and hopefully temperature • May be good way to vaporize oil or other liquid fuel	• Manifolding and metering • Design to avoid hot spots and injection tube failure

TABLE 5-2. CONTINUED

(e) Flue Gas Recirculation

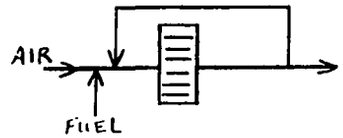
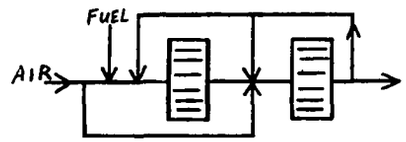
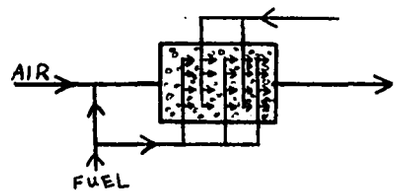
Combustor Concept	Description	Advantages	Disadvantages
1. Single Stage Catalytic 	• FGR introduction into – combustion air – combustion chamber prior to catalyst – the catalyst bed – gaseous fuel	• Applicable to many systems • Easy method to lower temperature	• May require auxiliary high temperature blower although natural draft feasible in some systems • Care must be taken to avoid condensation of H_2O in flue gas
2. Two Stage/Catalytic 	• FGR introduction into – combustion air – combustion chamber prior to catalyst – second stage air – second stage combustion chamber – either catalyst bed – gaseous fuels	• Same as (1)	• Same as above
3. Multiple Stage Catalytic 	• FGR introduction into – combustion air – gaseous fuel – bed at any location	• Same as (1)	• Same as (1)

TABLE 5-2. CONCLUDED

(f) Catalytic Combustion with Variable Catalyst Loading to Control Heat Release

Combustor Concept	Description	Advantages	Disadvantages
Variable Catalyst Loading	• Would probably require multiple thin beds	• Simple system	• May not work; after a minimum threshold of catalyst you may get full activity

(g) Combinations of A, B, C, D, E, and F

Combustor Concept	Description	Advantages	Disadvantages
For example, see C-3	• A unique combination of any of the above allowing cooling of the bed, staged combustion and flue gas recirculation may prove useful		

The choice of a cooling fluid is dictated by the type of catalyst support. For example, water cooling should not be considered using a monolith heat exchanger due to the high thermal stress that could occur. Conversely, if metal cooling tubes are buried in a packed bed, air cooling may not be sufficient to keep the tubes cool. It will probably be difficult to cool the felt pad arrangement except by radiation. Retrofit designs must carefully consider if there is sufficient cooling to accommodate a radiation cooled catalyst bed. Very likely those heat transfer surfaces that are air cooled will have insufficient heat transfer coefficients. Water backed units can probably accommodate the load.

5.1.5.2 Staging

Staging is an alternate method of maintaining low thermal NO_x emissions. As previously shown in Figure 5-1, the first stage can be either lean or rich. Some intercooling between stages will always be required to keep the peak flame temperature low in the second stage. Either stage could be catalytic or thermal. A thermal first stage has the advantage with oil that the fuel would not require vaporization in the first stage. However, a stable fuel rich condition might be difficult to achieve without sooting and possibly plugging the catalyst. Thus the first stage using oil (if the first stage is thermal) would most likely be fuel lean with a prevaporized fuel oil addition in the second stage. At this time the consideration of other fuels or two catalytic stages gives no evidence of a preferred first stage stoichiometry. In fact, for gaseous fuels there is no preference for which stages should be catalytic or thermal. In a retrofit application one might want to operate with the existing first thermal stage and add a catalytic second stage. Some retrofit applications might not lend themselves to staging. For example, it would probably be difficult to incorporate a staged concept into the existing gas fired home heating furnace. However, there is more than enough room for such a concept in the cast iron and firetube boilers. In particular, the turning point in the tube of a Scotch marine boiler is an excellent point to inject secondary air for a two-stage catalytic system.

At this point, too, it is difficult to judge whether a staged approach with internal cooling may offer some advantage. Some interstage cooling will certainly be required.

The choice of a catalyst support will not be influenced greatly if staging is used, although the packed bed may offer an advantage if the first stage is sooty. It seems likely that the monolith would plug more easily under those conditions and be more unlikely to cure itself.

5.1.5.3 Flue Gas Recirculation

Flue gas recirculation is another known method for NO_x reduction which might be very effective in lowering the peak flame temperature in a catalytic combustion

process. It would most likely be applied in a single stage system by introducing it with the combustion air. However, it can be applied in a two-stage concept as well. There are other locations where the flue gas might be introduced other than the combustion air to achieve different types of mixing, depending on the final physical configuration of the system. Combustion instabilities can be caused in conventional combustion systems by introducing the flue gas into the combustion air. However, with a premixed catalytic system this is not anticipated to be a problem. In fact, it may be desirable to use the combustion air blower to draw in flue gases as well. This can be done by appropriately sizing the ducts and/or orifices. This requires that the fan be able to take the higher exhaust gas temperatures and that the combined temperature of the combustion air and flue gas not be below the dew point of the mixture. Alternatively a separate fan could be employed. In the case of oil fired units the flue gas could be introduced upstream or downstream of the preheated air, again as along as condensation is avoided. From an applications point of view flue gas recirculation could be applied to any of the proposed applications; either new design or retrofit. The primary problem will be economic; can flue gas recirculation (fans, valves, ducting) be accomplished less expensively than other options.

Initially flue gas recirculation coupled with a single stage catalytic combustion system looks like one of the most promising schemes. The simple ducting coupled with a premixed arrangement may result in one of the least expensive systems, provided that significant benefits result. This is especially true for a retrofit application. However, flue gas recirculation may not work as well for fuel oil applications where fuel nitrogen could contribute to the total NO_x picture.

In the final analysis, the highest ranking scheme will probably be a combination of several of these schemes. For example, two-stage combustion combined with cooling the bed may prove to be the most promising technique. Of course, it should be kept in mind that what may be an optimum scheme for a new design may not be suitable for a retrofit application.

5.1.6 Fuels

The fuel to be considered can greatly influence the potential design, particularly if it is a liquid fuel. Several factors which must be kept in mind are noted below:

- Lightoff characteristics
- Flame speed
- Flammability limits
- Adiabatic flame temperature as a function of equivalence ratio

- Sooting characteristics
- Vaporization characteristics
- Sulfur content
- Nitrogen content

Most of the parameters were discussed in Section 4.2. From an applications point of view they can influence size, shape, equivalence ratio of a stage, residence times, degree of cooling, and startup procedures.

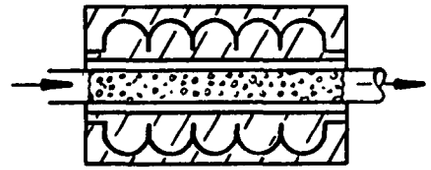
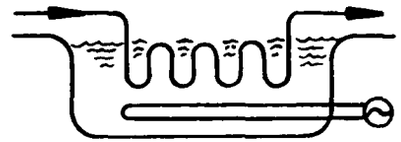
Problems associated with liquid fuels (No. 2 fuel oil) as applied to home heating can be significant. Conventional designs operate in a highly cyclic fashion to meet the load. Stricker (Reference 15) reported typical cyclic firing times on the order of 5 to 6 minutes (see Figure 3-15 of Section 3.2). (This will vary depending on the load and heater size per unit floor area.) Typical firing times in some West Coast furnace installations indicate a much shorter firing time, on the order of 2 to 3 minutes. Off cycles between firings can be on the order of 10 minutes to an hour depending on the load.

Typical catalyst warmup periods have recently been reduced to about 1 minute in an automotive application (Reference 65). However, until the bed is hot the combustor will require thermal combustion which will probably be a higher polluting regime. Thus, it can be seen that this polluting regime may be a significant fraction of the firing cycle. In addition, the cooldown cycles can be sufficiently long to allow the bed to cool, requiring a warmup period each time the furnace is cycled. This problem is most severe with No. 2 oil which requires either fuel atomization or an electric prevaporizer during warmup. (It is assumed that the liquid fuel will require vaporization during normal running in catalytic combustion.) An important task in designing an oil fired catalytic furnace will therefore be the development of a fast response oil vaporizer. Factors which must be considered in the vaporizer design are:

- Coking and cracking of the oil
- Flow instabilities due to boiling and two-phase flow (particularly during initial startup and shutdown)
- Turndown
- Start-up and shutdown.

The problem is to volatilize a liquid which has a range of boiling points from 325°F to 750°F and contains some ash and residue. Several approaches are listed in Table 5-3 with their advantages and disadvantages.

TABLE 5-3. OIL VAPORIZER DESIGNS

Approach	Advantages	Disadvantages
1. Use heat of combustion	• Does not require auxiliary heat source • Can be built into the apparatus	• Must start up on alternate method • Must be carefully designed to avoid coking • Shut down/soak down may be a problem
2. Clamshell electric heater-tube with small quartz balls 	• Smoothes out two phase flow problem • Good heat transfer • Can electrically maintain precise temperature control • Good capacitance	• High pressure drop • May clog up with time • Requires auxiliary power
3. Hot pot of Dowtherm G with oil coil 	• Good capacitance • Good temperature control	• Flow instabilities especially on start up may still be there. (May want to fill oil tube with quartz balls) • Requires auxiliary power

Cycling problems can be reduced if the furnace is modulated to meet the load. Modulation will probably require a turndown ratio of at least 10 to 1 and will also necessitate a corresponding turndown on the process side. Under the low fire condition care would have to be taken that the temperature in the catalyst bed did not fall below a critical level. It may be that the lowest firing level to sustain this critical level would be too high for sound energy conservation practices. That is, even though an energy saving (as well as emissions) could be realized by using a modulated approach, the required "pilot" for a catalytic combustor could negate those positive savings. It should also be noted that the combustion air will require preheating as well to avoid any condensation of the oil vapor. Thus, at this point, and without detailed analysis, there is no clear direction on which approach to take when designing an oil fired catalytic system. Perhaps the best approach would be to go with a two-stage approach, the first stage thermal followed by a catalytic second stage to overcome these startup problems. Other possibilities include dual catalyst systems involving noble metal startup or pilot catalysts (lower ignition temperature), and metal oxide operating catalysts (slower deactivation rate at high temperature).

5.2 OTHER DESIGN CONSIDERATIONS

As we have seen in the previous sections a great number of parameters must be considered when formulating a new design. There are in addition some practical design problems which are discussed briefly below:

- Flashback — Flashback to a stable thermal combustion zone as well as flashback in an unstable manner must be prevented for safety, for equipment lifetime, and to minimize pollutant emissions. This can be accomplished through quenching, maintaining velocities of a premixed mixture above the flame speed or remaining outside the flammability limits.
- Partial Plugging — This may be a serious problem. If for some reason local combustion produces soot and plugs the catalyst pores, the reactivity will fall off, the temperature will drop, thus producing a local instability.
- Nonuniformities Across the Bed — Likewise, nonuniform cooling might produce similar results. Local conduction will offset both the above problems and help maintain a uniform bed temperature.
- Mixing of Staged Air — As in any combustion process, proper mixing is a must to prevent bypassing of CO and UHC.
- Cooling the Bed — Methods of cooling the bed were discussed at some length in Section 5.1.4. However, the bed must not be cooled too much or the reactions will not be sustained.

- Sulfur Content of Liquid Fuels — The sulfur content is of concern for two reasons: (1) SO_2 and SO_3 emissions and (2) poisoning of the catalyst. It may be possible to combine catalytic combustion with a sulfate removal process such as insertion of a bed of ZnO to collect the S as ZnS.
- Pressure Drop Available — This will always be coupled to the overall cost allowed and also possibly to noise.
- Intermediary Cooling Fluid — Required heat absorption rates for cooling the catalyst bed by radiation may exceed the capability or pressure drop limitations using air. Consequently, an intermediary fluid could be used to remove the heat and then transport it to the process fluid.
- Thermal Shock — Thermal shock to refractory materials must be evaluated and avoided if possible.
- Thermal Stresses and Low Cycle Fatigue — One of the most serious problems in conventional furnace design is thermal fatigue of the heat exchanger. In any heat exchanger design great care must be taken to avoid severe thermal stresses.
- Size — Overall size is always a factor. It is conceivable that a new catalytic combustion system would be made more compact than conventional designs.
- Cost — Overall cost of the system will probably be the single most important factor. Unfortunately, most customers look only at the capital cost of the equipment as opposed to the overall operating cost.
- Maintenance — Ease of maintenance, and periods between maintenance must be considered.
- Retrofit Compatibility — Designs for retrofit should be considered as well as new designs.

5.3 OVERALL CONCLUSIONS

In general, it has been shown that the matrix of possible design choices for each of the application areas is quite large. The initial survey to this point does not indicate a clear direction to follow, except for a few isolated examples, either for a retrofit or new design application. Flue gas recirculation with a single stage catalytic combustor may be one of the better and least expensive variations for many of the applications. Gas fired home furnaces present special problems for retrofit due to limited volume, low existing heat transfer coefficient and their cyclic nature. Any oil fired unit also presents special problems including oil vaporization, startup and air preheating.

Section 6 following will examine several specific design problems and present suggested solutions for the following cases:

- Home heater – retrofit
- Home heater – new design
- Commercial boiler – retrofit
- Commercial boiler – new design
- Industrial boiler – retrofit
- Industrial boiler – new design.

SECTION 6

COMMERCIAL APPLICATION OF CATALYTIC CONCEPTS TO SELECTED SYSTEMS

This section presents a number of possible design concepts for several of the application areas. For three of these concepts detailed sizing calculations have been made. It should be emphasized that the concepts presented here are by no means the optimum for any candidate application, but only represent a possible design. Which of the many possible designs has the greatest potential for success will ultimately depend on the cost of the hardware. Many possible good design options (branches) could not be considered within the scope of this program.

Application areas where designs have been developed include

- Residential heating — retrofit
- Residential heating — new design
- Commercial boiler — retrofit
- Commercial boiler — new design
- Industrial boiler — retrofit
- Industrial boiler — new design

Summaries of the work performed on each of these areas is presented below.

6.1 HOME HEATER RETROFIT

Due to Aerotherm's prior experience with home heater design studies, a probably disproportionate number of design possibilities come to mind. However, it is also felt that this may be one of the most feasible applications for catalytic combustion. Also, although some of the concepts offered here are biased towards a home heater application, many of the same principles or concepts could be applied to the other areas. They must be evaluated in light of the system limitations (cost, pressure drop, etc.) of alternate applications.

There are basically four retrofit home heating applications which must be considered. These include

- Gas fired — warm air

- Gas fired — hot water
- Oil fired — warm air
- Oil fired — hot water

Although it is conceivable to design a room or floor heater using catalytic combustion, these do not significantly contribute to the population of furnaces, especially for new units being sold. Thus only the units listed above will be discussed in the following text.

As was shown in Section 3.2, nearly all gas fired burners, whether in a warm air or hot water application, consist of the typical naturally aspirated "stick" or "log" type burner. These burners are generally of the premixed type and rely on ample quantities of secondary excess air to keep the "combustion chamber" cool. In reality, there usually is not a combustion chamber as such; firing is direct to the heat exchange surface. The units have no control over the secondary air opening. Thus, in a retrofit application, if the overall excess air is to be controlled, the combustion chamber or volume will require modification to seal it around the burner. Furthermore, there will usually be little volume to work with and radiation heat transfer and maximum metal temperature must be considered in the design. There is generally no refractory lined or refractory fiber lined combustion chamber with gas fired units.

Figures 6-1 to 6-3 show several potential designs. All these units replace the conventional log burners. In the first case (Figure 6-1) heat is transferred from a monolithic or felt pad bed by radiation only. Preliminary calculations show that heat transfer rates are sufficient to keep the bed below 2800°F without exceeding a maximum metal temperature of 900°F. A summary of the calculations for Figure 6-1 is shown in Table 6-1. These calculations are based on some rather optimistic assumptions. For example, radiation heat transfer is calculated on the basis of a slab radiating to two perpendicular walls. The convective heat transfer from the metal heat exchange surface and the thermal entry length heat transfer relationships were used in combination with free convection coefficients. This combined coefficient is three to four times higher than the usual average heat transfer coefficient given for warm air furnaces. Thus it may be necessary to increase the heat transfer coefficient on the warm air side. This can be accomplished by increasing the local velocity around the heat exchanger, inducing turbulence, or adding heat exchange area by the use of fins. The first two options will increase pressure drop and may require a change in the air circulation fan. Testing of the concept will be required to verify these calculations. Figures 6-2 and 6-3 show convective cooling schemes. A summary data sheet on each design is included as Tables 6-2 and 6-3. The first scheme utilizes a monolith structure in the form of a crossflow heat exchanger. This ceramic heat exchanger, discussed in Section 4.2.1.1, is cooled using air

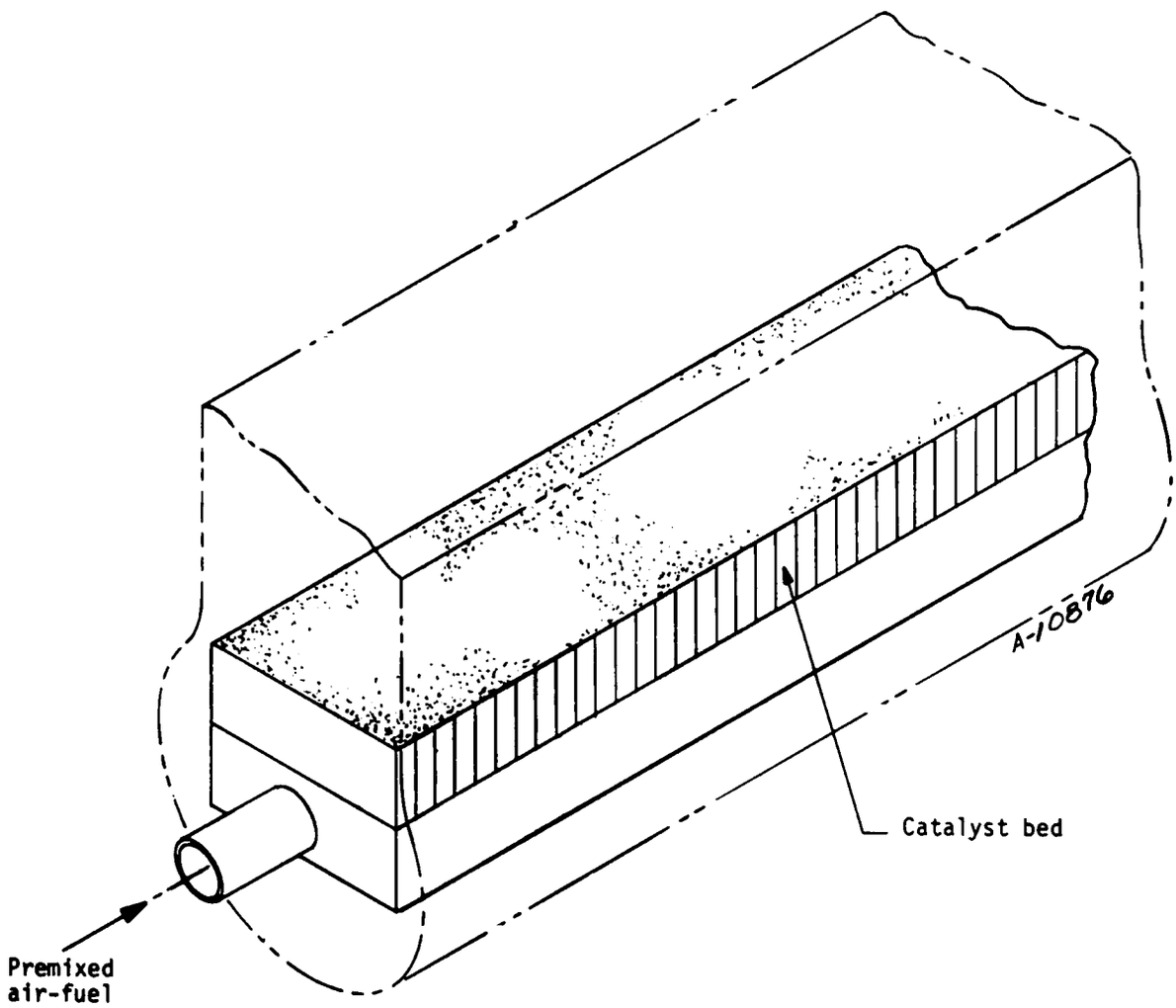


Figure 6-1. Home heater retrofit design #1.

TABLE 6-1. DATA ON DESIGN #1

Length: 15 inches
Width: 2 inches
Height: 0.5 inch
Volume: 15 in^3
Surface Area per Unit Volume: 50 ft^2/ft^3
Height Required to be Coated with Catalyst: 0.25 inch
Heat Release in Bed: 25,000 Btu/hr
Heat Transferred by Radiation: 11,400 Btu/hr
Heat Transfer Coefficient on Air Side: 8.9 But/hr-ft^2-°F
Pressure Drop through Bed: < 0.25"H_2O
Bed Temperature: 2200°F
Wall Temperature: 900°F
Type Bed: Celcor Honeycomb Monolith
Number of Units: 4

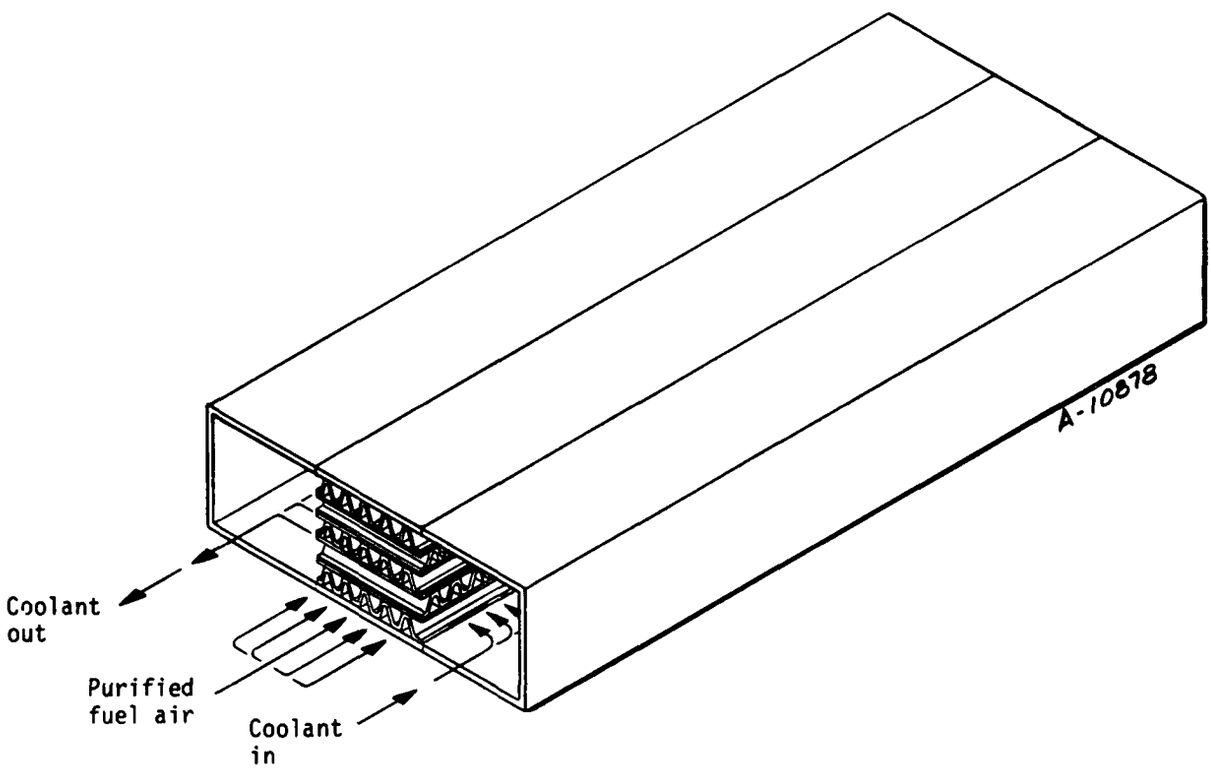


Figure 6-2. Design #2 cross flow ceramic heat exchanger.

TABLE 6-2. DATA ON DESIGN #2

Length: 15.00 inches
Width: 1.0 inch
Height: 0.50 inch
Heat Released in Bed: 25,000 Btu/hr
Heat Transferred by Radiation: 4612 Btu/hr
Heat Transferred by Convection: 6788 Btu/hr
Cooling Air Temperature Rise: 621°F
Cooling Air Flow Rate: 105 scfm
Cooling Air Pressure Drop Across Bed: ~ 3.0"H_2
Effectiveness of Heat Exchanger: 0.46
Number of Transfer Units (NTU): 0.825
Surface Area Per Unit Volume: 600 ft^2/ft^3

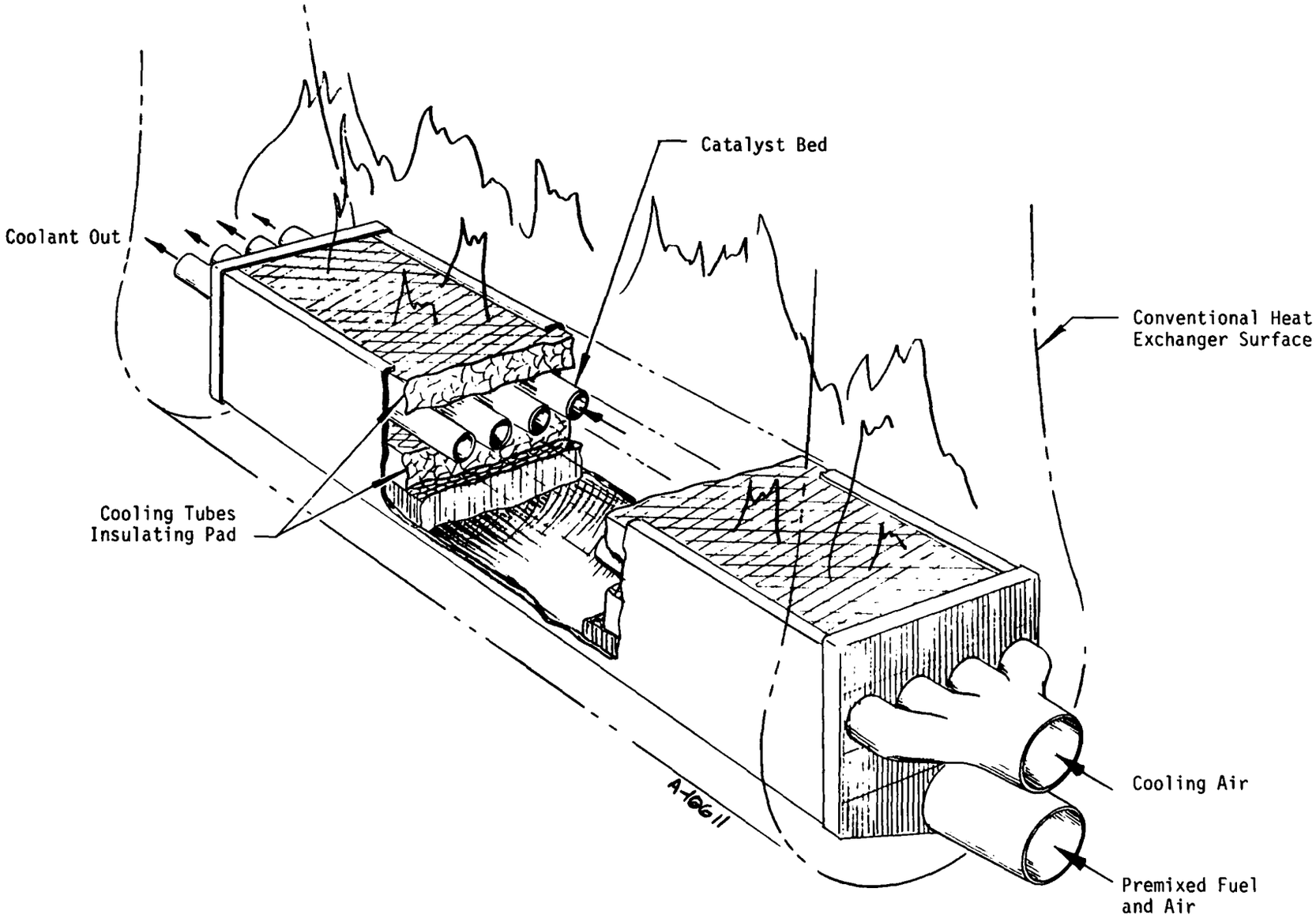


Figure 6-3. Home heater retrofit design

TABLE 6-3. DATA ON DESIGN #3

Width: 2 inches
Length: 15 inches
Height: 1.0 inch
Heat Release Per Burner: 25,000 Btu/hr
Total Number of Burners: 4
Number of Cooling U-Tubes: 6
OD of Cooling Tubes: 1/16"
Heat Transferred from Bed by Radiation: 4612 Btu/hr
Heat Absorbed by Tubes: 6788 Btu/hr
Coolant Flow Rate Per Burner: 21.5 gal/hr
Exit Gas Temperature: 2200°F
Coolant Inlet Temperature: 70°F
Coolant Exit Temperature: 120°F
Pressure Drop through Cooling Tubes: 11.16 ft H_2O

(water would cause excessive thermal shock). The cooling air is supplied using a separate small fan and the inlet and exit manifold are at the same end of the burner. The heat exchanger manifolding represents one of the most difficult technological problems. Representatives of the American Lava Corporation claim they have solved this problem, although the design is proprietary at this point and has only been tried on an experimental basis. In addition, in its present configuration the ceramic material from which the exchanger is made is permeable and will allow some leakage depending on the pressure differential. This situation cannot be tolerated if the leakage is to the coolant side (and perhaps even to the hot side). American Lava is developing a nonpermeable material which will soon be available in this cross flow heat exchanger form. In that case, this cooling air can then be fed back to the main cooling air or routed to a separate room or basement. Radiation heat transfer in this case was calculated using the assumption that the convective coefficient from the heat exchanger was the more conventional 2.7 Btu/hr-ft^2-°F. The heat exchanger surface is an American Lava Thermocomb material with approximately 8 corrugations per inch.

The last design, shown in Figure 6-3 (followed by a data sheet in Table 6-3), shows a pebble bed approach for the retrofit application to a gas fired furnace utilizing small U-tubes of cooling water.

The heat absorbed by the cooling water is then transferred to the circulating air just prior to entering the furnace. This arrangement requires an auxiliary pump and finned tube heat exchanger. The water cooling circuit is arranged to come on after the catalytic bed has reached a specified temperature. It may also be possible to run cooling coils between a sandwiched monolithic bed or just above the bed. In the latter case the cooling water must be flowing during the initial light-off, where thermal combustion will occur. The entire transient problem must be studied in detail in any of these designs to insure that an unsafe condition does not occur. For example, in conventional furnaces the burner comes on for a minute prior to the circulating air fan. Depending on the length of time required for the water system to heat, it may be necessary that the circulating air fan come on sooner than current practice to insure that heat is extracted from the water and boiling does not occur. Similarly, in the pebble bed case (Figure 6-3) timing of the cooling water flow and recirculating air flow must be carefully controlled.

The three designs just discussed cover the gas fired warm air and hot water retrofit applications. There remain the oil fired applications.

Oil fired warm air heaters utilize a refractory or refractory felt combustion chamber connected to a heat exchanger of varying design (unlike the gas fired units which are all very similar in design). All the heat exchanger designs are low pressure drop devices, resulting in low velocities, low heat transfer coefficients, and thus large heat transfer areas. Generally a relatively small fraction of the heat is

transferred from the combustion chamber. This fact presents a difficult design problem for a cooled retrofit catalytic combustor. However, it may lend itself to a multistage configuration where a larger volume may be required.

There are a number of problems that will be common to any potential design using oil. These are:

- The oil will require prevaporization when operating in the catalytic mode
- The combustion air must be preheated above 600°F to avoid condensation of vaporized oil
- The oil may be vaporized using the heat of combustion or electrically
- Sooting of a thermal combustion phase must be avoided
- Light-off and heat-up of the catalyst system will either require a thermal combustion phase or air electrical preheating scheme
- Thermal combustion of the vaporized fuel must be avoided prior to the catalyst bed during the normal operating mode.

The designs previously discussed and shown in Figures 6-1 through 6-3 could be applied to oil combustion by adding an air preheater and oil vaporizer. However, it may be more appropriate to develop a design more suited to the combustion volume of the oil fired furnace.

A design that initially seems ideally suited to this volume is the concept developed by JPL and shown in Figure 4-27 of Section 4.4.6. This design would fit into the combustion volume and solves the six common problems mentioned earlier. The heat up period for this design has been reduced to about 1 minute, which may be acceptable in a home heater application. It is important to note that the JPL design operates only in the fuel-rich mode at this time. One drawback is that little heat is extracted from the bed. As with the gas fired design, in order to achieve low NO_x the maximum combustion temperature must be reduced. This can be achieved by cooling the bed or going to a two-stage or flue gas recirculation concept. Cooling the bed is easily adaptable to the JPL design. Water cooling coils can be embedded in the packed bed. This heated water then exchanges heat with the incoming house recirculating air using a finned tube heat exchanger. Alternatively, a ceramic heat exchanger (monolith) using a separate cooling air supply can be incorporated. The principal problem is in ducting and manifolding the air. Flue gas recirculation in conjunction with the JPL approach is also feasible.

Another potential problem with the JPL design is assuring that sooting does not occur with the relatively cold combustion chamber walls when firing #2 fuel oil. JPL has achieved a no-sooting condition on kerosene, and it is conceivable that the design would work on #2 oil.

It would be convenient to utilize an existing burner in a retrofit application to provide combustion air as well as to provide the light-off and heat-up capability. Several factors discourage this approach:

- During normal catalytic running, the combustion air must be preheated; this would necessitate diverting the flow downstream of the burner blower — a difficult task.
- Conventional burners soot or smoke during light off when the walls are still cool.
- The blowers are pressure drop limited.
- The burners are not built to handle preheated air.

Another approach, shown in Figure 6-4, utilizes a catalyst impregnated felt pad. The chief design questions with this approach for a retrofit oil system are as follows:

- Lightoff — What type of lightoff system should be used with this design? Unless the combustion air and all structural parts are above the boiling point of the oil it is likely that condensation of the oil will occur and perhaps plug the pad.

  In order to achieve preheating either a thermal combustion system or electrical preheating of both the combustion air and oil vaporizer may be employed. Electric preheating offers the advantage of simplicity. Since electrical power will be required in any case to operate fans, etc., it seems to be the preferred method with this design.

- Heat Transfer

  — In a cylindrical or conical arrangement, as shown in Figure 6-4, there has to be sufficient heat transfer by radiation alone to get the flame temperature below the acceptable limit for low NO_x; especially when minimum excess air is used. Heat must be transferred to three places: (1) to the combustion air, (2) to the room recirculating air, and (3) to the oil to be vaporized. In the first case this heat transfer does not aid in lowering the combustion temperature since the air is part of the combustion process. In the second case current heat transfer coefficients on the heat exchanger may not be sufficiently high to achieve low enough combustion temperatures. Therefore, it may require some auxiliary heat transfer surface, possibly water cooled.

- Oil Vaporization — The best arrangement in this case would be to wrap coils around the combustor in the proper temperature regime. Care must be taken to avoid overheating.

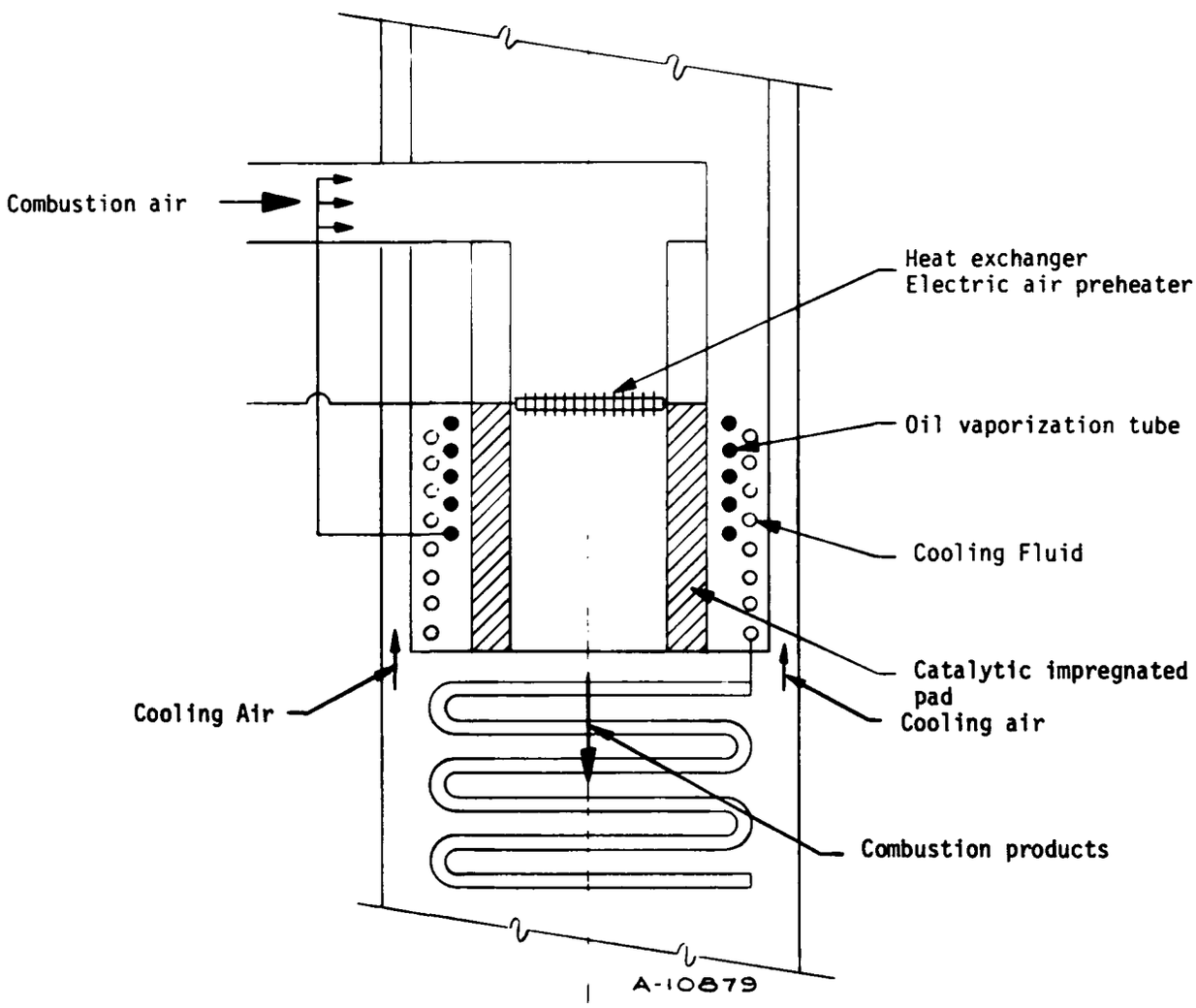


Figure 6-4. Catalytic pad oil burner.

- Shutdown and Standby

  Since the nature of a home heating system is currently a cyclic one, it may be desirable to keep the oil vaporizer hot during standby periods. This is accomplished through auxiliary electrical heating or burying the tubes in a high heat capacitance material. (This requires a longer initial warm up period.)

Although this design is feasible it requires considerable modification and new hardware. It may be more appropriate to consider it for a new design concept.

In summary, it appears that the most reasonable approach for an oil fired retrofit application is a single catalytic system using a thermal lightoff and warm up. The oil would be vaporized during the normal running and the catalyst bed would be actively water or air cooled.

6.2 HOME HEATER — NEW DESIGNS

The freedom of a completely new design presents fewer constraints on physical size and heat transfer arrangement. There will still be an overall size limit (similar to current practice) but that is easily met. Two other basic criteria which will not be as easy to meet are cost and noise, the latter because of the higher pressure fans that may be required to achieve higher heat transfer rates. Within these limits literally thousands of arrangements are potential candidates, as seen in Section 5.1. Gas and oil fired warm air and hot water heating systems are considered. For oil fired units the requirements of preheated combustion air and vaporized oil still exist. For either fuel it is necessary to take into consideration either cyclic operation or modulation to match the variation in load. Coupled with those aspects is the transient response of the furnace. At this point it appears quite feasible to design a gas warm air or hot water furnace. Oil fired units present considerably more problems, none of which are insolvable. Following are descriptions of several designs which warrant further study.

Home Heater Design #1

This design, pictured in Figure 6-5, involves radiant cooling of the catalyst bed, lean catalytic first stage, addition of fuel before the second stage, and catalytic combustion of the second stage. The unit is compact, involving a concentric cylinder arrangement of the catalyst bed, fuel addition units, and outer shell. The outer shell can either be water or air cooled, with additional fins placed in the outer shell if it were air cooled. The catalyst bed could either be a packed bed, a fiber mat, or possibly a monolith bed. Fuels for this application would most likely be the gaseous fuels, but a prevaporized oil could also be used. Thermal or electrical start up similar to the retrofit design would be required for oil to

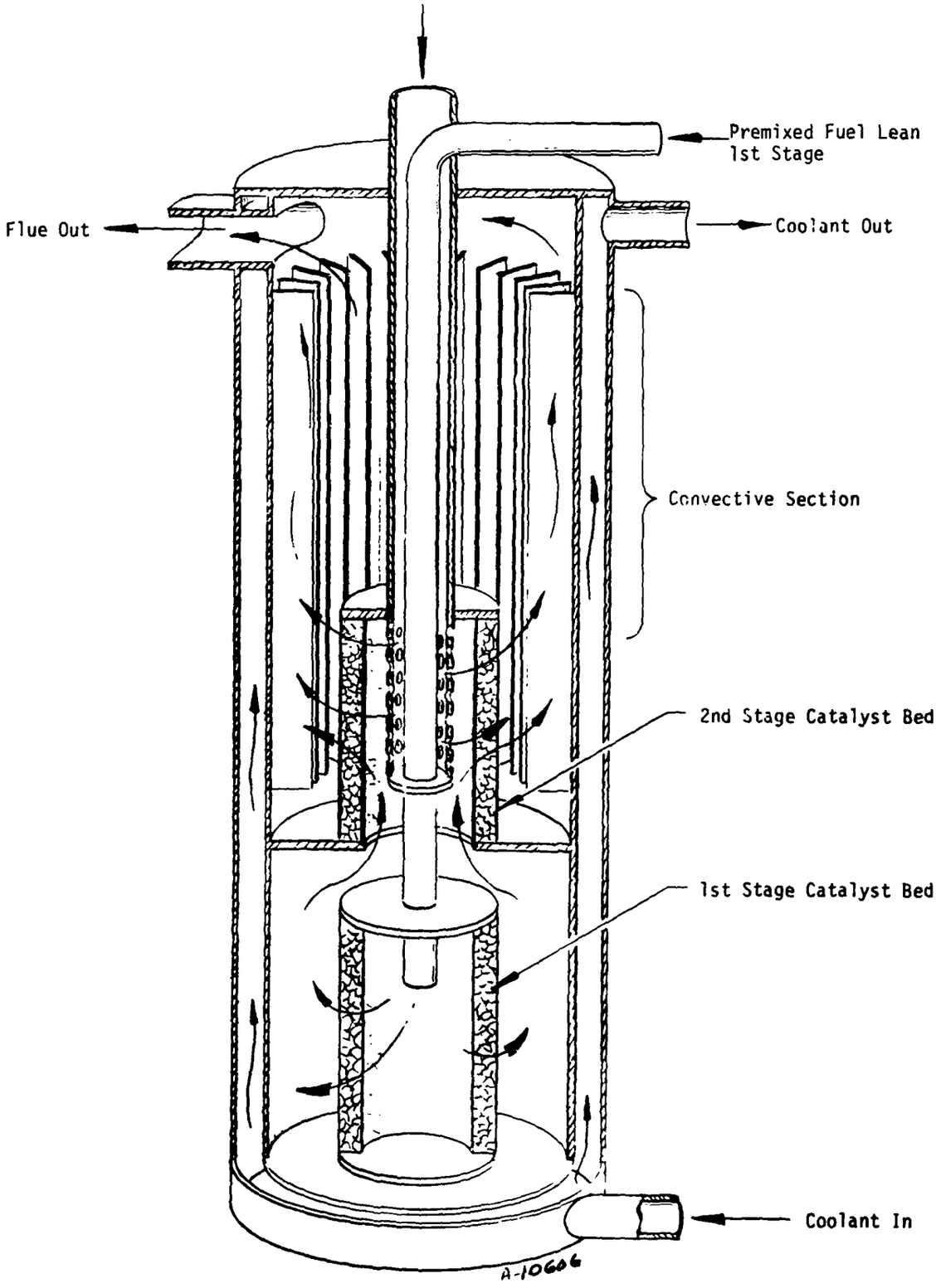


Figure 6-5. Home heater design #1.

vaporize the fuel and preheat the combustion air. Oil vaporizing tubes would be placed between the cold shell and the catalytic surface. Preliminary calculations have been made on this design to size the first and second stage catalyst beds and the heat transfer area. Table 6-4 summarizes the important design parameters calculated. Figure 6-6 shows this design to scale. This unit is air-cooled and could utilize an existing house air recirculation fan; it could also be designed as a water-cooled unit. Note that the overall dimensions are well within current practices, although the room air fan, combustion blower, and fuel controls must be packaged into the unit as well.

It must also be noted that sufficient heat must be extracted from the first stage to achieve two goals:

- To insure the maximum flame temperature in the second stage does not exceed 2200°F → 2500°F to achieve low NO_x and be within the limits of the catalyst
- To lower the temperature sufficiently to prevent thermal combustion prior to the second stage catalyst bed after introduction of the second stage fuel.

The latter criterion can be circumvented if the velocities are greater than the flame speed. This can certainly be achieved by appropriately sizing the passages.

The catalyst volume calculation was based on ~ 11,000 Btu/hr-ft^2 of catalyst surface area, based on experimental JPL criteria. Within this constraint, the sizes shown in Figure 6-6 and Table 6-4 depend on radiative and convective heat transfer calculations.

Home Heater Design #2

Figure 6-7 shows a variation of design #1. Premixed fuel and air (fuel lean or rich) passes through a cylindrical catalytic bed which transfers heat by radiation and convection to water cooled tubes connected with sintered copper balls. The exhaust products are passed through a second stage with fuel or air addition and finally out through additional heat exchange area. In this case the first stage is catalytic, whereas the second stage is thermal. The heat transfer surface could be tailored to achieve the proper temperature distribution or be designed with more surface on the process side if air cooling were incorporated. No detailed calculations were performed on this design.

Home Heater Design #3

This concept, shown in Figure 6-8, is patterned after the Bratko furnace design with some improvements. A conical fibrous catalyst surface radiates to an outer

TABLE 6-4. DATA SUMMARY HOME HEATER DESIGN #1, 100,000 BTU/HR

	1st Stage	2nd Stage
Heat Release (Btu/hr)	68,750	31,250
Stoichiometry	1.60	1.10
Gas Inlet Temperature (°F)	70	1401
Gas Exit Temperature (°F)	2200	2591
Catalytic Surface Requirement (ft^2)	6.12	2.78
Surface Area/Unit Volume (ft^2/ft^3)	200	200
OD (inches)	2.86	2.43
ID (inches)	2.00	2.00
L (inches)	4	4
Pressure Drop ("H_2O)	~ 0.04	> 0.1

Heat Transfer Area Downstream: 12.26 ft^2

Average Overall U = ~ 5 Btu/hr-ft^2-°F

Exit Gas Temperature: 400°F

Use 28 Fins 1.3 inches long on either side

Cooling Air Flowrate: 1000 scfm

Pressure Drop Air Side: 0.122"H_2O

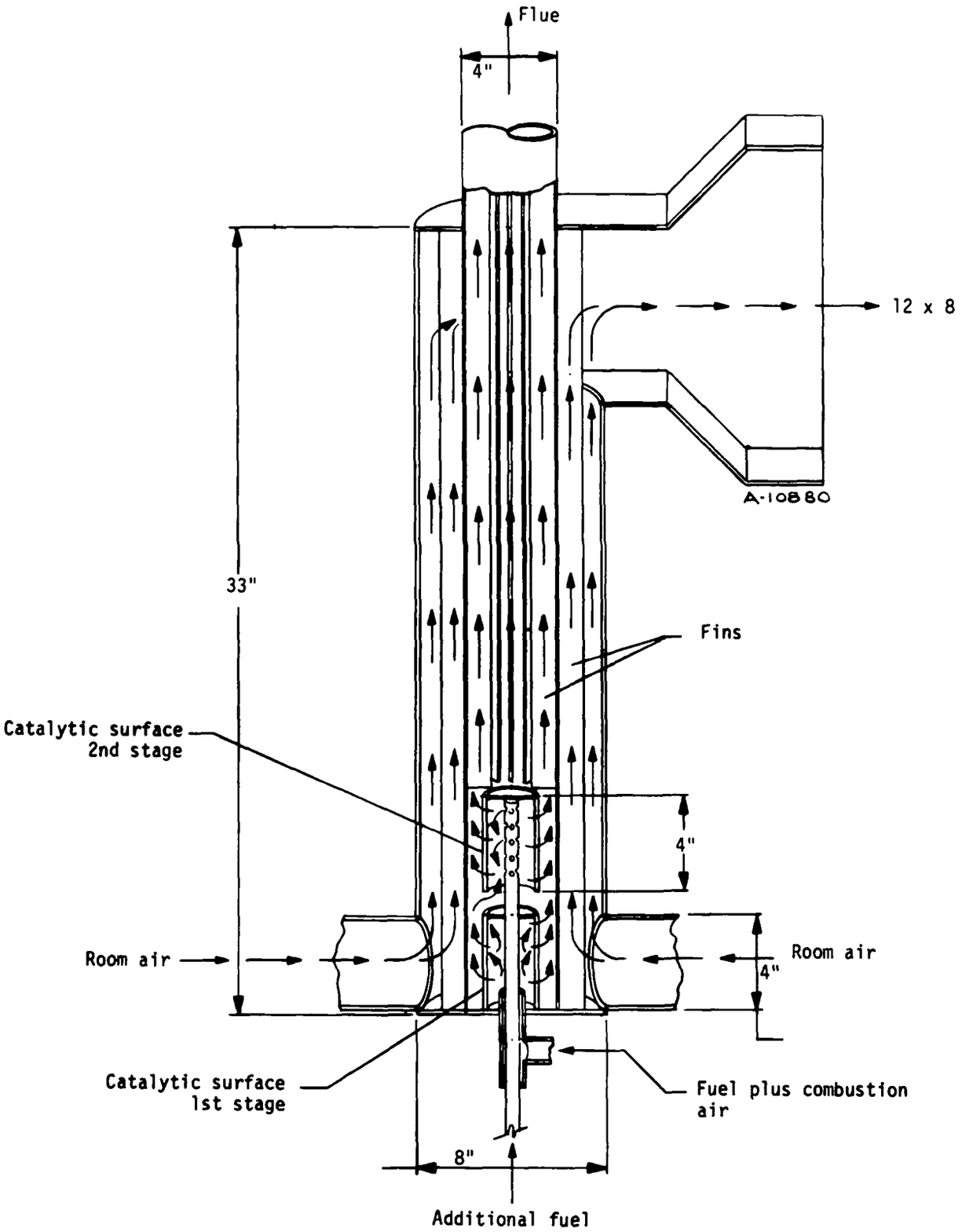


Figure 6-6. Scaled home heater design #1.

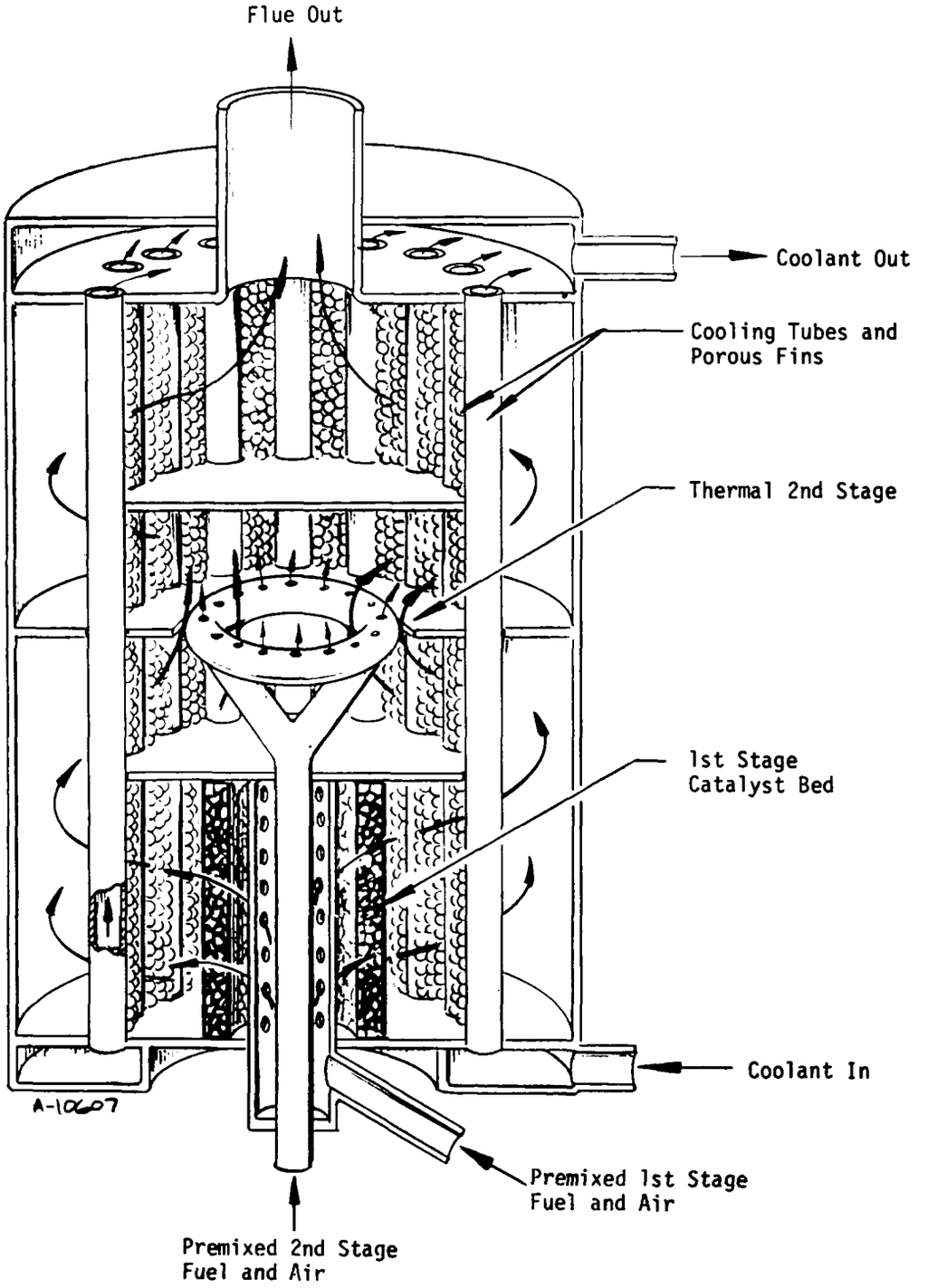


Figure 6-7. Home heater design #2.

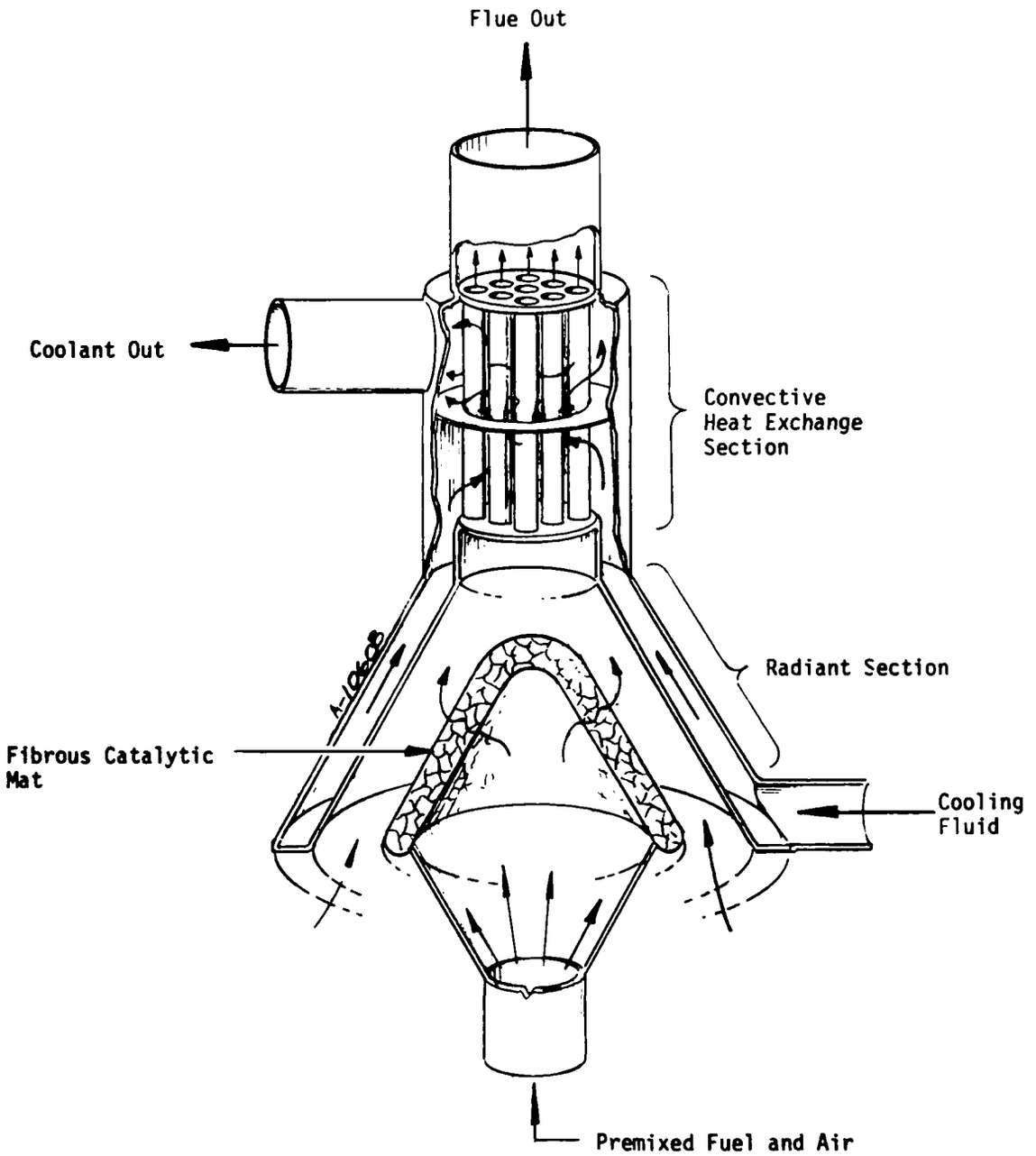


Figure 6-8. Home heater design #3.

air or water cooled shell. A premixed mixture of air and fuel would be routed behind the felt pad and ignited at the outer surface. After exchanging heat radiatively with the outer shell the flue gases are passed through the tubes of a convective section. The process stream is passed through in a multipass crossflow arrangement outside the tubes. This design is single stage, operating with minimum excess air but relying on radiation cooling to keep the catalyst surface cool. It could be designed to operate on oil.

Home Heater Design #4

Figure 6-9 shows a concept utilizing heat pipes between sections of catalysts. The heat is picked up by the room air stream flowing adjacent to either side of the combustion chamber. This design could easily use oil or gaseous fuel. The first combustion chamber would be modified to utilize a startup oil spray nozzle firing thermally and later switched to vaporized oil. The oil vaporization tubes could also be located between catalyst beds. The remaining heat is finally extracted through a convective section at the right hand side of the figure.

Home Heater Design #5a, b, c

Figure 6-10 shows three variations of a common design. This unit could be built as a single test rig and modified for the alternate approaches. The concepts include staged combustion, first-stage thermal or catalytic, second-stage thermal or catalytic, integrally cooled catalyst bed or radiatively cooled catalyst bed. This concept is probably the most versatile as far as testing numerous concepts. Flue gas recirculation could be added to any of these schemes.

6.3 COMMERCIAL BOILER — RETROFIT

As indicated in Section 3.3, the principal existing commercial boiler styles in use are the cast iron and firetube designs. Within the firetube design, packaged scotch and firebox are prevalent. All of these designs have relatively large initial combustion volumes, whether gas or oil fired. The firebox designs, including some of the cast iron boilers, employ a refractory or refractory felt-lined combustion chamber. The others (packaged scotch) utilize a large water backed volume for the initial combustion chamber. The on-off cycles again are highly dependent on the individual load and can conceivably be as short as the home heater application.

The principal difficulty is to extract sufficient heat from the bed to achieve low NO_x. All the problems associated with oil fired home heater applications also apply in this instance. The most significant difference is that the capital cost of these units is an order of magnitude higher than the home heating systems. This will allow considerably more latitude in potential designs.

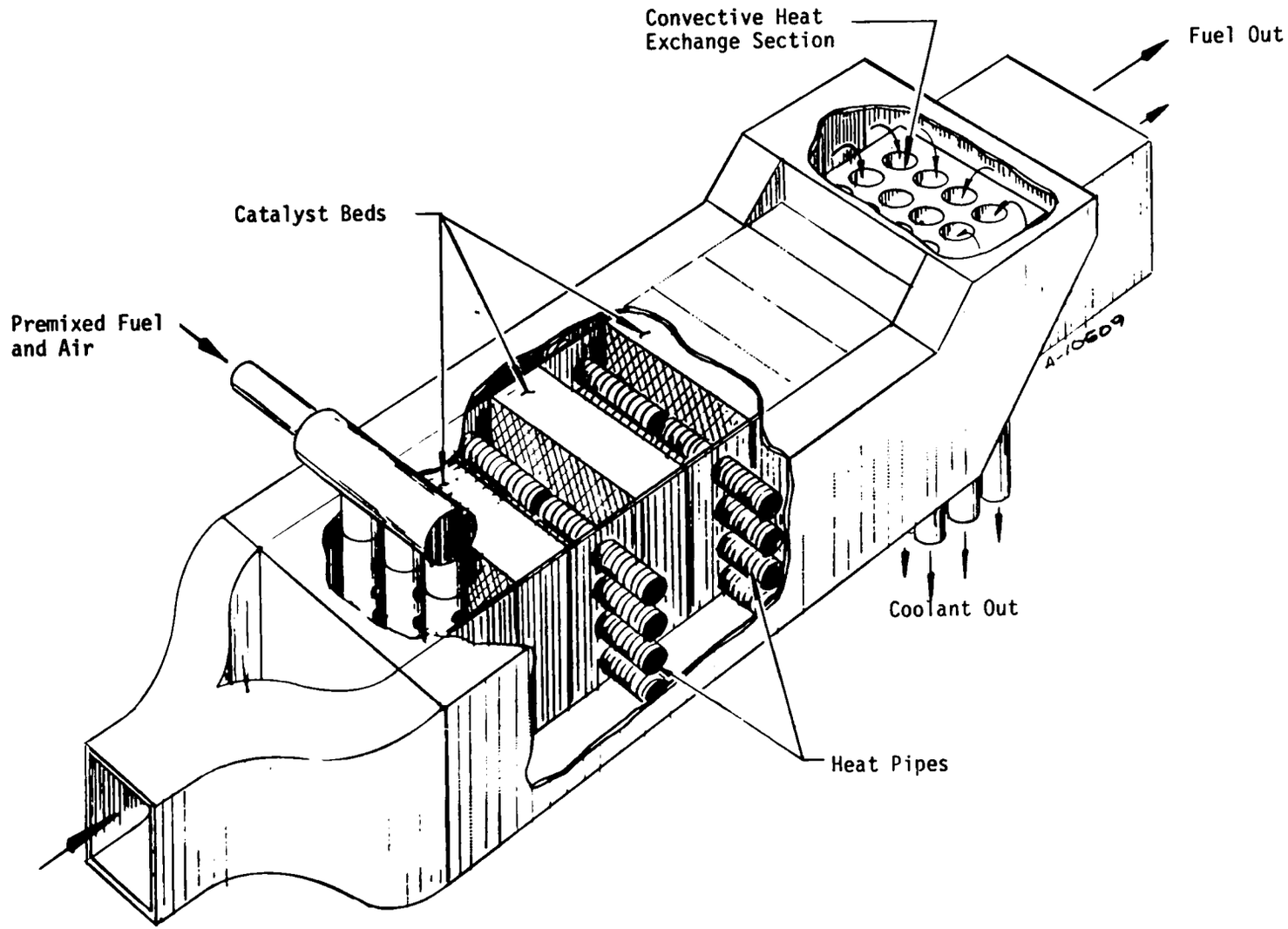
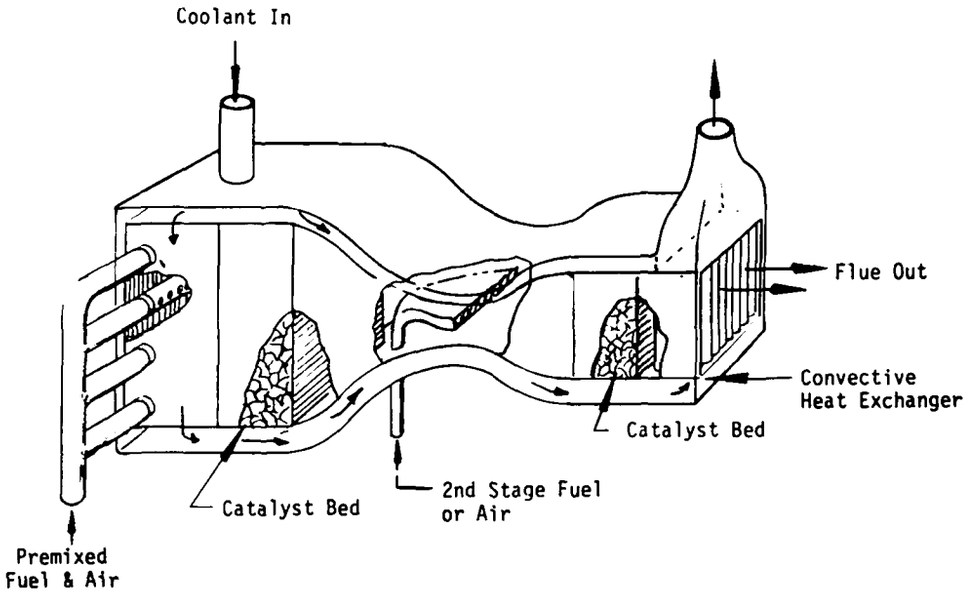
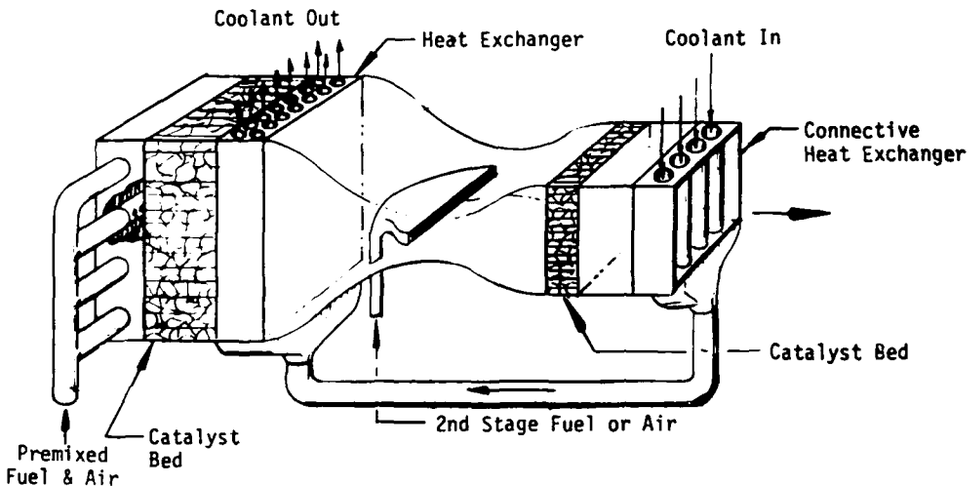


Figure 6-9. Home heater design #4.



(c)



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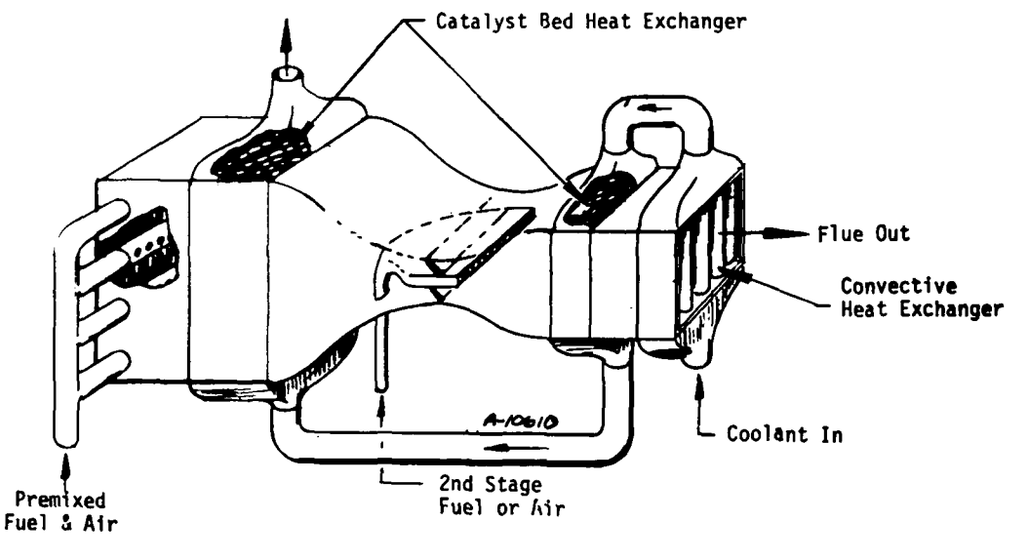

(a)

Figure 6-10. Home heater design #5.

First consider a design with a refractory lined firebox. In this case a larger version of the home heater retrofit design shown in Figure 6-3 could equally well be applied. In the case of internal cooling of the catalyst bed a portion of the feed water or circulating water could be used as the coolant. If it is desirable to use air as the internal catalyst coolant, as with a monolith heat exchanger, it should not be the combustion air but rather an auxiliary air supply which would than transfer heat to the recirculating water. This does not seem to be a very logical approach and therefore a monolithic heat exchange catalyst would not be chosen for this application.

The felt pad in a conical or cylindrical arrangement is also a possibility for a retrofit combustor. Much commercial equipment, being oil fired, presents the problem of incorporating oil firing with the felt pad mentioned in previous sections.

6.4 COMMERCIAL BOILER — NEW DESIGN

Figure 6-11 shows a potential new design concept for a firetube boiler. The firetubes are filled with pellets of catalyst or coated with a catalytic material. A combustion chamber is added of any desired length for first-stage thermal combustion, if required. In addition, a second-stage can be added as desired, followed by additional cooling. FGR can be added to this design as well.

A catalytic water wall design is shown in Figure 6-12. Actually, this is very similar to the Home Heater Design #1 in that it employs a cylindrical catalytic combustor radiating to the water wall. This radiant section is followed by a convective section. This design is a single stage and relies on the high radiant cooling.

6.5 INDUSTRIAL BOILERS — RETROFIT

The retrofit designs for the firetube commercial boilers could equally well apply to the small industrial boiler. The problems associated with a watertube design were briefly discussed in Section 5. Figure 6-13 shows one approach, incorporating a single stage catalyst and flue gas recirculation. This unit would be built as a replacement combustor and would be required to fit into an existing burner port. For oil firing preheated air and an oil vaporizer are required.

6.6 INDUSTRIAL BOILERS — NEW DESIGN

As mentioned in Section 5, it may be advantageous to incorporate radiation cooling of the catalyst bed into a new design for an industrial waterwall boiler. This approach is shown in Figure 6-12 under new commercial boiler designs. Figure 6-14 shows slight modification of that approach. This design looks more like the luminous wall furnace as built by Holden (Reference 69).

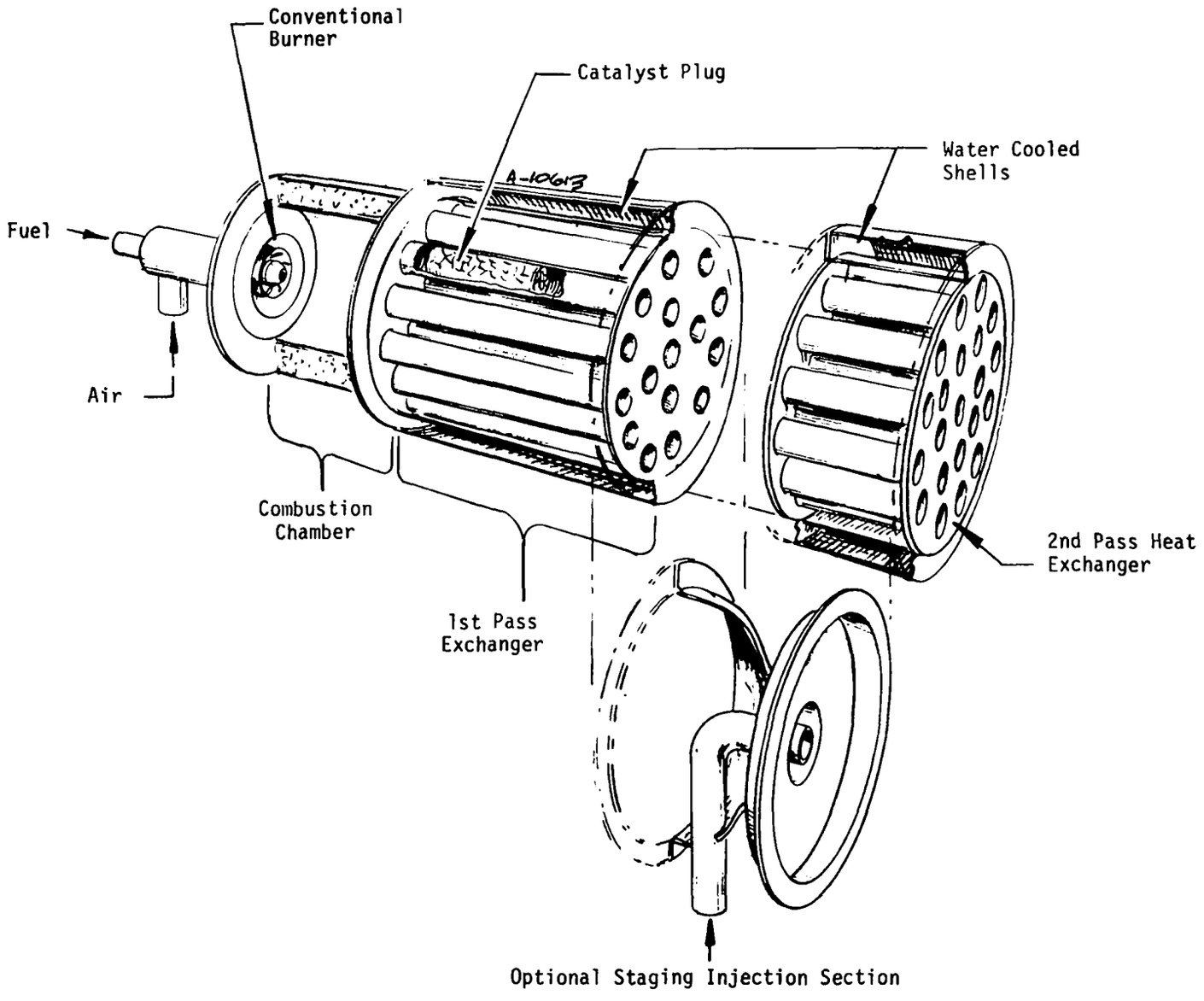

Figure 6-11. Commercial boiler design #1 Firetube boiler.

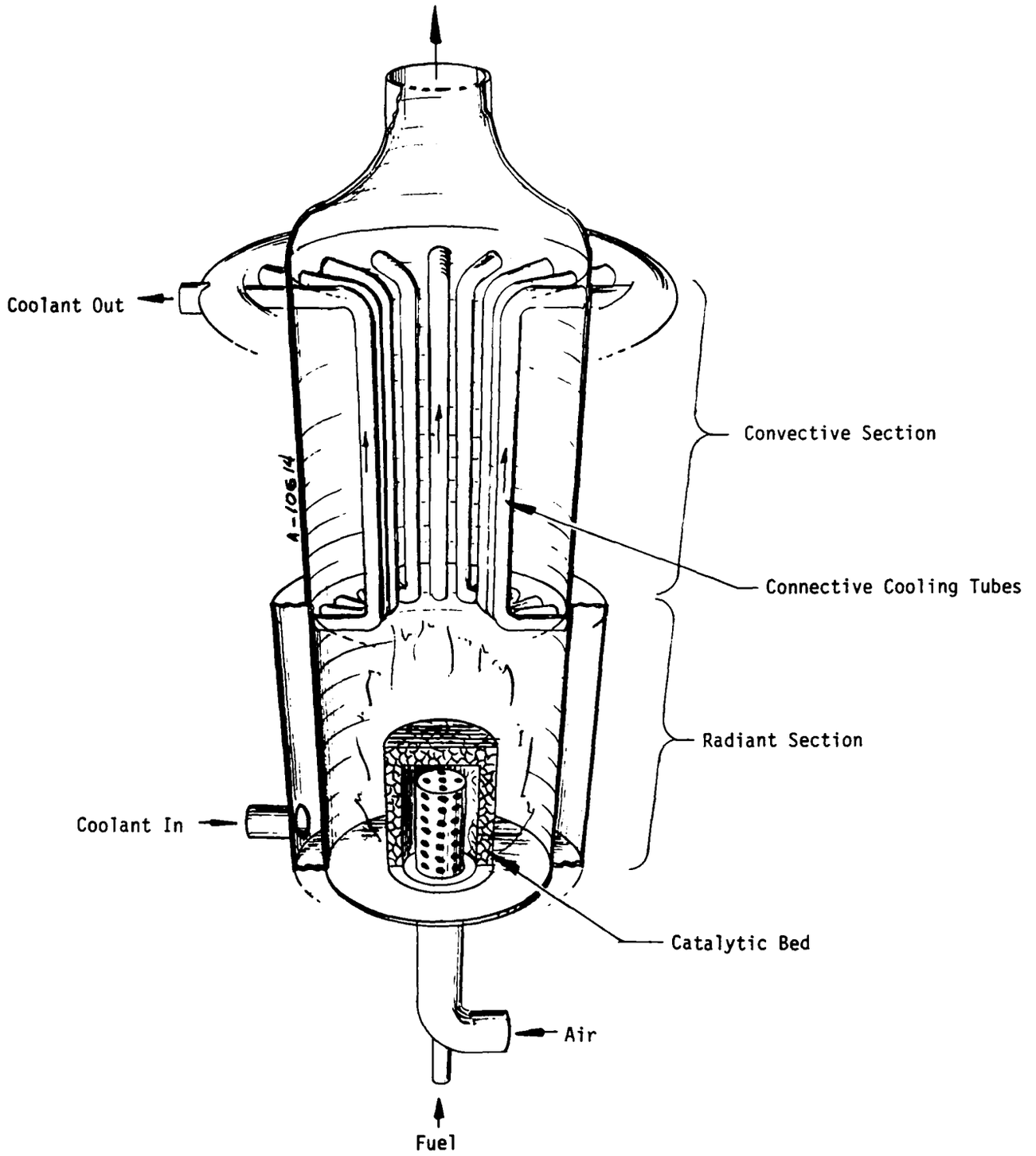

Figure 6-12. Commercial boiler design #2 water wall configuration.

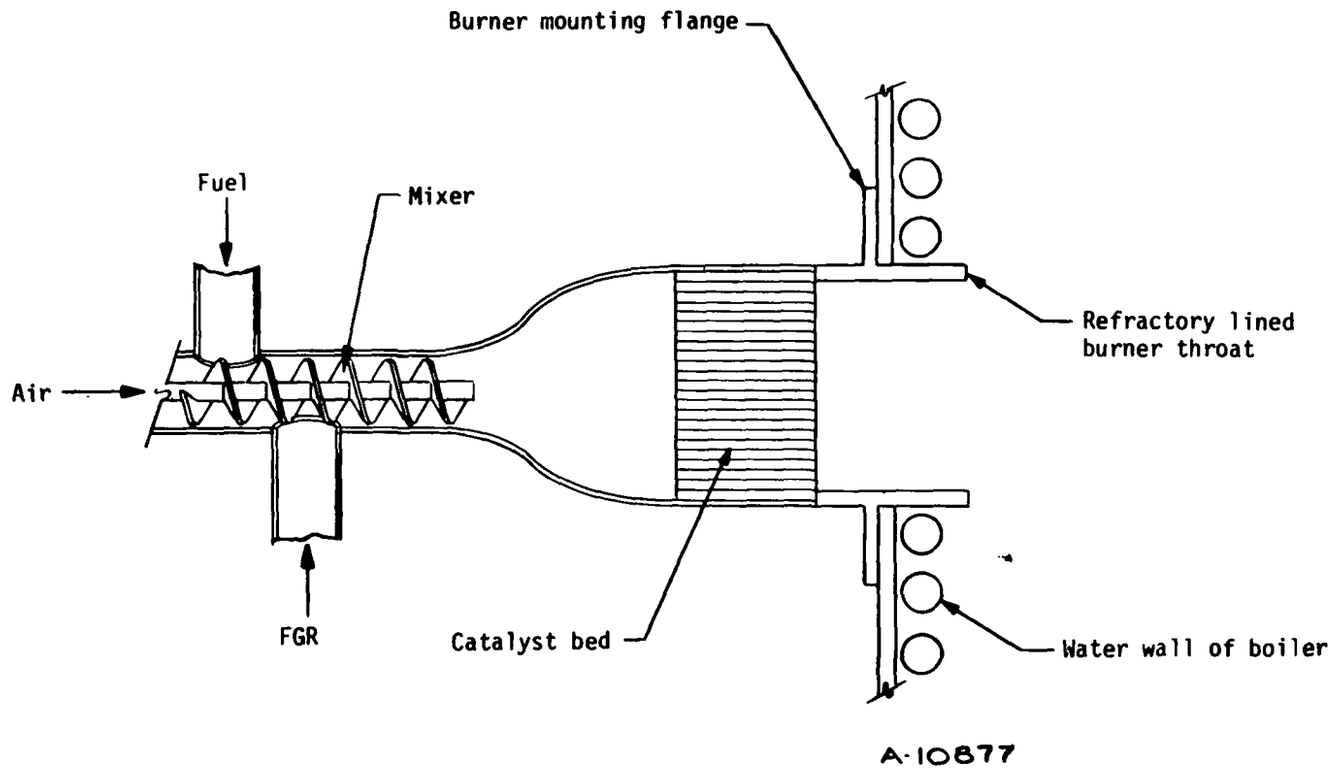

Figure 6-13. Industrial boiler replacement catalyst burner.

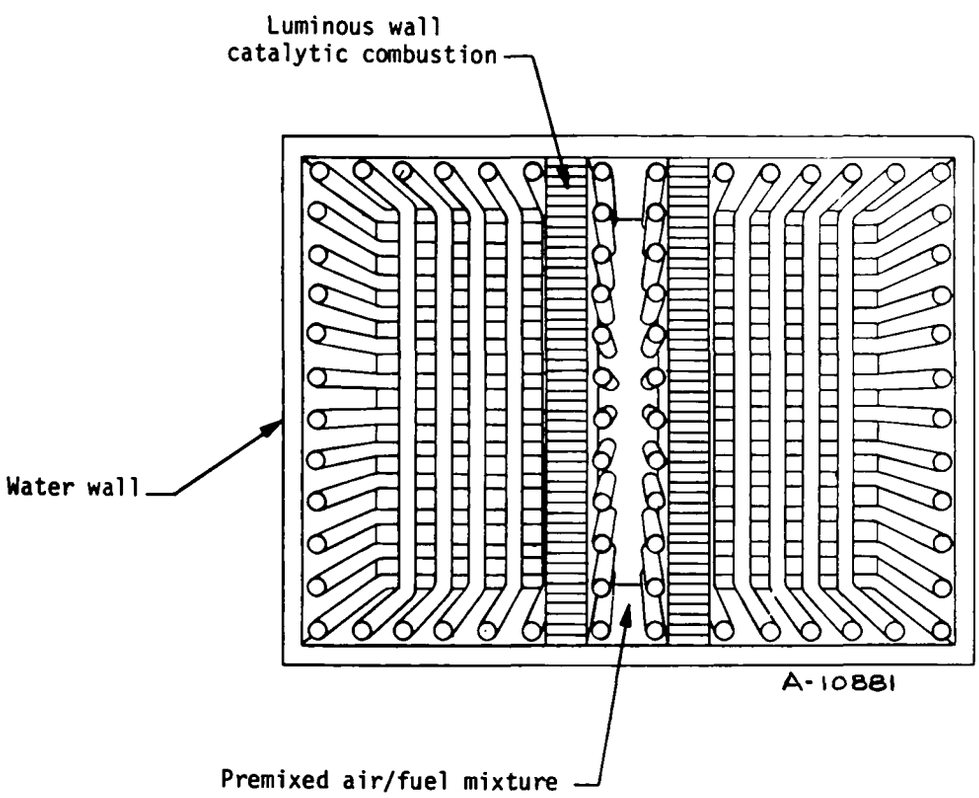

Figure 6-14. Luminous wall catalytic furnace.

6.7 CONCLUSIONS

Data which would be useful to the design for sizing the catalyst bed and calculating heat release rates are almost nonexistent. Nevertheless, several possible designs have been generated.

- Gas fired warm air and hot water retrofit designs appear to be feasible, and although problems exist, are the easiest retrofit methods to accomplish.
- Oil fired warm air and hot water retrofit designs present special problems concerning oil vaporization prior to combustion, and oil preheating without thermal combustion occurring.
- The necessity for preheated air for some catalyst-fuel combinations to activate the catalyst bed must be taken into consideration in any final design.
- New designs based on oil- or gas-fired warm air and hot water furnaces offer fewer constraints than retrofit designs. Based on limited existing information, these designs appear feasible.
- Designs of both retrofit and redesign systems for commercial and industrial boilers have been made. These new designs stress radiative heat transfer, while retrofit designs stress catalyst bed cooling and flue gas recirculation. All appear feasible.
- At the present time it is not possible to make a reasonable cost estimate of catalytic combustors, due to a general lack of knowledge concerning bed depth required. This information must be obtained to allow cost analyses to be made.

SECTION 7

RECOMMENDATIONS

Based upon extensive reviews of stationary combustion source characterizations and existing catalytic combustion knowledge, a complete design matrix has been defined, and several conceptual designs from this matrix have been completed. Because of the proprietary nature of most of the existing data on catalytic oxidation, the designer is severely hampered in his ability to do realistic calculations. It is therefore recommended that a comprehensive testing program on high-temperature catalytic oxidation be conducted, in order to provide the designer with firm data for use in sizing calculations. This program should include:

- Screening tests of various catalyst-support combinations with a variety of fuels, in order to determine activation energies and kinetic rate constants, and to study heat release limits, catalyst life, poisoning effects, ignition and light-off for various air/fuel ratios, preheat temperatures, and surface temperatures.
- Development of a mathematical model for combined homogeneous/heterogeneous combustion which will be capable of predicting the performance of a catalytic bed. This model will make use of the data obtained in the screening tests.
- Tests which demonstrate the feasibility of catalytic combustion in flue gas recirculation, catalyst bed cooling, and two-stage combustion concepts. Since the goal of low NO_x emissions is dependent on holding the bed temperature down, the mechanisms of active bed cooling must be studied in detail.
- Prototype design and development of catalytic furnaces using flue gas recirculation, catalyst bed cooling, and/or two-stage combustion. Since little data of any value presently exists to aid the designer in sizing a catalytic combustor, this data must be obtained experimentally before further prototype design is attempted.

The results of such a test and analysis program would provide a base of design information, currently lacking, sufficient to allow an accurate assessment of the prospects for NO_x reduction by catalytic combustion concepts and of the commercial prospects of catalytic combustion in area-source applications.

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(Please read Instructions on the reverse before completing)

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7. AUTHOR(S) J. P. Kesselring, R. A. Brown, R. J. Schreiber, and C. B. Moyer		8. PERFORMING ORGANIZATION REPORT NO.
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15. SUPPLEMENTARY NOTES

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16. ABSTRACT The report gives results of a review of the state-of-the-art of catalytic combustion concepts, and of an assessment of the applicability of catalytic combustion to gas- and oil-fired home heaters and commercial and industrial boilers. Newly developed high-temperature support materials will greatly enhance the field of high-temperature catalytic combustion, but current catalyst systems are limited by the calatyst coating to much lower temperatures than the supports. To keep combustor temperatures below those that would cause catalyst degradation, to achieve high system efficiency, and to prevent NOx formation, combustion system concepts such as two-stage combustion, flue gas recirculation, and bed heat removal appear necessary. Application of these concepts to home furnaces appears feasible, but their application to larger size units may be more attractive because of their greater initial cost, generally more sophisticated controls, better supervision of equipment, and heat transfer characteristics.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution	Hydrocarbons	Air Pollution Control	13B
Combustion		Stationary Sources	21B
Nitrogen Oxides		Area Sources	07B
Catalysis		Staged Combustion	07D
Oxidation		Flue Gas Recirculation	07C
Fuels		Bed Heat Removal	21D

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