

Reduction of Combustion Generated Pollution: Process Modifications and Energy Efficient Power Cycles*

János M. BEÉR

*Massachusetts Institute of Technology
Cambridge, Massachusetts USA*

Received 13.2.1997

Theoretical bases of combustion process modifications aimed at the reduction of pollutant emission are examined. It is shown, as an example, of how the minimization of emissions of nitrogen oxides leads to a design protocol that translates results of modeling and of bench scale experiments into guidelines for industrial design. The formation and emission of polycyclic aromatic compounds is also considered, because their formation is strongly favored in "low NO_x flames". In power generation the pollutant emission can be reduced effectively by the improvement of the "heat rate," i.e., the thermodynamic efficiency of the power cycle. Combined gas turbine-steam cycles which have strong potential for high thermal efficiency may, however, present new challenges to combustion research. Technology responses to such problems are discussed.

Introduction

Orientation of applied combustion research has taken an important turn in the 1960s towards the reduction of combustion generated pollution. Interest has changed from problems of high intensity combustion in restricted combustion spaces to the processes of formation and destruction of minor constituents, such as oxides of nitrogen, polycyclic aromatic compounds, and submicrometer organic (soots) and inorganic (metals) particulates in practical flames. In contrast to earlier studies in which fluid dynamics and heat transfer dominated, in the present investigations the chemistry of the processes of pollutant formation and reduction play a central role. For purposes of low emission engineering design, chemical kinetics provides the guidance, and fluid dynamics and heat transfer are the tools for the realization of the preferred temperature and concentration "histories" of the fuel. Of the many combustion generated pollutants nitrogen oxides deserve special attention, because of their wide ranging effects on the atmosphere: visibility reduction, tropospheric ozone formation, stratospheric ozone depletion (NO , NO_2 , N_2O); and also, because nitrogen oxides, more than other pollutants, are amenable to reduction by combustion process modification. Such process modifications, however, always involve a high temperature, fuel-rich flame zone favorable for the formation of polycyclic aromatics and fine particulates, the emission of which may represent health hazards.

* This work is presented at 35th IUPAC-İstanbul Congress as an invited lecture

It is necessary, therefore, to include them in the discussion of NO_x emission control.

Design Protocols For Low NO_x Emission From Practical Plant

The kinetics of formation and destruction of nitrogen oxides are discussed in two excellent reviews by Miller and Bowman (1989) and Bowman (1992). The three principal sources of NO in combustion are:

- 1 attack by atomic oxygen on atmospheric nitrogen at high temperature and in oxidizing atmosphere (**"Thermal" or Zeldovich NO**)
- 2 attack of hydrocarbon fragments on atmospheric nitrogen in fuel-rich environments (**"Prompt" or Fenimore NO**), and
- 3 oxidation of heterocyclic nitrogen compounds organically bound in coals and fuel oils. (**Fuel NO**).

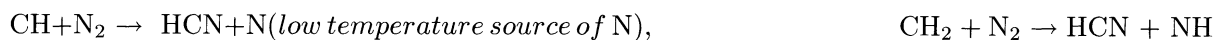
Thermal NO

The "atom shuttle" reaction: $N_2 + O = NO + N$, and $N + O_2 = NO + O$ was first identified by Zeldovich et.al., (1947). This mechanism dominates in fuel-lean high temperature systems (at 1800K the NO formation rate doubles for a 35K temperature rise). Later it was found that NO concentrations in methane/air pulsating combustor significantly in excess of that predicted by the Zeldovich mechanism assuming equilibrium O and O_2 concentrations, but results were in good agreement with calculations using a modified rate equation in which account was taken of superequilibrium O atom concentrations. The latter were calculated from H_2 concentration measurements in the flame and partial equilibrium considerations: $O/O_{\text{equ}} = H_2/(H_2)_{\text{equ}}$.

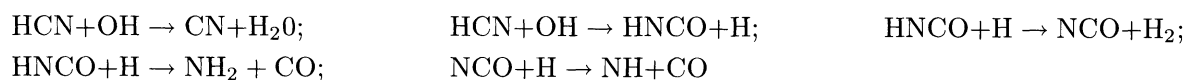
Prompt NO

In fuel-rich combustion, molecular nitrogen in the air is captured by reactions with hydrocarbon fragments, as first described by Fenimore (1971). The NO formed by this reaction is popularly termed "prompt" because of its very early appearance in the flame at the flame front. The reaction paths are :

- a) reactions of hydrocarbon fragments and N_2 generate hydrogen cyanide (HCN):



- b) hydrocarbon abstraction generates ammonia radicals:



- c) ammonia radicals generate NO: $NH + O \rightarrow NO + H;$ $N + OH \rightarrow NO + H$

As the fuel/air ratio falls so does the relative contribution of Prompt NO, which is considered to be between 20 and 30% of the total NO formed at $\cong \phi$ 0.8. (ϕ is fuel/air ratio in the flame normalized by the stoichiometric fuel/air ratio). It is noteworthy that because of the relatively slow formation of thermal NO short residence time experiments, e.g., stirred reactor studies, show higher Prompt/Thermal NO ratios than flame reactor experiments in which there is sufficient time for thermal NO formation.

Fuel NO

Heterocyclic nitrogen compounds organically bound in the fuel molecules of coal and oil readily oxidize to form NO in fuel-lean atmospheres. The Fuel-N can, however, be converted to N_2 in high temperature fuel-rich pyrolysis reactions. The primary product of the pyrolysis is HCN which is converted via oxycyanogen radicals to amines and then to N_2 . In this way the Fuel-N is rendered innocuous for NO formation. It is noteworthy for practical applications that the rate of oxidation of Fuel-N to NO is only slightly dependent upon temperature, but is a strong function of the local oxygen concentration, while its conversion to N_2 benefits from elevated temperatures in the fuel-rich flame, because the activated reactions run faster towards equilibrium at higher temperature.

NO Reduction by “Reburn”

The reactions between NO and hydrocarbon fragments provide the basis for the method of NO reduction by fuel staging termed “NO Reburn” (Wendt et. al., 1971). When a hydrocarbon fuel such as a natural gas is injected into the hot NO bearing combustion products of some primary fuel (coal, oil or gas) so that the fuel-air ratio is turned locally fuel-rich a fraction of the NO is converted to cyanides, e.g., $NO + CH \rightarrow HCN + O$, or $NO + CH_2 \rightarrow HCN + OH$. The cyanides then form amines, which can further react with NO to produce N_2 . Following the reduction of NO, further air injection is necessary to complete the combustion

Examination of the above mentioned modes of NO formation and destruction, their chemical mechanisms and kinetic rates (Kee et. al., 1980, 1989) leads to the following engineering methods for NO_x minimization.

- a) *reducing the peak flame temperature* in fuel-lean combustion by heat extraction in boilers and furnaces, by “in furnace” recirculation of burned gas, by “external” recirculation of flue gas through the burner, and by premixing gaseous fuel with air and with flue gas prior to ignition:
- b) *staging the combustion air* to convert organic, fuel-N to N_2 by fuel-rich/lean sequencing in coal and oil flames, and
- c) *staging the fuel (NO Reburn)* to convert NO to N_2

In gas turbine applications dilution of the combustion products by large amounts of air is used to cool the gas before entry to the gas turbine to a temperature limited by structural properties of turbine blade materials. At “state-of-the-art” combustor exit temperatures in industrial gas turbines ($< 1650K$) the rate of NO formation is low, but large amounts of NO may form in the first stage of combustion prior to the addition of the dilution air. In modern combustor designs the gaseous fuel is premixed with the combustion air right at the beginning of the combustion process, this reduces significantly the NO_x formation, but leaves other problems, such as flame stability and trace combustibles of CO and HC emissions as challenges of combustor designs.

Polycyclic Aromatic Compounds (PACs)

PACs are of interest as a group of combustion generated pollutants because of their potential mutagenic activity. PACs may originate in the fuel or may form by pyrosynthesis in fuel rich regions of flames. Pyrolysis followed by oxidation, one of the preferred routes for the reduction of nitrogen oxides in flames also favors

the formation and emission of trace concentrations of PACs. Fluxes of PAC specie determined in fuel-rich natural gas turbulent diffusion flames show the build-up of hydrocarbons of increasing molecular weight along the flames (Fig. 1.), in a trend similar to that observed in laminar premixed flames by Bittner et. al., 1983. It is postulated that PACs are formed by the successive addition of C_2 through C_5 hydrocarbon rings (Fig. 2.). The mutagenic potential of PACs can be illustrated by results of bacterial mutation assays. The mutagenicity of flame samples (Fig. 3.) shows that the specific mutagenicity of pyrosynthesized PACs from a natural gas-air flame is significantly higher than that which originates from unburned fractions of a highly aromatic fuel.

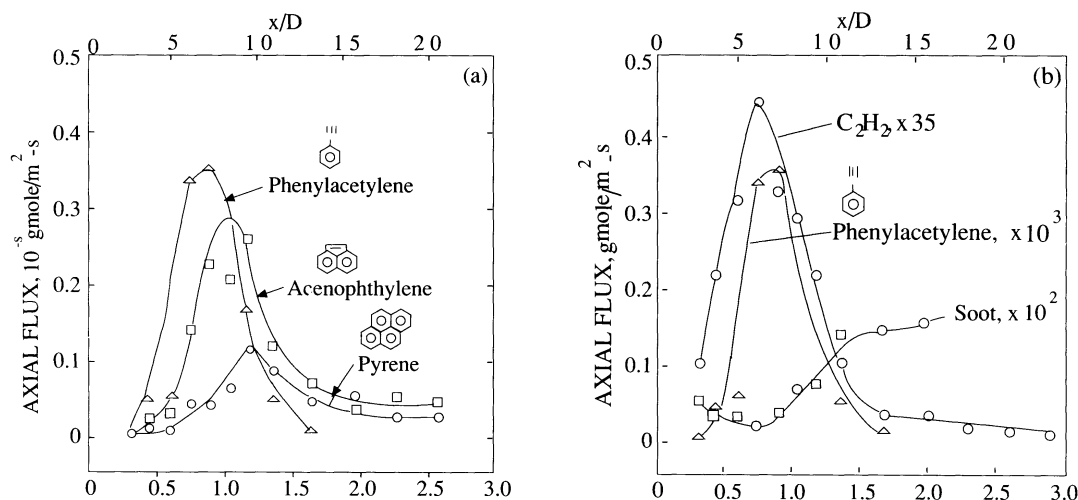


Figure 1. (a) Axial fluxes of phenylacetylene, acenaphthylene, and pyrene in a fuel-rich natural gas turbulent diffusion flame, (b) Axial fluxes C_2H_2 , phenylacetylene, and soot in a fuel-rich natural gas turbulent diffusion flame (Topan et. al. 1984).

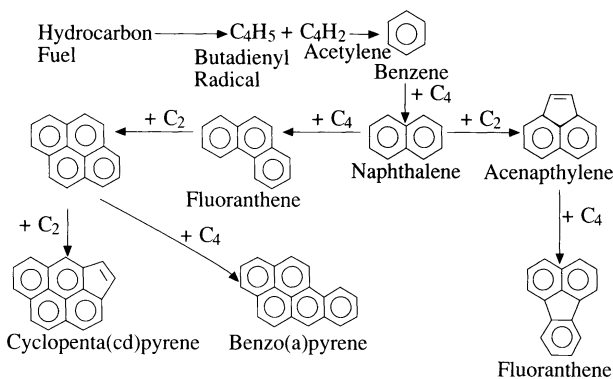


Figure 2. Mechanism of formation of polycyclic aromatic compounds during combustion: cyclization via butadienyl and acetylene, followed by addition of C_2 to C_5 hydrocarbons (Cole et al. 1984).

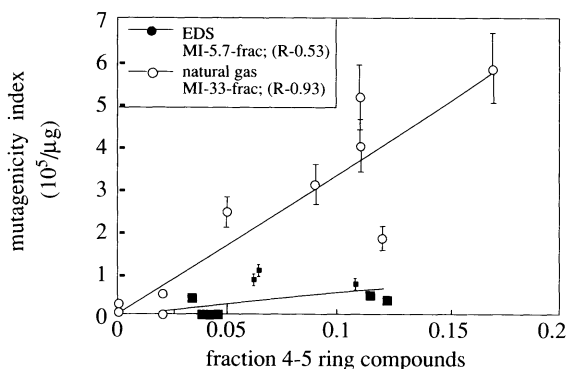


Figure 3. Indirect specific induced mutagenicity vs the fraction of 4- and 5-ring compounds of the PACs. The mutagenicity index is a measure of the mutagenic potential of a complex mixture of combustion products (Thijssen et. al. 1993).

Because of the need for very high destruction efficiencies of PACs in practical plant ($>99.99\%$) the mixing process in the final oxidative zone of the staged combustion process ought to perform to a very high standard. Interest is focused on the high wave number region of the turbulent-energy spectrum, on the smallest eddies in which the turbulence energy is dissipated by molecular processes leading to chemical reaction.

Reduction of Pollutant Emission by the use of High Efficiency Combined Gas Turbine-Steam Power Cycles

Improved thermodynamic efficiency of power generating systems leads to fuel conservation and because pollutant emission is directly proportional to fuel use, to reduced pollutant emission. In general, Gas Turbine-Steam Combined Cycles use two power generating cycles in tandem. Because of the complementary temperature ranges of the gas turbine or Brayton cycle (1700-900K) and the Steam or Rankine cycle (878-288K) the GT exhaust gases can be cooled in a heat recovery steam generator (HRSG) to produce additional power in a steam turbine. The usual thermodynamic efficiency of the GT cycle, 33%, can be raised to about 38% by its combination with the steam cycle. The gas turbine requires premium fuel, but coal or residual fuel oil can be added in the HRSG as supplementary fuel (Fig. 4.). The gas turbine exhaust gas contains typically 12 to 18% O_2 depending on the thermal load. At the lower end of the oxygen concentration range flame stability and complete burn out of the supplementary fuel may present problems, while at high O_2 levels the NO_x emission needs special attention, e.g., low NO_x "Duct Burners".

In the Air Heater Combined Cycle (Fig. 5.) coal burns at atmospheric pressure in a high temperature furnace preheating compressed air and also raising steam. The compressed air is further heated in a natural gas fired "topping combustor" before entering the gas turbine. In this case the gas turbine is entered by a clean high temperature gas, the coal's contribution to the gas turbine cycle is made through the air preheat. The cycle efficiency can exceed 50%; the fractional gas use being a strong function on the air preheat. Because of the high air temperature the fuel equivalence ratio must be very lean to avoid high NO emissions. The R&D tasks of the Ultralean Premixed Topping Combustor will be the fuel air premixing without flashback, and the combustor wall cooling. A design is necessary in which all the combustion air is used as cooling air before premixing with the fuel-gas.

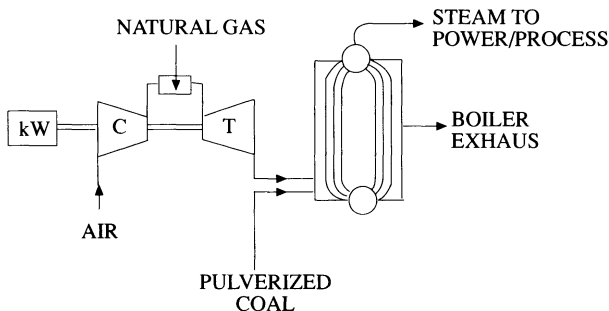


Figure 4. Gas turbine cycle with coal fired heat recovery steam generator.

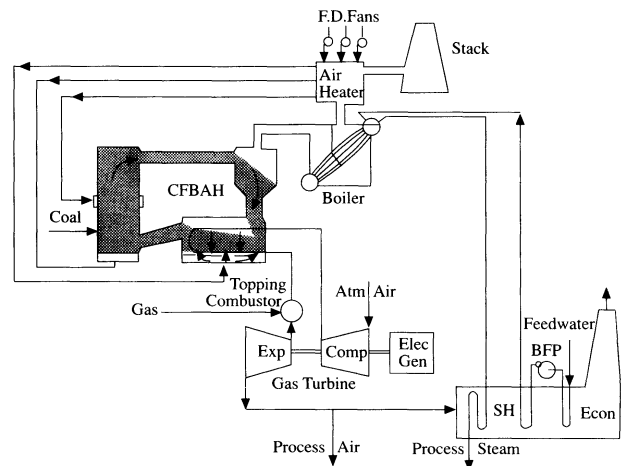


Figure 5. Atmospheric circulating fluidized bed air heater cycle with natural gas-fired topping combustor.

The major challenge to combustion technologists lies in solving the problems of direct coal use in gas turbines. A notable example of such an effort is the development of Pressurized Fluidized Bed Combustion (PFBC). Fluidized combustion is capable of sulfur retention by additive limestone and of low NO_x emission. Also, at the relatively low temperature of the fluidized bed combustor vaporization of metals in the coal ash and their emissions in submicrometer aerosols is greatly reduced which simplifies the gas clean-up before entry to the gas turbine. The low temperature, however, has also disadvantages, as it reduces the GT cycle efficiency and favors the emission of nitrous oxide, N_2O . Nitrous oxide is a "greenhouse gas" and because its long lifetime in the lower atmosphere, it reaches the stratosphere where it takes part in (Fig. 6.) reactions

leading to the depletion of ozone. In the Second Generation PFBCs the coal undergoes mild gasification and the resulting char is burned in the PFBC. The flue gases leaving the PFB at a temperature of about 1150K and having sufficient excess air to burn the fuel gases generated in the gasifier, enter a Topping Combustor where the gas temperature is raised to about 1600K, the state-of-the-art industrial gas turbine entry temperature. This raises the cycle efficiency to about 47% and also eliminates the N_2O emission.

Hot gas clean-up and the topping combustor are areas of development for this cycle. In the area of gas cleaning the problem is to provide protection of the turbine from solid particulates and corrosive alkali metal vapors. The cleaning has to be done at PFBC and gasifier exit gas temperatures because of the loss in efficiency due to the loss of the sensible heat when the gas is cooled to facilitate cleaning. A DOE sponsored program for the development of porous ceramic "candles" is well on its way to the solution of this problem (Robertson, et. al., 1988.)

The technical problems in the topping combustor development are the adequate cooling of the combustor with the high temperature PFBC exhaust gas, and the low emission combustion of the fuel-nitrogen bearing fuel gas. An example of the technology response to these challenges is the Multiannular Swirl Burner (MASB) (Beér 1965, 1989, 1986; Garland et. al., 1986, 1990; Robertson et.al., 1993; Domeracki et. al., 1994). The conceptual design of the MASB is shown in (Fig. 7.). In the MASB thick layers of concentric annular passages of air flow cool the high alloy metal walls of the combustor, and the concentric conduits of air axially displaced to permit air staging for low NO_x operation. Results of recent tests carried out by a Westinghouse team at the University of Tennessee Space Institute's Coal Fired Flow Facility have shown that combustor metal wall temperatures can be maintained at reasonable levels even though most cooling is done by 870 C flue gas. The MASB was fired by a low calorific value ammonia bearing gas in a Fuel-Rich/Fast Quench/Fuel-Lean mode which resulted in very low NO_x , emissions, less than 10% conversion of the fuel-N to NO_x , and without fuel-N in the feed an increase of only 8ppm NO_x on top of the NO_x concentration of the combustion products entering the BASB.

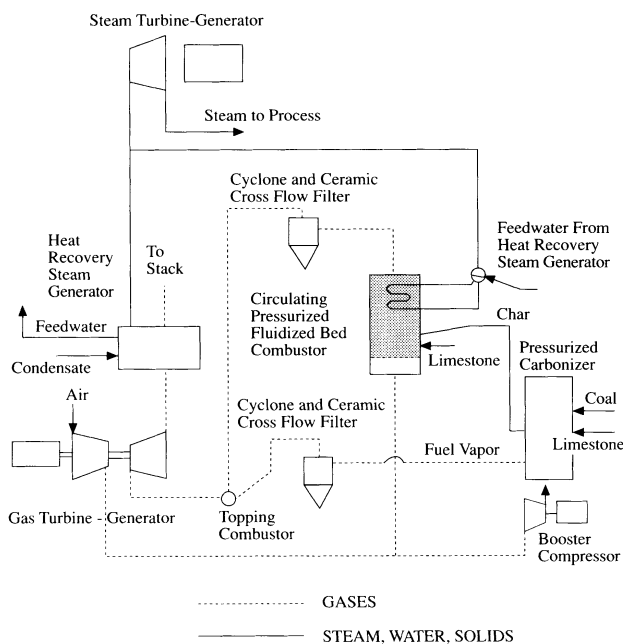


Figure 6. 2ND generation PFBC cogeneration cycle.

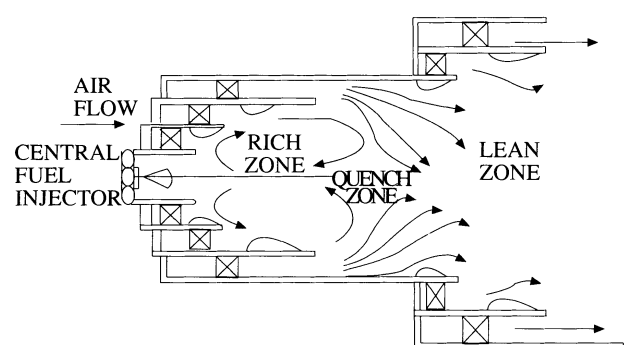


Figure 7. Multi-annual swirl burner (beér, US. Patent, 1989).

The effect of improved thermal efficiency of power generating cycles upon CO_2 emission is shown in (Fig. 8.). It can be assumed that the emission of other pollutants also scale with that of the CO_2 . By taking

a condensing pulverized coal fired power plant as the base with about 1kg CO_2 /kWh emission it can be seen that this value can be reduced by more than 50% through the application of advanced thermodynamic cycles.

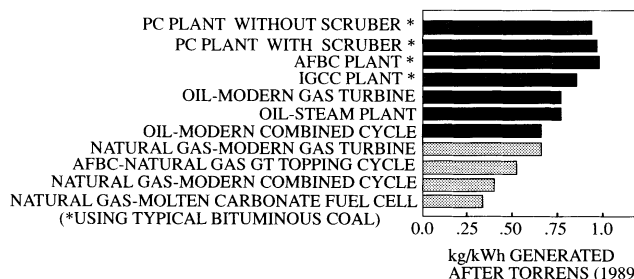


Figure 8.

Conclusions

Combustion and pollutant formation are inseparable processes. Because of the central role of combustion in fossil fuel utilization for the foreseeable future, major efforts are being made to ameliorate the environmental effects. New clean combustion technologies are being developed based on the better understanding of the physical-chemical bases of pollutant formation and emission from flames and design protocols are formulated for the translation of the scientific results to industrial design.

Energy conservation in the form of increased thermal efficiency of power generating cycles is also an effective way to reduced pollutant emission. The combined Gas turbine-Steam Cogeneration plants in the future raise some challenging questions for combustion scientists and engineers on the stability of premixed flames at mixture strengths close to the lean flammability limit, the reduction of nitrogen oxides (both NO and NO_2), hydrocarbons and CO , when burning natural gas, oil or a coal-fuel directly in the gas turbine. Mention is made of recent engineering solutions to these problems applied to practical plant or in the stage of industrial R&D. It can be expected that combustion technology will continue to respond to the challenge and seek novel ways in a drive towards the lower bounds of combustion generated pollution.

Acknowledgments

Stimulating discussions with colleagues Majed Toqan, Jan Thijssen, Laszlo Barta are acknowledged with thanks. Research support from ABB-CE, ENEL, EPRI, ESEERCO, and Westinghouse Electric Corp. are gratefully acknowledged. Thanks are due to Ms. Julie-Marie Andersen for producing this manuscript with professional efficiency.

References

1. J.M. Beér, U.S. Patent No. 484540, 1989.
2. J.D. Bittner, J.B. Howard, H.B.s Palmer, "Soot Formation in Combustion Systems and Its Toxic Properties." "J. Laheve and G. Prado, eds., p. 95. Plenum (1983).
3. C.T. Bowman, "Twenty-fourth Symposium (International) on Combustion, Invited Lecturer", pp. 859-878, 1992. The Combustion Institute, Pittsburgh, PA.

4. J.A. Cole, J.D. Bittner, L.P. Longwell and J.B. Howard, "Formation of Aromatic Compounds in Aliphatic Flames," *Comb. Flame.* 56, p. 51 (1984)
5. W.F. Domeracki, T.E. Dowdy, D.M. Bachovchin, "Topping Combustor Development for Second-Generation Pressurized Fluidized Bed Combined Cycles." Proceedings of the ASME, IGTI 1994 Gas Turbine Conference, 1994.
6. W.F. Domeracki, T.E. Dowdy, and D.M. Bachovchin, ASME-IGT Conference, Houston, TX Paper No. 95-Gt-106, 1995.
7. C.P. Fenimore, "Thirteenth Symposium (International) on Combustion". The Combustion Institute, p. 373, 1971.
8. R. Garland, P. Pillsbury, "Status of Topping Combustor Development for Second Generation Fluidized Bed Combined Cycles," ASME paper 90-GT-30, 1990.
9. R. Garland, P. Pillsbury, and G. Vermes, "Generic Studies of Advanced Fluidized Bed Air Heater Technology," DOE/DE/40543-5. Westinghouse Electric Corporation, 1986.
10. R.J. Kee, J.A. Miller, and T.H. Jefferson, "CHEMKIN" DOE Sandia Laboratories, New Mexico, Doc. No. SAND 80-8003 (1980).
11. R.J. Kee, F.M. Rupley, and J.A. Miller, CHEMKIN II. Sandia Report SAND 89-8009 Sandia National Laboratories, Livermore, CA, 1989.
12. J.A. Miller, and C.T. Bowman, "Progress in Energy and Combustion Science" 15, 287, 1989.
13. A. Robertson, R. Garland R. Newby, J. Patel, and L. Rubow, "Second-Generation PFB Combustion Plant Performance and Economics," EPRI Seminar on Fluidized Bed Combustion Technology for Utility Applications, 1988.
14. J.H. Thijssen, M.A. Toqan, J.M. Beér and A.F. Sarofim "Comb Sci and Techn", 90, p. 101, 1993.
15. M.A. Toqan, W.F. Farmayan, J.M. Beér, J.B. Howard, and J.D. Teare, Twentieth Symposium (International) on Combustion, p. 1075, The Combustion institute, 1985.
16. M.A. Toqan, J.M. Thijssen, J.M. Beér, and A. Lafleur, *Inst. E.* 66, pp. 119-125. Wendt. J.O.L., Sternling, C.V. and Matovich, M.A., 1971, Fourteenth Symposium (International) on Combustion. The Combustion Institute, Pittsburgh, PA, PP. 874-904, 1995.
17. J.O.L. Wendt, C.V. Sternling, and M.A. Matovich, "Fourteenth Symposium (International) on Combustion." The Combustion Institute, Pittsburgh, PA, pp. 897-904, 1971.
18. Y.B. Zeldovich, P.Y. Sadvonnikov, and D.A. Frank Kamenetskii, Oxidation of Nitrogen in Combustion (trans. by M. Shelef). Academy of Sciences of USSR, institute of Chemical Physics, Moscow-Leningrad, 1947.