NEW RESULTS CONCERNING THE EMISSION OF POLLUTANTS FROM COMBUSTION PROCESSES IN GAS TURBINES

G. Kappler*), Th. Just**), G. Winterfeld***)

Abstract

The development of practical gas turbine combustors designed to meet the imposed air pollution standards presupposes results from both, basic reaction kinetics research and combustion modeling. Therefore, in a joint cooperation between German research institutes and a gas turbine manufacturing company investigations were carried out on NO formation in flames with special emphasis on the fuel-rich regime, on numerical methods to describe pollutant formation in post-flame gases, and on the technical feasibility of modifications for emission reduction of conventional combustors. The investigations have shown that the formation of "prompt NO" at equivalence ratios > 1 can not be described by the Zeldovich mechanism and that, besides inhomogeneities in the fuel distribution and other parameters already discussed, combustor modeling must also account for inaccuracies of reaction kinetics data and heat losses due to flame radiation. Simple modifications on a conventional combustor led to simultaneous reduction of CO, NO, and unburned hydrocarbons.

I. Introduction

The current design of combustors for gas turbine engines is subdued not only to the traditional design requirements like

*)
MTU, Munich, (Section IV),

**)
DFVLR, Inst.fur Reaktionskinetik,
Stuttgart, (Section II),

high combustion efficiency at all main operating conditions, wide ignition and stability limits, low pressure loss, long durability and low production costs, but also to exhaust emission control. To reduce pollutant formation and emission it is neccessary to gain more insight into the basic reaction kinetics processes. In particular, it is of great interest to improve the knowledge of the "prompt NO" formation in fuel rich flame zones. To link results from basic kinetics to the complex combustion and flow processes in a combustor, numerical modelling techniques are used. However, the realistic matching of combustor models to actual combustor behaviour is still a matter of great concern. To make such models as simple as necessary for practical applications the great number of possible parameters has to be reduced regarding their relative degree of influence. Also, the technical feasibility of modifications on conventional combustors aimed to achieve low exhaust emission rates has to be investigated, while maintaining as much as possible their initial performance.

To make best use of the available basic research and developments potentials the efforts of the DFVLR-Institutes for Reaction Kinetics and Air Breathing Engines and MTU Gas Turbine Development Department were joined, for low emission combustor design. According to the outlined problem areas, in this paper results of research efforts are reported in three parts.

DFVLR, Inst.fur Luftstrahlantriebe, Porz-Wahn (Section III).

II. NO Formation in Fuel-Rich Flames Zones

Recent investigations have shown that not only the well known Zeldovich-mechanism may be responsible for the NO formation in flames but other mechanisms may be important, too. Various reaction channels can contribute to the NO formation whereas their relative importance depends strongly on flame conditions as given mainly by temperature T. and equivalence ratio \emptyset . In lean, but not necessarily laminar flames with $\emptyset \leq 1$ under convenient conditions it is possible to predict the NO formation with reasonable accuracy by

$$\Delta NO \approx 2 \text{ k [O] [N_2]} \Delta t$$
 (1)

if the oxygen atom concentration is assumed to be in local thermodynamic equilibrium and if for k a value of $k = 5 \cdot 10^{13}$ exp (-75 400/RT)cm3/mole · sec is adopted. The applicability of this formula should be not overestimated since it is often not simple to predict proper values for T, [0] and At in the flame zone of interest. In particular at lower temperatures increasing contributions of non-equilibrium oxygen concentrations have to be considered occasionally. These effects have been discussed at length (1) and will not be dealt with in this paper. However, much more difficulties arise if accurate predictions of the NO formation in fuel-rich hydrocarbon flames are required. Recent investigations on such flames, which were initiated by the pioneer work of Fenimore (2) have shown without doubt that reaction channels like:

$$C_2 + N_2 \rightarrow 2 \text{ CN}$$
 (R1)

$$CH + N_2 \rightarrow HCN + M$$
 (R3)

grow rapidly in importance with increasing flame richness. Applying for example the simple formula (1) on laminar alkane flames with $\emptyset = 1.4$ and assuming 1 bar and adiabatic flame temperature, a NO concentration

of 0.06 ppm after 5 msec is calculated. In contrast to this prediction the measured NO concentrations range from 40 - 50 ppm (3). Strong evidence for the assumed (2) participation of radicals like C2 and CH in the NO formation process was found by measurements of HCN concentrations in fuel rich flames (3). In general HCN appears as an intermediate, but at 0 > 1.5, HCN even seems to be a rather stable product in the post flame gases. For flames with an equivalence ratio $\emptyset > 1$ it is typical that a fast NO production takes place in and near to the zone where the original hydrocarbon molecule is decomposed to smaller hydrocarbon molecules or to carbon containing radicals. The adjacent flame zones show then in general comparatively low or even zero production rates of NO. For cases of nonzero production rates these zones are generally the main sources of NO if the gas is hold long enough at sufficient high flame temperature. The described behaviour of NO in the first flame zone is denoted as "prompt NO" formation (2). "Prompt NO" formation at $\emptyset < 1$ was also observed (3), but the main reason for the formation is here very probably the existence of a superequilibrium oxygen atom concentration in the first part of the flame. This mechanism will be not discussed in this paper. At 1 bar it was not possible to resolve properly the "prompt NO" respectively the HCN profiles in laminar, fuel-rich flames (3), therefore measurements at reduced pressures were initiated (4). As an example, Fig. 1 shows the results obtained at 72 torr. According to the low pressure, the flame zone in which the hydrocarbon is decomposed has a length of about 15 to 20 mm. This length is sufficient for application of a probe sampling technique. As the most interesting result it should be noted here that the decrease of HCN behind its maximum, corresponds closely to the increase of NO. About 70 % of the formed "prompt NO" behind the maximum of HCN seems to come from reacted HCN.

The obvious important role of HCN and carbon containing radicals is supported

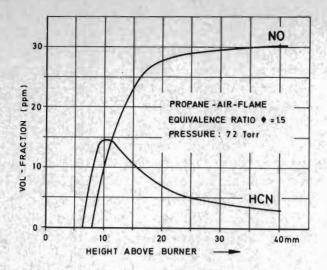


FIGURE 1. "PROMPT NO" FORMATION IN LAMINAR PROPANE-SYNTHETIC AIR FLAMES.

further by qualitative spectroscopic measurements of CH, C2 and CN emissions in low pressure flames (4). As it was anticipated, typical emission peaks of CN, C2 and CH in the zone of fast HCN production were observed. Even at an equivalence ratio Ø of about 0.9 a C, emission peak occured, which led to the preliminary conclusion that on the basis of a comparison of peak intensities between lean and rich flames it might be correct to assume that about 20 % of the "prompt NO" in the investigated lean flame stems from hydrocarbon radicals and not from excess oxygen atoms. Although it is not possible at present to give a very detailed reaction scheme for the "prompt NO" production by hydrocarbon radicals some facts concerning the general scheme become more and more established. In the first flame zone a rapid destruction of hydrocarbon has to be assumed which leads at 0 > 1 to increasing amounts of C2 and CH. C2 for example reacts fast with No forming CN. In the next step under the typical conditions of a fuel rich flame the produced CN will soon build up a quasi-equilibrium between CN and HCN:

This is strongly favoured by the great excess of H2 and H over oxygen atoms in fuel

rich flames. The reaction enthalpy ΔH_{298} for

$$CN + H_2 \rightarrow HCN + H$$
 (R6)

is about - 20 kcal/mole, which is of course sufficiently low for a fast establishment of a quasi-equilibrium. The most probable reactions of CN in the direction of NO formation are

$$CN + O \rightarrow CO + N$$
 (R7)

or

$$CN + O_2 + (?) CO + NO$$
 (R8)

The N atoms react further with oxygen containing compounds to NO and the corresponding products. It becomes clear now, that HCN is an intermediate which is closely linked to the "prompt NO" formation in hydrocarbon flames. Of course the reaction (R6) is not the only source for HCN. The reaction

$$CH + N_2 \rightarrow HCN + N$$
 (R3)

has to be considered, too.

Further support of this general scheme can be found by measurements of the temperature dependence of "prompt NO" concentrations in fuel-rich and slightly lean flames (5). The adiabatic flame temperature was varied by using "synthetic air" with nitrogen to oxygen ratios greater or smaller than 4 to 1. Fig. 2 shows the results. For an equivalence ratio 0 > 1 and temperatures below 2 400 K a relative small temperature dependence of the "prompt NO" concentrations was found in contrast to a very strong dependence for Ø < 1 and temperatures greater than 2 200 K. This interesting result should be considered with respect to the proposed reaction scheme:

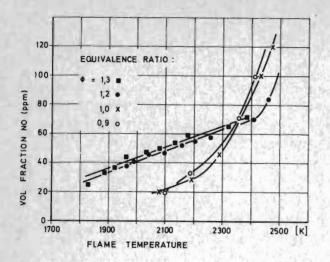


FIGURE 2. FORMATION OF "PROMPT NO" AND HCN.

The explicitly written reactions have reaction enthalpies and therefore also most probably activation energies which are equal or less than + 20 kcal/mole. For the production of C2 (CH) it is also possible to develop a plausible sequence of reactions which lead from hydrocarbons to C2 (CH) by a number of steps which have just as well activation energies not greater than about 20 kcal/mole. A sequence in that respect can be imagined for example by considering reactions of hydrocarbons or hydrocarbon radicals with H or OH. The measured variation of "prompt NO" with temperature according to Fig.2 can be described for 0 > 1.2 by an empirical formula (5):

$$NO \approx 0.0745 \cdot T - 106 \text{ (ppm, } ^{O}K) \text{ (2)}$$

(T = adiabatic flame temperature), which is in fact roughly compatible with a sequence of reactions with associated activation energies in the order of 20 kcal/mole. However, on the contrary in stoichiometric or lean flames it is not possible to construct a similar "low activation energy" sequence of reactions, since under these conditions the dominant NO formation process is:

$$O + N_2 \rightarrow NO + N \tag{R9}$$

with an activation energy of 75 kcal/mole.

If in these mixtures "prompt NO" occurs, it is mainly formed by excess oxygen atoms and will show consequently a much more pronounced temperature dependence. This behaviour is reflected by the much steeper lines for $\emptyset \le 1$ in Fig.2.

In conclusion of this section it is stated that in fuel-rich flames other mechanisms than the Zeldovich-mechanism for NO formation play without doubt an important role. For a complete and a priori prediction of NO concentrations more investigations have to be carried out which should concentrate in particular on hydrocarbon destruction to C2 and CH and on the rate constants according to the proposed sequence. At present careful measurements of prompt NO under various pressures, temperatures and equivalence ratios will provide usable semiempirical data for theoretical prediction procedures of NO concentrations in gas turbines and other propulsion systems.

III. Relative Influence of Parameters Entering Combustor Models

It is generally agreed that computational combustor models as described for example in (6), (7) or (8) would greatly assist practical combustor development, insofar, as they will allow the evaluation of different combustor designs with respect to their pollutant emissions. However, the accuracy of the predictions of such computational models is still a matter of great concern. Therefore, at DFVLR, Porz-Wahn, combustor models are investigated, primarily with the aim to find out how well such calculations can predict the actual conditions in practical flames, and to compare the relative importance of various parameters used in the model. Presently, a combustor model using the well-stirredreactor (WSR) principle is investigated, which is based on a computer programme developped by Jones and Protheroe (9). A comparison is carried out between model calculations and measurements in a simple

one-dimensional post reaction zone of a flame in a homogeneous propane-air-mixture. In this way, the influence of reaction kinetics including the scattering of rate constant data, flame gas radiation and initial gas temperature on the NO-concentration in the model and the flame were compared.

For this purpose a burner was used, on which an atmospheric propane-air flame was stabilized by a perforated plate containing 200 regularly spaced holes of 2 mm dia. A homogeneous propane-air mixture, which can be heated up to 580 K is fed through the holes so that a large number of small flame cones are formed in the issuing combustible jets. Due to the high viscosity in the burning gas behind the flame front, any differences in gas composition, temperature and velocity are equalized very rapidly. Thus, a few millimeters downstream of the flame cone tips the flame resembles a quasi-onedimensional post-reaction zone, with an approximate diameter of 70 mm. In this zone, the concentrations of CO, CO, and NO were measured by gas sampling with a water-cooled probe. The measurements were carried out at different heights above the flame cone tips - that is the flame front - corresponding to different residence times. The gas velocity in the post-reaction zone was varied between 4 and 30 m/s. Gas analysis was done by conventional methods, using NDIR for CO, and CO, and chemiluminescence for

For the comparison of measured and calculated NO-concentrations the one-dimensional post-reaction zone, which resembles a plug-flow-reactor was modelled by a sequence of small WSR-elements. The residence time in each element had to be prescribed. Since presently the reaction kinetics of higher hydrocarbons with air are only poorly understood, a simplified reaction scheme was introduced into the WSR-programme. Following a proposal by Hammond and Mellor (6), for near-stoichiometric and fuel-lean mixture ratios the complicated hydrocarbon de-

composition is replaced by the following equation:

$$C_a H_b + \left[\frac{a}{2}(1+\alpha) + \frac{b}{4}\right] O_2 + a[(1-\alpha)CO] + \alpha CO_2] + \frac{b}{2} H_0 O_s.$$
 (R10)

This reaction which proceeds to the right-hand side infinitely fast, describes the well-established fact (for example (15)), that the first rapid step of the hydrocarbon oxidation generally yields large amounts of $\rm H_2O$ and $\rm CO$, whereas $\rm CO_2$ appears only in small quantities. The quantity

$$\alpha = \frac{{}^{n}_{cO_2}}{{}^{n}_{cO} + {}^{n}_{cO_2}} \tag{3}$$

can be chosen according to ratios of CO_2/CO experimentally observed at the end of the fuel decomposition zone. For fuelrich mixtures, the first step will probably have to be replaced by a reaction which produces CO and H_2 in stead of H_2O , as proposed by Edelmann (10). The second step of the reaction concerns the CO conversion according to:

$$CO + OH + CO_2 + H$$
 (R11)

completed by the well-known set of C-free radical reactions as well as the recombination reactions for all species involved. From the envisaged equations the following 9 reactions have been introduced in the WSR-model:

OH + OH	(R12),
STORY OF THE PARTY	(R13.),
	(R14),
	(R15),
	(R16),
	(R17),
	(R18),
PERSONAL PROPERTY AND ADDRESS OF THE PERSON.	(R19),
H ₂ O+ M	(R20).
	OH + OH H ₂ O+ H OH + O OH + H OH + OH H ₂ + M O ₂ + M OH + M H ₂ O+ M

Finally the extended Zeldovich-mechanism for NO formation was added:

$$N_2 + 0 \stackrel{?}{=} NO + N$$
 (R9),
 $N + 0_2 \stackrel{?}{=} NO + O$ (R21),
 $N + OH \stackrel{?}{=} NO + H$ (R22).

One disadvantage of the strong simplification of the hydrocarbon decomposition lies in the inability of the model to predict unburnt hydrocarbons. The simplification is clearly more of an advantage than the use of global reaction rate equations, like in ⁽¹¹⁾, or the assumption of equilibrium conditions, as in ⁽⁷⁾, because the actual radical levels are better approximated by the reaction scheme used.

The amount of prompt-NO in the hydrocarbon decomposition zone, was specified according to test results (3). Rate constants were taken from Baulch et al (12). For the CO consuming reaction (R11) the rate constants were adapted to the temperature range; that means, that the activation energy suddenly increases from a low to a higher value at about 1 500 K. The effectiveness of different collision partners in the recombination reactions was approximately allowed for according to results of Homer and Hurle (13). A rough estimation of the temperature loss due to radiation of the flame gases showed that the temperature drop per unit time changes only slightly during the first ten milliseconds of residence time, and hence, a constant value for this quantity was used in the comparison.

First checks aimed to save computer time showed that, for the experimental conditions used, it was sufficient to retain in the reaction scheme only the equations R10, R11, R13-R16, R20, R9, R21, R22. Furthermore, for the NO formation the approximation according to equation (1) was used. Further calculations revealed that, in order to describe a post-reaction zone of a premixed flame, with a total residence time of 10 milliseconds it is sufficient to use ten elemental reactors. Increasing this figure to 30 steps resulted in a negligible small change of the calculated concentrations (+ 2 %), a decrease to 5 steps yielded a decrease of approximately 10 to 12 %.

A comparison between the measured and

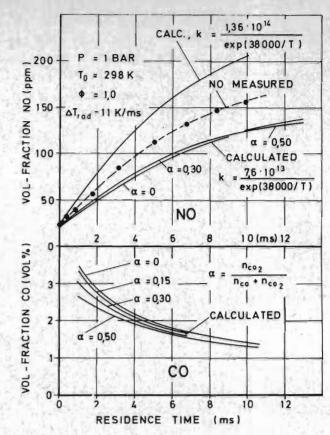


FIGURE 3. CALCULATED AND MEASURED NO- AND CO-DISTRIBUTION IN A POST-REAC-TION-ZONE.

the calculated NO distribution in the postreaction zone of a stoichiometric propaneair-flame shows the upper part of Fig. 3. For the calculation of NO according to equ.(1) two values for the rate constant were used; the upper curve corresponds to $k = 1.36 \cdot 10^{14} \exp (-38 \cdot 000/T) \text{ cm}^3/\text{mole·sec},$ recommended by Baulch (14) in 1969. The lower curves correspond to $k = 7,6 \cdot 10^{13}$ exp (- 38 000/T), a value recently recommended by Baulch et al (12). The calculated trend reproduces the actual behaviour of the NOformation quite good. However, there are larger differences between calculated and measured NO-values. Considering furthermore that the accuracy, by which rate constants are known presently, is at best a factor of 2, it follows that simplified combustor models would more or less be able to predict trends of emission levels only.

For the calculation of the lower curves the ratio a of CO2/CO + CO2 production in the hydrocarbon decomposition (R10) was varied between $\alpha = 0$ and $\alpha = 0.5$, which results in changes of the temperature and the radical level in the first part of the flame zone. No major net effect is observed on the NO-level, but if α exceeds 0.5, the calculated NO values decrease rapidly, as a consequence of a decreasing O-atom-concentration. The lower part of Fig. 3 shows that, for the same reasons, different values of a lead to different CO oxidation rates in the first part of the flame zone. A comparison with measured values for CO, presently suffers from measuring errors due to probe effects. Considering experimental results from low-pressure-flames (15), values for α in the order of 0.15 - 0.3 should be close to actual conditions.

It should be noted, that both CO- and NO-concentrations depend on the level of the radicals present in the flame. Due to the assumption of the decomposition reaction (R10), the WSR-model for the post-reaction zone starts with a zero initial radical concentration, whereas in practice at this stage high levels of radicals are found. A repetition of the stepwise calculation with very small WSR-elements corresponding to an elemental residence time of 10 µs showed that OH-, O-, and H-radicals are formed very quickly so that a partialequilibrium state of the three radical concentrations is reached after approx. 60 us. The concentration level of the radicals is well above the local equilibrium value; for example a peak O-concentration of 3 · 10 ppm is found for an initial temperature of 298 K. After attainment of the partial-equilibrium the radical concentrations begin to decrease according to the progress of all reactions. This behaviour shows that for residence times in the order of 1 ms for the elemental reactor the assumption of zero initial radical concentration does not present a deficiency.

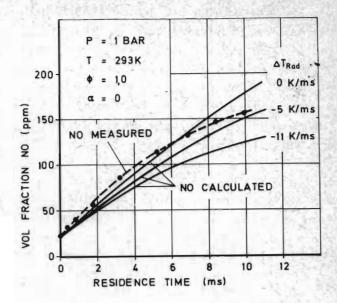


FIGURE 4. INFLUENCE OF TEMPERATURE DROP TO RADIATION ON NO-FORMATION.

The effect of a temperature drop due to flame radiation on NO formation is shown by Fig.4. The highest temperature drop $\Delta T = -11$ K/ms results from an estimation of the actual flame radiation. For lower temperature drops (-5 and 0 K/ms), the trend of the calculated curves deviates considerably from the measured trend. Thus, flame radiation must be accounted for in combustor models if the trends in pollutant fromation, in particular NO, are to be predicted correctly.

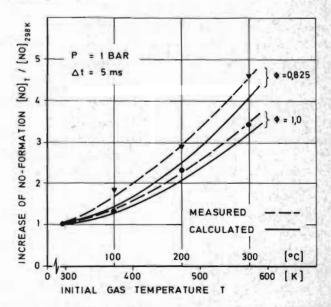


FIGURE 5. EFFECT OF INITIAL GAS TEMPERATURE ON NO-FORMATION.

Fig. 5 shows the influence of initial temperature on NO formation. In it the ratio of NO produced at initial temperature T to NO produced at a reference temperature of 298 K is plotted for a residence time of 5 milliseconds. For a stoichiometric mixture the coincidence between the measured and the calculated values is remarkably good. For a fuel-lean mixture, Ø = 0.825, the measured trend is again reproduced by the calculations; however, larger deviations from the actual NO-values are observed. If the model is applied to fuel-rich mixtures the trend of NO formation with temperature is also represented wrongly, which indicates that the first reaction step of the simplified reaction scheme (R10) is inadequate for this regime.

IV. Technical Feasibility of Some Combustor Modifications for Exhaust Emission Reduction

At MTU-Munich investigations have been carried out to test the technical feasibility of modifications on conventional combustors to achieve low exhaust emission rates while maintaining the initial performance requirements. It is well known that as a consequence of NO, CO and unburned hydrocarbon formation and consumption processes, combustor design changes which improve NO, emission generally worsen the other pollutant performance and vice versa. Therefore, the modifications which for low cost reasons had to be of simple design, were optimised in a manner to yield emission reduction of all of the pollutants over the whole range of engine operation.

The combustion chambers were installed in a automotive regenerative gas turbine and tested over the full range of operating conditions. Exhaust emission measurements were taken mainly at idle and full power conditions and only at some intermediate stages. Due to technical restraints the gas sampling probes could not be placed at the combustion chamber outlet but were in-

stalled in the gas generator exit and power turbine entry duct. The sampling probe design, the sampling procedure and the analytical system set up for the measurements were in agreement with SAE specifications. The pollutants measured were carbon monoxide oxides of nitrogen and unburned hydrocarbons (UHC). Sampling validity was checked by comparing combustion efficiency determined from thermocouple measurements and fuel air ratios determined from fuel and airflow measurements with combustion efficiency and fuel air ratio determined from gas sampling measurements.

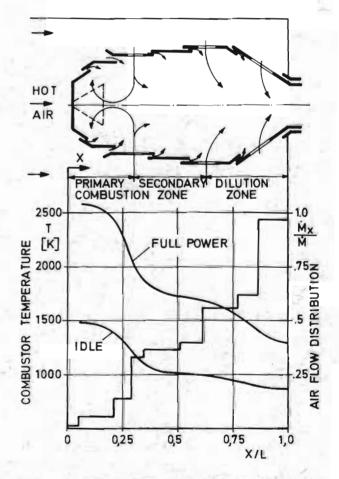


FIGURE 6. TEMPERATURE AND AIR FLOW-DISTRI-BUTION IN CONVENTIONAL COMBUSTOR TC 003.

Fig. 6 shows a scheme of the conventional combustion chamber (TC 003) initially designed according to engine operating requirements. The combustor uses a pressure atomizing fuel nozzle with only minor air assistance. The air flow entering the

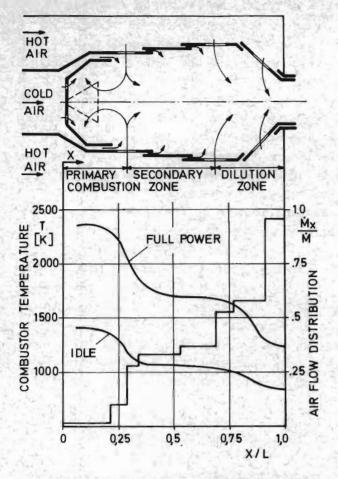


FIGURE 7. TEMPERATURE AND AIR FLOW DISTRI-BUTION IN MODIFIED COMBUSTOR TC 033.

combustor zones through the various openings of the liner and the total temperature distribution along the combustor length for idle and full power operating conditions are also shown on Fig. 6. The combustor was fed with hot air from the regenerator, the air entry temperature varying between 750 and 980 K. To obtain a wide combustor ignition and stability region the combustor had a relatively rich primary zone fuel air ratio.

The total temperature distribution for idle and full power condition shows that the temperature drops stepwise from the highest value which is reached in the primary combustion zone, along the secondary combustion zone and the dilution zone to the design value at the combustor exit. The maximum temperature in the primary com-

bustion zone is 2 580 K for full power and 1 500 K for idle condition.

Reaction kinetics analysis has shown that the formation of NO_X is favored by high temperature, long residence time and high pressure, the temperature having the strongest effect because it relates to NO_X formation exponentially. These conditions are the same which favor CO consumption. To obtain a true technological gain, an approach was chosen by which the temperature peaks in the primary combustion zone were reduced and the residence time in the secondary combustion zone lengthened.

To reduce the temperature peaks cold air was injected into the primary combustion zone. The amount of cold air which bypassed the rotating heat exchanger and was fed directly from the radial compressor into the combustor, did not exceed 7 % of total air flow rate in order to keep the total engine efficiency loss lesser than 3 %. Longer residence time was obtained by moving the second row of air injection holes farther downstream and by changing the mass flow distribution. The increase of residence time amounts to approximately 50 %.

Fig. 7 shows a scheme of the modified combustor (TC 033) with cold air injection into the combustion zone. By ducting the cold air along the combustor head better cooling of this 'ot part was obtained, and hence as an additional bonus, the combustor durability was increased. Although only one third of the cold air is entrained by the recirculating air vortices into the primary combustion zone the peak temperatures are markedly reduced. In comparison to the conventional combustor, Fig.6, the temperature peak in the primary combustion zone of the modified combustor, Fig. 7, decreased at full power condition by 250 K. The temperature reduction at idle condition is smaller because of the lower temperature differences between hot and cold air.

The comparison of air flow and total temperature distribution in Fig. 6 and Fig. 7 shows that the secondary combustion zone length was stretched while keeping the mean temperature constant. The temperature of the secondary combustion zone was kept constant at 1 700 K because at this temperature hydroxyl radicals are still present. These radicals strongly favor CO and unburned hydrocarbon oxydation processes. Since the peak temperature was reduced for the modified combustor the temperature gradients between the primary combustion zone and the secondary combustion zone became less steeper than those of the conventional combustor. As a result consumption of UHC was aided because the combustion products were not suddenly frozen.

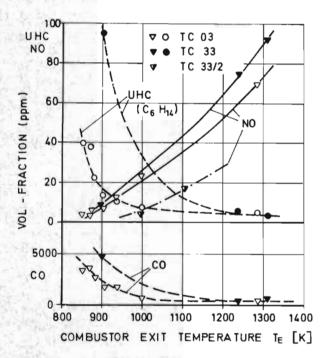


FIGURE 8. MEASUREMENTS OF CO, UHC AND NO BEHIND CONVENTIONAL AND MODIFIED COMBUSTOR.

In Fig.8 the nitrogen oxide and unburned hydrocarbon emission measurements of the conventional and modified combustor are plotted as a function of the combustor exit temperature i.e. the engine operation condition. The measurements show that the NO emission from the modified combustor was less than that of the conventional combustor. For full power condition

(T_E = 1 300 K) the reduction amounts to 23 %, whereas at idle condition the NO emission is, as expected, the same for both combustors. Improving the homogeneity of the primary combustion zone by a new cost saving method of fuel injection a more significant NO reduction was obtained. The corresponding measurements are shown in Fig.8 the reduction being represented by the point dotted line. The degree of reduction corresponds with what one would expect from combustor modeling assuming well stirred reactor conditions.

In Fig. 8 also the measured values of CO and UHC emissions (the latter measured as C6H11) are represented. It follows from the results that the consumption rate of the unburned hydrocarbons during idle operation is much larger for the modified combustor than for the conventional combustor. This result stresses the importance of the long hot secondary combustion zone in which only metal cooling air is provided. At full power conditions the same UHC emission rates where measured for both combustors due to the high temperature which greatly improves the consumption processes. The comparison of carbon monoxide exhaust emission measurements for both combustors at various operating conditions clearly demonstrates that the CO emission of the modified combustor during idle conditions is lower than that of the conventional combustor, the reason partly being the improved oxidation process in the secondary combustion zone.

V. General Conclusions

In the first section of the paper it was stated that in fuel-rich flames other mechanisms than the Zeldovich-mechanism for NO formation play without doubt an important role. For a complete and a priori prediction of NO concentrations more investigations have to be carried out which should concentrate in particular on hydrocarbon destruction to \mathbf{C}_2 and CH and on the rate constants according to the proposed sequence.

At present careful measurements of prompt NO under various pressures, temperatures and equivalent ratios will provide usable semiempirical data for theoretical prediction procedures of NO concentrations in gas turbines and other propulsion systems.

The comparison between pollutant levels predicted from combustor models and those from flame measurements showed clearly the deficiencies of the presently available hydrocarbon reaction schemes and kinetic data. The deviations due to the scatter of rate constant data are of similar order of magnitude as the influence of a heterogeneous fuel distribution as shown in [7] b Because of the demonstrated large influence of the actual reaction kinetics, any simpli- k fied reaction scheme has to be verified experimentally. It has also been shown that flame radiation cannot be neglected because of its pronounced effects on reactions which are strongly temperature-dependend. Suitable expressions for its introduction into combustor models have to be proven experimentally.

The analysis of the practical investigations described in the third section has shown that cold air injection into the combustion zone which is followed by an axially extending hot secondary combustion zone represents a technical feasible method for exhaus emission reduction from automotive regenerative combustion chambers. Employing a simple approach of fuel injection which greatly improves the homogeneity of the primary combustion zone NO emission values were reduced. It will be the aim of further investigations to determine if emission reductions which can be accomplished by making design modifications on conventional combustors do satisfy imposed emission regulations.

VI. Acknowledgements

The authors acknowledge the financial support of parts of the work by the Deutsche Forschungsgemeinschaft. The cooperation of Dr. H. Eberius, Dr. F. Suttrop and G. Meikis is greatly appreciated. Thanks are also due to MTU, Munich, for the permission to publish results of development work.

VII. List of Symbols

- a (-) number of C-atoms in hydrocarbon molecule,
 - (-) number of H-atoms in hydrocarbon molecule,
 - k cm3/mole·s rate constant
 - n; mole number of moles of component i,
 - R kJ/mole deg universal gas constant,
 - K gas temperature
 - T_E K combustor exit temperature
 - At sec time interval
 - [x] mole/mole mole fraction of species x
 - α (-) see equ.(3),
- Ø (-) fuel equivalence ratio.

- Bowman, C.T., Investigation of Nitric Oxide Formation Kinetics in Combustion Processes. The Hydrogen-Oxygen-Nitrogen-Reaction. Comb. Sci. Techn., 3, 1971, p.37.
- Fenimore, C.P., Formation of Nitric Oxide in Premixed Hydrocarbon Flames. 13th Symp.on Comb., 1971, p.373.
- Bachmaier, F., Eberius, K.H. and Just, Th, The Formation of Nitric Oxide and the Detection of HCN in Premixed Hydrocarbon-Air Flames at 1 Atmosphere. Comb.Sci., Techn., 7, 1973, p.77.
- 4. Eberius, K.H., to be published.
- 5. Eberius, K.H., Just, Th., NO Formation in Fuel-Rich Flames; A Study of the Influence of the Hydrocarbon Structure AGARD CP 125, 1973, paper 16.
- Hammond, D.C., Jr. and A.M. Mellor, Analytical Calculations For the Performance and Pollutant Fmissions of Gas Turbine Combustors. AIAA-Paper 71-711, 1971.
- Heywood, J.B. and T. Mikus, Parameters Controlling Nitric Oxide Emissions from Gas Turbine Combustors.
 AGARD CP 125, (1973), Paper 21, 1973.
- Mosier, Roberts, R. and Henderson, R.E.
 Development and Verification of an
 Analytical Model for Predicting Emissions from Gas Turbine Combustors During
 Low Power Operation.
 AGARD CP 125, 1973, paper 25.

- 9. Jones, A., Prothero, A. The Solution of the Steady-State Equations for an Adiabatic Stirred Reactor.
 Combustion and Flame, 12, 1968, p.457.
- 10. Edelman, R., Some Problems in Combustion Controlled by Coupled Mixing and Kinetics.

 Paper presented at ESCI-Meeting, Atlanta, 1970.
- Clarke, A.E., Odgers, J., Stringer F.W., and A.J. Harrison. Combustion Processes in a Spherical Combustor. 10th Symp.on Combustion, 1965, p.1151.
- 12. Baulch, D.L., Drysdale, D.D., Horne, D.G., and Lloyd, A.C. Evaluated Kinetic Data for High Temperature Reactions, Vol.2, Butterworths, London, 1973.
- 13. Homer, J.B. and Hurle, J.R., The Kinetics of the Dissociation of Water in Shock Waves. Paper presented at the Symp. on Gas Kinetics, Szeged, Hungary, July 1969.
- 14. Baulch, D.L., Drysdale, D.D., Horne, D.C. and Lloyd, A.C., Critical Evaluation of Rates Data for Homogeneous Gas Phase Reactions of Interest in High Temperature Systems., Part 4, Dept. of Chem., Univ. Leeds, 1969.
- 15. Porter, R.P., Clark, A.H., Kaskan, W.F. and Browne, W.E., A Study of Hydrocarbon Flames. 11th Symp.on Combustion, 1967, p.907.

DISCUSSION

- Y.M. Timnat (Dept. of Aeronautical Engineering, Technion I.I.T., Haifa, Israel):
- How are the kinetic results, obtained at low pressure (72 Torr) affected by pressures - which would be considerably higher in an aircraft combustor?
- 2. The injection of cold primary air into the combustion chamber presents difficulties for aircraft combustors since the air entering from the compressor is hot. How is this problem going to be met?
- G. Kappler, Th. Just and G. Winterfeld:
- 1. Kinetic measurements at low pressures were initiated in order to make the flame zone in which the hydrocarbons are decomposed sufficiently long for probe sampling technique. Once the reaction scheme for the formation of prompt NO is established, the kinetic results can be scaled to higher pressure by using the proper rate constants. The required kinetic data for scaling is still a matter of research. Qualitatively one expects that the NO formation in fuel rich zones at higher pressures will also be largely due to reacted HCN.
- 2. As pointed out in the paper, cold air injection was applied for an automotive regenerative gas turbine by using a bypass duct from the compressor directly to the combustion chamber head. Thereby air heating by the regenerator was omitted. For aircraft combustors the method of cold air injection is not applicable and can be used only in conjunction with bypass air heat exchangers for blade cooling as treated in some projects.