Oxides of Nitrogen in Combustion

Turbulent Diffusion Flame

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THE STUDY of combustion processes is usually complicated by the lack of steady conditions. In a turbulent diffusion flame the local situation is subject to wide fluctuations with time; therefore, any detailed analysis of the combustion process may fall short of explaining the behavior in terms of available molecular kinetic data and the normal principles of fluid mechanics. To avoid duplication, earlier work in the field of combustion is not reviewed here.

Many combustion processes involving air produce measurable amounts of the oxides of nitrogen (*13*), and these oxides are more likely to persist in the products of reaction under conditions of rapid cooling from high temperatures (*1*). In a turbulent flame, in which rapid cooling occurs, the local rates of cooling are thought to be a function of the level and scale of turbulence. In studying the nature of combustion processes, therefore, particularly the formation of the oxides of nitrogen, it appeared that level of turbulence would be a pertinent variable.

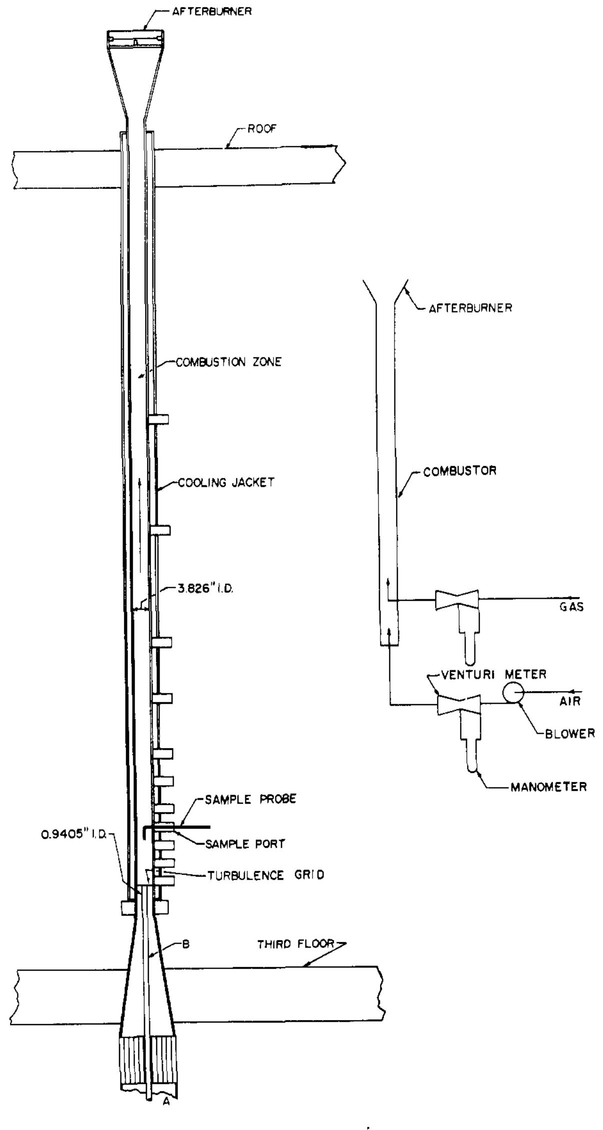


Figure 1. Combustion tube

The microscopic nature of combustion in turbulent flames is not well understood. The transport processes involved and the interrelation of the several fluxes present many theoretical difficulties. At the current state of knowledge of the nature of turbulence, it is extremely difficult to interrelate the local perturbations, molecular kinetics, and gross flow characteristics of the system with the composition of the products of reaction. Therefore the influence of mixture ratio and level of turbulence upon the macroscopic nature of the combustion process was studied. Particular emphasis was placed upon the formation of oxides of nitrogen, which is important in respect to air pollution.

EQUIPMENT AND METHODS

The combustion tube (Figure 1), used for earlier studies of combustion in turbulent diffusion flames (*4*), was mounted in a vertical position. Air was introduced at *A*, and natural gas was introduced through the coaxial tube, *B*. The combustion zone was 3.826 inches in inside diameter and approximately 162 inches long. A cooling jacket surrounded the tube, and sampling ports were located along its side. The gases were discharged through an afterburner on the roof of the laboratory.

A flow of air at the desired rate was initiated, after which a flow of natural gas was introduced and adjusted to the desired rate. Combustion was initiated by an electric spark located just above the turbulence grid. In the afterburner at the upper end of the combustion chamber, another nearly continuous electric spark ensured relatively complete combustion of the products of reaction.

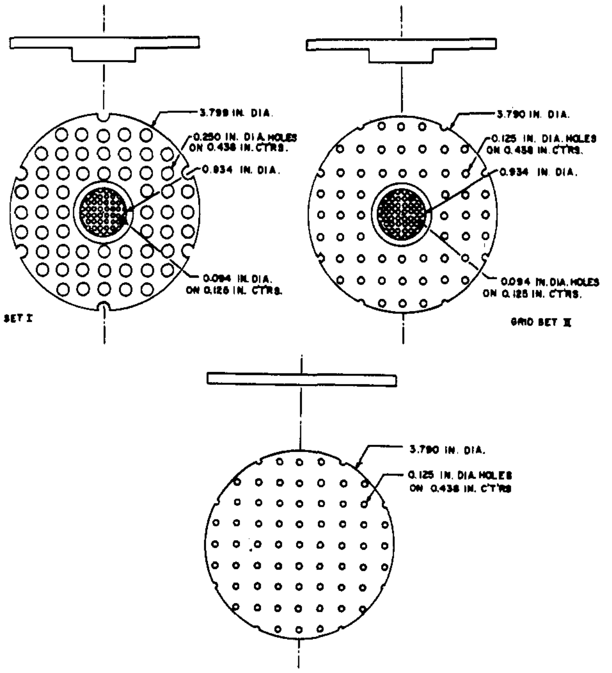


Figure 2. Grid sets

Studies were made at the level of turbulence realized in the free stream of air and natural gas, and at three levels of turbulence induced by the three sets of grids shown in Figure 2. The grids were located at the end of tube *B* and completely covered the cross section of the combustor. An effort was made to maintain the same velocity in the holes in the brass grid plates for both the gas and air streams.

The experimental work is described in terms of shear flow and of grid sets I, II, and III. The apparent level of turbulence which results from use of these grids is presented in Figure 3. This information, based on experimental work of Davis (*5*), can be used only as a frame of reference, because the size of the grids used for the present investigation differed greatly from those used by Davis. Recent experimental information (*6*) confirms the fact that such induced turbulence is far from homogeneous. In the wake of the grids significant variations exist in the macroscopic velocity from point to point across the channel at small downstream distances (*6*). At a distance downstream equal to eight times the size of the hole spacings in the grid, however, no significant variation in point velocity attributable to the individual openings in the grid remains.

The composition of the natural gas is set forth in Table I. Fourteen typical specific weight measurements, made gravimetrically or with an Edwards gas density balance, varied from 0.04401 to 0.04543. The variation was small enough to make it possible to use the composition of gas given in Table I for the entire series of measurements.

The rate of flow of natural gas was determined, for the early part of the work, by an orifice meter, and for the later part, by a Venturi meter. Differential pressure was measured with a kerosine-in-glass manometer, and differences in elevation were determined by means of a cathetometer. The pressure of the natural gas in the main transmission lines was so steady that it was not necessary to introduce automatic equipment to control the rate of flow. Variations in flow rate of more than 1% were infrequent. It is believed that the calibration of the Venturi meter as a function of Reynolds number was known within 0.5%.

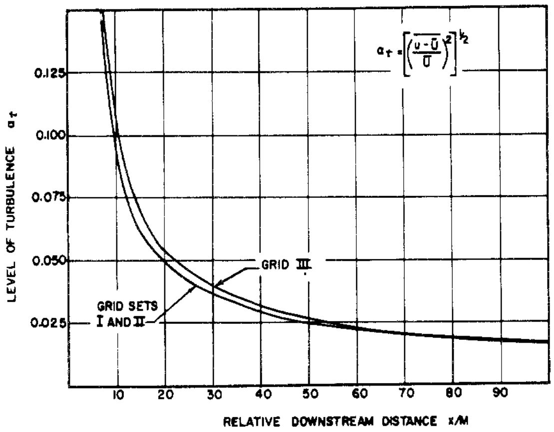


Figure 3. Level of turbulence as a function of downstream distance

Based on data of Davis (5)

Table I. Composition of Natural Gas

Component	Mole Fraction Component
Methane	0.880
Ethane	0.064
Propane	0.028
n-Butane	0.006
Isobutane	0.004
n-Pentane	0.001
Isopentane	0.001
Hexane	0.001
Carbon dioxide	0
Nitrogen	0.015
Oxygen	0
Water	0

Air Supply. The equipment for the supply of air (*7*) consisted, in essence, of two blowers driven by a direct current motor. The speed of the motor was controlled by a quartz oscillator and a predetermined counter (*9*). The humidity of the air was measured, and the air flow rate was determined by a Venturi meter, the calibration of which had been established within 0.5% over the range of Reynolds numbers covered in this investigation. The speed control was sufficiently accurate to prevent detectable variation in the flow of air during a set of measurements. It is believed that the weight rate of flow was known within 0.8% for all the conditions covered in this investigation.

Auxiliary Equipment. In determining apparent temperatures, a probe thermocouple was employed (*4*). A platinum, platinum-10% rhodium thermocouple 0.003 inch in diameter was placed along the axis of a shield of aluminum oxide 0.188 inch in diameter and approximately 1 inch long. The shroud was held in place by a cooled support, and the leads from the thermocouple were brought out through a cooled copper fitting. The shrouded thermocouple was not employed at apparent temperatures in excess of 2000° F. because of rapid deterioration.

Available information (*12*) upon the electromotive force of a platinum, platinum-10% rhodium thermocouple was employed in determining the apparent temperatures. At many points in the turbulent diffusion flame the temperature varied significantly with time as a result of the instability of the combustion process. The frequencies of such instabilities were of the order of 1 or 2 cycles per second.

After steady state was approached, samples of the products of combustion were withdrawn from the combustor through a sample tube introduced through one of the ports shown in Figure 1. Glass bulbs were provided for receipt of the samples, and a high vacuum system, including a mercury diffusion pump and mechanical pump, was used to evacuate the sample bulbs and the tube connecting the sample bulb with the combustion chamber. During actual sampling of the gas stream, the gas was allowed to flow slowly through the sample tube into the sample bulb. The bulb was filled in about 2 minutes.

It was not necessary to water-cool the sample tube inside the combustion zone. The sample tube was heated outside the combustion zone by the circulation of warm air and maintained at approximately 200° F., to avoid condensation of water and absorption of oxides of nitrogen in the tube before they reached the sample bulb. One of the reactants used in the analytical procedure (*2*, *3*) was present in the sample bulb, so that the oxides of nitrogen were rapidly absorbed after entering the bulb.

Samples were taken at various longitudinal positions, at the center line, and at several radial positions. All longitudinal positions are reported in terms of distance from the exit of the coaxial gas tube (*B*, Figure 1). The radial positions are reported in terms of distance from the center line.

Analytical Methods. The oxides of nitrogen and carbon dioxide, carbon monoxide, and oxygen were determined. The values reported are based upon the assumption of a perfect gas and ideal solution for the products of reaction at atmospheric pressure. Carbon dioxide, carbon monoxide, and oxygen were determined by conventional Orsat methods, and it appears that the mole fraction of these products was established within 0.003. From time to time duplicate analyses were made; it is believed that the standard deviation of the mole fraction of the principal components was not greater than 0.002.

Oxides of nitrogen were determined by a phenoldisulfonic acid method (*2, 3*). The mole fraction of oxides of nitrogen is reported in nitrogen dioxide equivalent. The quantity of oxides of nitrogen in the sample withdrawn would be expected to differ somewhat from that in the flame, because the rate of approach to equilibrium of the reactions associated with the formation and decomposition of the oxides of nitrogen is significant at flame temperatures and the equilibrium shifts markedly with temperature. However, near the exit of the combustor, the temperatures of the reaction products are lower and the composition of samples from this point should nearly reflect that of the reaction products. In the present investigation the sample was not cooled as rapidly as desirable during its passage from the portion of the sample tube in the combustor to the portion which was maintained at approximately 200° F. by the circulation of warm air. However, at the higher temperatures, rates of cooling were of the order of 100° per millisecond. Furthermore, the quantities of the oxides of nitrogen in the flame are small and far from equilibrium, and the reaction rates are apparently much slower than those in a system made up of nitrogen and oxygen in equal atomic proportions. Experiments with a ballistic piston apparatus (*8*) confirm the marked influence of diluents on reaction rates. For these reasons, it is believed that the results obtained are indicative of the conditions existing in the combustor, although the reported quantities of the oxides of nitrogen are undoubtedly smaller than actually exist in the reaction zone.

Some uncertainties exist in the absolute value of the mole fraction of the oxides of nitrogen, but agreement with premixed samples indicates that the standard deviation in the evaluation of the mole fraction of nitrogen dioxide equivalent in the gas samples was not more than 5×10^{-6}. Additional uncertainty as a result of the nature of the sampling of the combustion process increased the standard deviation of the data for duplicate samples to 6×10^{-6} mole fraction.

The data upon the principal components are reported to 0.0001 mole fraction and upon the mole fraction of oxides of nitrogen to 1×10^{-6}. The number of significant figures recorded is greater than justified by the accuracy of the experimental data. Nevertheless, they are included so that local variations in behavior may be recognized, even though the differences are smaller than the absolute uncertainty of measurement.

EXPERIMENTAL RESULTS

The experimental conditions for the investigation in a turbulent diffusion flame are recorded in Table II.

The apparent temperatures, measured with the probe thermocouple described, are available in tabular form (*10*). Typical experimental data are illustrated in Figures 4 and 5. Figure 4 indicates a rapid rise in apparent temperature in the mixing zone, followed by a gradual decrease in temperature as the energy distribution becomes more uniform in the stream and as thermal transfer to the water-cooled copper walls of the combustor takes place. The radically different behavior at 17% stoichiometric apparently results from the much lower flame temperature and smaller combustion zone.

It was not feasible to extend temperature measurements above 2000° F. because of rapid deterioration of the thermocouple. This limit in maximum temperature accounts for the absence of apparent temperature data for mixture ratios near stoichiometric. The temperature data are termed apparent temperatures, because it is doubtful that the shrouded thermocouple used in these measurements was a proper instrument for obtaining actual temperatures. The platinum and the platinum-rhodium, as well as the aluminum oxide of the shroud, may have had a significant catalytic influence on the temperature measured by the

Table II. Experimental Conditions

	Air		Gas				Unreacted Composition, Mole Fraction				
Test No.	Entrance velocity[b], ft./sec.	Weight rate of flow lb./sec.	Entrance velocity[b], ft./sec.	Weight rate of flow, lb./sec.	Mixture Ratio[a], % Stoichiometric	Weight Fraction Water in Air Stream	Methane	Ethane	Heavier	Oxygen	Nitrogen
					Shear Flow						
1	7.73	0.04305	0.122	0.4329×10^{-3}	16.6	0.0113	0.0136	0.0010	0.0063	0.2066	0.7782
2	7.99	0.04483	0.610	2.227	82.0	0.0102	0.0635	0.0046	0.0030	0.1947	0.7340
3	7.79	0.04289	1.024	3.627	138.6	0.0134	0.1029	0.0075	0.0048	0.1854	0.6992
4	21.20	0.1185	0.321	1.185	16.5	0.0107	0.0136	0.0010	0.0063	0.2067	0.7783
5	21.20	0.1167	1.690	5.874	83.0	0.0077	0.0643	0.0047	0.0030	0.1946	0.7336
6	21.25	0.1174	2.712	9.631	135.0	0.0058	0.1015	0.0074	0.0047	0.1857	0.6990
	21.15	0.1181	2.779	9.968	139.4	0.0092	0.1027	0.0075	0.0048	0.1854	0.6979
					Grid Set I						
8	7.49	0.04281	0.117	0.4341×10^{-3}	16.5	0.0052	0.0137	0.0010	0.0006	0.2066	0.7782
9	7.66	0.04362	0.613	2.264	85.7	0.0068	0.0661	0.0048	0.0031	0.1941	0.7321
10	20.85	0.1197	0.3215	1.180	16.0	0.0062	0.0134	0.0010	0.0006	0.2067	0.7784
11	21.47	0.1172	1.7134	6.015	85.5	0.0098	0.0654	0.0048	0.0030	0.1943	0.7325
					Grid Set II						
12	7.87	0.04291	0.3669	1.268×10^{-3}	50.1	0.0111	0.0389	0.0028	0.0018	0.2006	0.7557
13	7.94	0.04307	0.6268	2.206	84.6	0.0092	0.0653	0.0047	0.0030	0.1943	0.7327
14	7.97	0.04334	0.7309	2.541	96.8	0.0057	0.0741	0.0054	0.0035	0.1922	0.7249
15	12.95	0.06706	0.9704	3.496	86.0	0.0060	0.0664	0.0048	0.0031	0.1941	0.7316
					Grid III						
16	7.88	0.04298	0.6283	2.181×10^{-3}	84.4	0.0086	0.0647	0.0048	0.0030	0.1945	0.7334
17	7.85	0.04321	0.723	2.586	99.6	0.0119	0.0753	0.0055	0.0035	0.1919	0.7238
18	7.85	0.04303	1.0529	3.667	141.0	0.0124	0.1036	0.0075	0.0048	0.1852	0.6987
19	12.68	0.06725	0.9872	3.442	85.3	0.0111	0.0653	0.0047	0.0030	0.1943	0.7327
20	12.58	0.06748	1.5480	5.530	135.3	0.0068	0.1000	0.0073	0.0047	0.1860	0.7019
21	12.15	0.06542	1.6020	5.773	145.7	0.0026	0.1068	0.0078	0.0050	0.1844	0.6960

[a] Mixture ratio expressed as per cent combustibles relative to stoichiometric quantity required.
[b] Av. velocity of fluid stream in combustion tube approaching combustion zone.

thermocouple. The flow pattern and the local course of the combustion process were undoubtedly changed by the presence of the shroud and thermocouple. Furthermore, in a turbulent diffusion flame the local fluctuations in temperature are significant, and it is difficult to ascribe a value to the temperature at a given point. The bias in the apparent temperature may well vary from a few degrees below 1000° F. to at least 100° in the major combustion zone with temperatures of the order of 2000° F.

Composition of Products. The mole fractions of carbon dioxide, oxygen, and carbon monoxide, determined along the center line for many of the experimental conditions described in Table II, are recorded in Table III on a dry basis.

The mole fractions of carbon monoxide and carbon dioxide in the product are shown in Figure 6 as a function of longitudinal position for several conditions of flow. The exit quantities of carbon monoxide decrease with a decrease in mixture ratio. The decrease in carbon monoxide with longitudinal position probably results from radial diffusion and associated reaction with oxygen to yield carbon dioxide.

It is evident from the data shown in Figure 6 for grid III and shear flow at a mixture ratio of 140% stoichiometric that the turbulence grid significantly increases the quantity of carbon monoxide and carbon dioxide at the center line, probably because the rate of reaction in the combustion zone is higher with the grid than with shear flow. The shorter primary reaction zone with the turbulence grid is clearly shown in Figure 4 for the same conditions. The difference in behavior between grid III and shear flow for 140% stoichiometric is not pronounced at the exit.

The mole fractions of carbon dioxide, oxygen, carbon monoxide, and inert gases at the center line are shown in Figure 7 as a function of longitudinal position. The conditions of flow are the same as those used in portraying apparent temperatures in Figure 5. The radial distribution of the major products of reaction was not measured in this investigation. Such data for the same combustor, however, are available (*4*). In the present study, the combustor

Table III. Composition of Products in Combustion Zone at Center Line

Sample No.	Longitudinal Position[a], In.	Composition, Mole Fraction			
		CO_2	O_2	CO	Inert[b]
		SHEAR FLOW			
		Test 1			
748-3	8	0.0392	0.0035	0.0350	0.9223
748-12	22	0.0633	0.0551	0.0251	0.8565
755-2	52	0.0287	0.1603	0	0.8110
755-8	76	0.0198	0.1828	0	0.7974
755-10	100	0.0184	0.1745	0	0.8071
		Test 3			
875-3	8	0.0084	0.0708	0.0047	0.9161
875-11	22	0.0203	0.0569	0.0222	0.9006
883-1	52	0.0523	0.0202	0.0544	0.8731
883-9	76	0.0653	0.0223	0.0497	0.8627
883-10	100	0.0711	0.0217	0.0490	0.8582
		Test 4			
425-4	12	0.0433	0.1196	0.0113	0.8258
440-5	40	0.0282	0.1248	0.0152	0.8318
		Test 5			
694-2	8	0.0032	0.1794	0.0028	0.8146
737-8	8	0.0148	0.0961	0.0070	0.8621
737-2	28	0.0376	0.0808	0.0222	0.8594
730-8	76	0.0589	0.0613	0.0139	0.8659
730-1	100	0.0638	0.0602	0.0123	0.8637
		Test 6			
97-2	8	0.0174	0.0577	0.0074	0.9175
		Test 7			
97-14	22	0.0197	0.1002	0.0152	0.8649
105-4	52	0.0523	0.0624	0.0267	0.8586
105-11	76	0.0601	0.0412	0.0354	0.8633
105-15	100	0.0669	0.0348	0.0299	0.8684
		GRID SET I			
		Test 8			
489-10	12	0.0306	0.1367	0.0112	0.8215
489-18	40	0.0117	0.2091	0	0.7792
489-2	100	0.0210	0.1706	0	0.8084
		Test 9			
470-3	8	0.0298	0.0486	0.0298	0.8918
482-1	40	0.0650	0.0215	0.0447	0.8688
464-3	100	0.0872	0.0499	0.0184	0.8445
		Test 10			
541-22	8	0.0264	0.1446	0.0083	0.8207
		Test 11			
716-9	22	0.0548	0.0643	0.0179	0.8630
723-4	52	0.0722	0.0515	0.0087	0.8676
723-10	76	0.0769	0.0432	0.0168	0.8631
723-13	100	0.0845	0.0342	0.0059	0.8754
		GRID SET II			
		Test 13			
560-3	8	0.0593	0.0527	0.0278	0.8602
566-2	52	0.0539	0.0982	0.0083	0.8396
		Test 14			
571-16	22	0.0662	0.0424	0.0397	0.8507
571-9	52	0.0772	0.0430	0.0246	0.8552
571-6	76	0.0867	0.0336	0.0174	0.8623
571-5	100	0.0889	0.0282	0.0163	0.8666
		Test 15			
137-8	8	0.0327	0.1203	0.0127	0.8343
137-4	22	0.0674	0.0641	0.0166	0.8519
129-12	52	0.0780	0.0449	0.0194	0.8577
129-10	76	0.0815	0.0187	0.0032	0.8966
129-1	100	0.0105	0.0834	0.0176	0.8885
		GRID III			
		Test 16			
810-6	8	0.0542	0.0024	0.0634	0.8800
810-2	22	0.0510	0.0277	0.0659	0.8554
802-13	52	0.0821	0.0212	0.0195	0.8772
802-11	76	0.0234	0.1561	0.0047	0.8158
802-1	100	0.1023	0.0090	0.0085	0.8802
		Test 17			
850-9	8	0.0066	0.1077	0.0206	0.8651
850-2	28	0.0638	0.0057	0.0628	0.8677
842-2	100	0.1043	0.0030	0.0169	0.8758
		Test 18			
786-3	8	0.0299	0.0975	0.0130	0.8596
794-1	22	0.0542	0.0173	0.0692	0.8593
794-7	52	0.0547	0.0106	0.0749	0.8598
794-14	76	0.0703	0.0033	0.0639	0.8625
794-16	100	0.0752	0	0.0589	0.8659
		Test 20			
121-1	76	0.0961	0.0370	0.0432	0.8237
121-4	100	0.0854	0.0043	0.0452	0.8651
		Test 21			
113-11	22	0.0659	0.0268	0.0462	0.8611
113-16	52	0.0813	0.0026	0.0494	0.8667

[a] Longitudinal position measured from point of mixing.

[b] Predominantly nitrogen and small quantities of hydrocarbons.

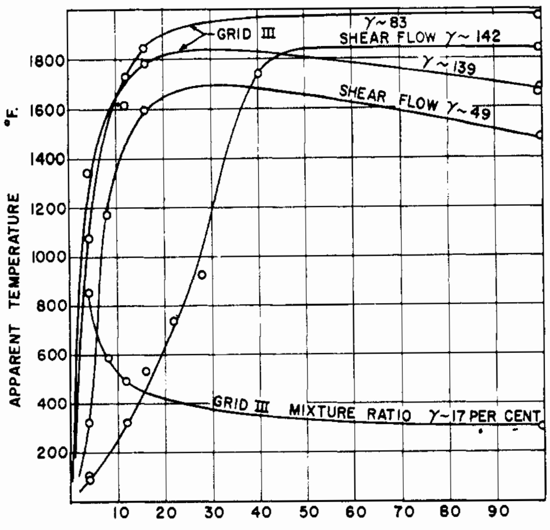


Figure 4. Apparent temperatures at center line for several conditions

Entrance velocity 8 feet per second

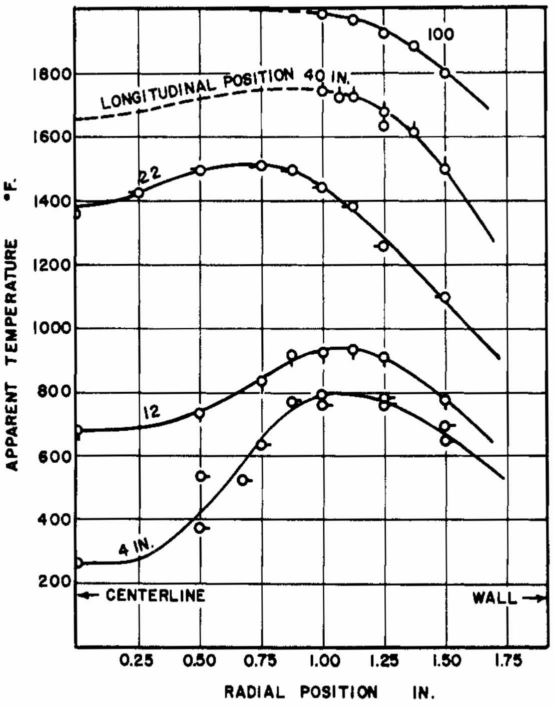


Figure 5. Radial variation in temperature at several longitudinal positions for shear flow

Entrance velocity 21 feet per second; mixture ratio 83.5% stoichiometric

was mounted in a vertical position to eliminate a lack of radial symmetry encountered in the earlier study (*4*).

The variations in the mole fractions of carbon dioxide, oxygen, and carbon monoxide follow earlier trends (*4*). The marked variation in oxygen content at longitudinal positions smaller than 10 inches is typical of turbulent diffusion flames. There exists a significant instability which results in large variations in the composition of samples withdrawn at different times. These relatively long-term variations are probably associated with minor changes in flow rate and other variables which affect the character of the turbulent diffusion flame near the point of mixing.

Attempts to use the data as presented to make a carbon balance between the reactants and products yielded an average discrepancy of 7% of the carbon present. However, this is not considered to be excessive since samples were obtained only along the center line, and previous investigations (*4*) indicated that significant radial variations in composition exist. At mixture ratios equal to or greater than stoichiometric, the analyses of samples taken near the exit of the combustor show that an appreciable fraction of the natural gas was not reacted. No attempt was made to measure the quantities of unoxidized reactants.

Oxides of Nitrogen. For all the experimental conditions recorded in Table II, the oxides of nitrogen were measured as a function of longitudinal and redial position. The experimental measurements for shear flow and for the three grids are available in tabular form (*10*). The standard deviation of all the duplicate samples taken at substantially the same time was 5.6×10^{-6} mole fraction. For samples

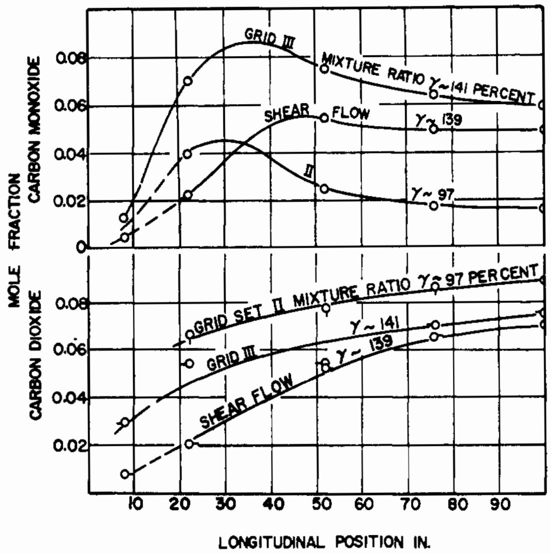


Figure 6. Mole fractions of carbon monoxide and carbon dioxide at center line

Entrance velocity 8 feet per second

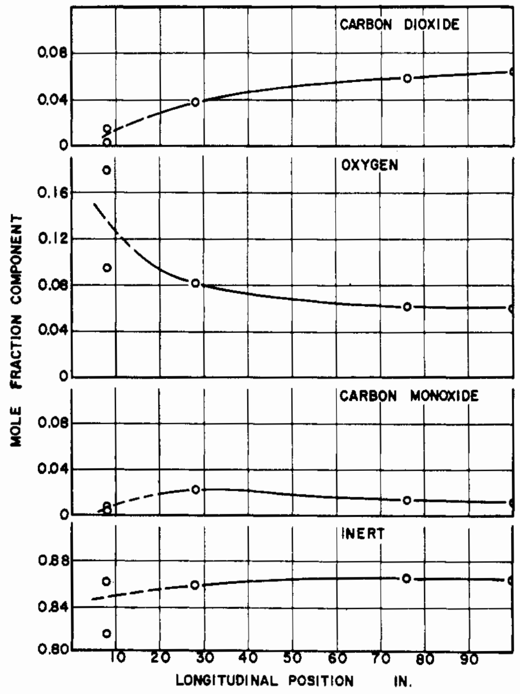


Figure 7. Mole fraction of carbon dioxide, oxygen, carbon monoxide, and inert gases at center line for shear flow

Entrance velocity 21 feet per second; mixture rotio 83% stoichiometric

Table IV. Smooth Values of Oxides of Nitrogen at Center Line

Longitudinal Position, In.	Per Cent Stoichiometric Mixture Ratio				
	17	82	138	16	86
	Shear Flow			Grid Set I	
	Entrance Velocity 8 Feet per Second				
10	35×10^{-6}[a]	0	3×10^{-6}	41×10^{-6}	18×10^{-6}
20	41	6×10^{-6}	6	41	32
30	39	12	10	34	38
40	26	18	12	23	42
50	18	23	14	17	45
60	15	28	15	16	46
80	12	34	16	15	48
100	11	36	16	15	49
σ[b]	4	2	2	3	4
	Entrance Velocity 21 Feet per Second				
10	8×10^{-6}	7×10^{-6}	4×10^{-6}	8×10^{-6}	12×10^{-6}
20	23	18	8	13	27
30	35	26	13	14	48
40	34	31	18	11	61
50	25	34	23	6	66
60	18	35	27	5	68
80	14	37	31	4	69
100	12	37	32	3	70
σ	2	4	2	2	4

	Per Cent Stoichiometric Mixture Ratio					
	50	85	97	85	100	141
	Grid Set II			Grid III		
	Entrance Velocity 8 Feet per Second					
10	30×10^{-6}	41×10^{-6}	24×10^{-6}	4×10^{-6}	6×10^{-6}	9×10^{-6}
20	37	60	36	10	13	21
30	33	63	41	19	20	17
40	30	57	43	31	24	4
50	29	48	43	42	27	2
60	29	47	43	53	29	1
80	29	46	43	71	31	1
100	29	46	43	80	32	1
σ	7	2	2	15	10	2
	Entrance Velocity 12.9 Feet per Second			Entrance Velocity 12.7 Feet per Second		
10	...	21×10^{-6}	...	20×10^{-6}	...	15×10^{-6}
20	...	39	...	36	...	26
30	...	43	...	47	...	28
40	...	38	...	53	...	24
50	...	32	...	57	...	19
60	...	31	...	60	...	16[c]
80	...	30	...	65	...	12[c]
100	...	30	...	68	...	12[c]
σ	...	3	...	10	...	10

[a] Nitrogen oxides reported in mole fraction of nitrogen dioxide equivalent.

[b] Standard error of estimate defined by $\sigma = [\sum_{1}^{N} \{ (\mathbf{n}_{NO_2})_m - (\overline{\mathbf{n}_{NO}})_e \}^2/N]^{1/2}$ [c] Extrapolated and thus subject to greater uncertainty.

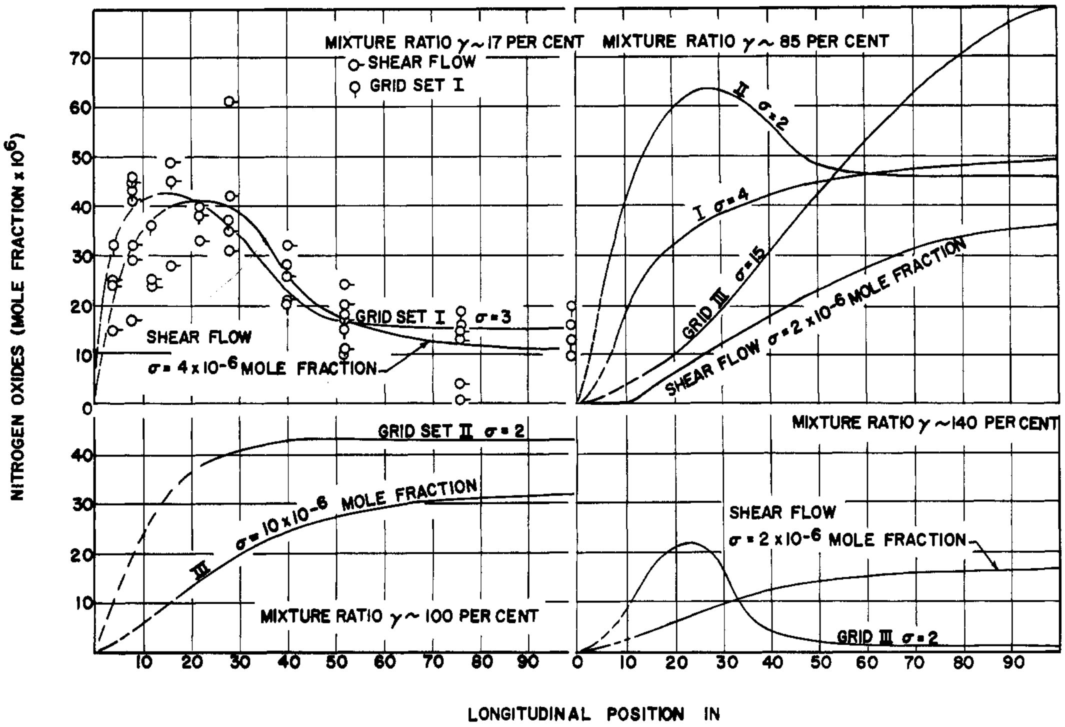
taken from the same position for the same entrance conditions at different times, however, the standard deviation was 11.6×10^{-6} mole fraction. This indicates the lack of reproducibility in the combustion conditions and illustrates the limitation in the detailed analysis of the results. Minor changes in the composition of the natural gas, the humidity of the incoming air, the surface temperature of the combustor, and possibly in the mixture ratio, materially influence the nature of the local perturbations in the turbulent mixing zone. Such variations in local conditions influence the residual quantities of the oxides of nitrogen to an extent sufficient to cause the above-mentioned increase in standard deviation. The behavior is similar in the regions of oscillatory combustion with premixed flames *(11)*. The standard deviation was calculated as the root-mean-square of the deviation of replicates from the average of the replicates at that condition of combustion and location.

Data on oxides of nitrogen at the center line were smoothed with respect to longitudinal position for shear flow and for each grid. Smoothing with respect to mixture ratio did not appear necessary, because the variations with mixture ratio were fairly regular. Also, only a few different compositions were investigated. The smoothed data, given in Table IV, are relatively orderly, although the effect of flow conditions is pronounced. Table IV includes the standard error of estimate of the experimental data, assuming all the uncertainty to lie in the mole fraction of oxides of nitrogen. The standard error of estimate is not considered excessive, in view of the fact that the standard deviation of replicates in the analytical procedure was of the order of 6×10^{-6} mole fraction. In arriving at the standard error of estimate, the arithmetic average of all data obtained at a single point in the combustor for a given set of conditions was employed.

The influence of flow conditions upon the quantity of the oxides of nitrogen at the center line is illustrated in Figure 8 for an entrance velocity of 8 feet per second. For a mixture ratio of 17% stoichiometric, a rather regular and stable variation in the mole fraction of nitrogen oxides occurs with longitudinal position. With this lean mixture ratio most of the oxides of nitrogen are formed near the

Figure 8. Oxides of nitrogen at center line

Entrance velocity 8 feet per second →



lower part of the tube, and the mole fraction of nitrogen oxides rapidly decreases at the center line as radial diffusion or secondary chemical reactions proceed. Little difference exists between the behavior with shear flow and grid set I. Furthermore, the standard error of estimate of the experimental data from the smooth curves shown is within the uncertainty of analytical measurement. This indicates that combustion is stable and that little random variation with time occurs. Experimental points are included in the illustration for a 17% stoichiometric mixture ratio to show the type of agreement encountered but are omitted in the rest of the figure.

At a mixture ratio of approximately 85% stoichiometric, a much more complicated situation exists. Shear flow yields relatively stable combustion, as indicated by a small standard error of estimate of 2 × 10^{-6} mole fraction oxides of nitrogen. The oxides of nitrogen continue to increase with longitudinal position as a result of the much larger region of active combustion. The quantity of oxides of nitrogen in the exhaust is about 36 × 10^{-6} mole fraction. Grid set I yields behavior similar to that with shear flow. However, combustion takes place somewhat more rapidly, and most of the oxides of nitrogen appear to be formed 60 inches from the point of mixing. In the case of grid set II, combustion is unusually rapid, and some diffusion is evident between 28 and 60 inches downstream from the point of mixing. Little difference exists in the oxides of nitrogen for grid sets I and II after mixing is realized. In the case of III a surprisingly large and continued increase in the oxides of nitrogen is indicated. The reasons for the pronounced difference between the behavior with III and grid sets I and II are not entirely clear.

Under stoichiometric conditions, the situation is relatively simple. With grid set II the nitrogen oxides increase regularly to a maximum of approximately 43 × 10^{-6} mole fraction at the exit of the tube. The rate of reaction with grid III again is relatively slow, as for III with an 85% stoichiometric mixture ratio. Oxides of nitrogen, however, do not reach a quantity much in excess of 30 × 10^{-6} mole fraction at the exit.

The standard error of estimate of the experimental measurements from the smooth curves for stoichiometric conditions is small in the case of grid set II and not excessive for III. It is probable that with grid III the much larger mole fractions of carbon monoxide and smaller mole fractions of oxygen inhibit considerably the formation of the oxides of nitrogen. Why the effect is not as pronounced in the case of grid set II is not entirely clear. These trends illustrate the complexity of the kinetics of the carbon-nitrogen-oxygen-hydrogen system under the conditions of combustion encountered in a turbulent diffusion flame.

At 140% stoichiometric under conditions of shear flow the oxides of nitrogen increase gradually to a maximum of about 15 ×10^{-6} mole fraction at the exit of the combustor. With grid III they reach 22 × 10^{-6} mole fraction 22 inches from the point of mixing and then decrease rapidly to 2 or 3 × 10^{-6} mole fraction. The combined effect of carbon monoxide in inhibiting the formation of the oxides of nitrogen and the nearly complete absence of oxygen in accelerating their decomposition is evident near the end of the combustor.

Mixture ratio exerts a pronounced influence upon the formation of the oxides of nitrogen, and a mixture ratio between 80 and 100% corresponds approximately to the maximum quantity of the oxides of nitrogen in the products of reaction. Perturbation, maximum temperature, approach to equilibrium, and inhibiting effects of carbon monoxide all appear to be important in establishing the formation of the oxides of nitrogen.

ACKNOWLEDGMENT

The experimental work described was made possible through the Air Pollution Control District of Los Angeles County, California. The interest and assistance of H.H. Reamer in connection with the experimental program were most helpful. Joan McFarland assisted in the reduction of the experimental data. Ann Taylor contributed to preparation of the manuscript.

NOMENCLATURE

M = size of grid mesh, inches
N = number of experimental points
n_{NO_2} = mole fraction nitrogen oxides
$\overline{U}$ = mean velocity, feet/second
u = instantaneous velocity in the longitudinal direction, feet/second
x = distance from turbulence grid, inches

a_t = apparent turbulence level (fractional)
γ = mixture ratio, expressed as per cent combustibles relative to stoichiometric quantity required
σ = standard error of estimate

Subscripts

e = experimental value
m = smoothed value

Superscript

$\bar{\ }$ = time average

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RECEIVED for review February 19, 1960. Accepted November 21, 1960. Material supplementary to this article has been deposited as Document No. 6661 with the ADI Auxiliary Publications Project, Photoduplication Service, Libary of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $3.75 for photoprints or $2.00 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to Chief, Photoduplication Service, Library of Congress.

Thermal Decomposition and Partial Oxidation of Ammonia

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THE PRESENT STUDY was stimulated in part by reports in the Russian literature (*2, 4, 9, 12*) of the synthesis of ammonia at high pressures and temperatures in a ballistic piston apparatus. It appeared that some low-entropy hydrogen-nitrogen compounds, such as hydrazine (*1, 3*), might be obtained as secondary products from the synthesis of ammonia. It was desired also to study the thermal decomposition and partial oxidation of ammonia as a possible approach to the formation of such products. The present investigation was carried out in a ballistic piston apparatus (*5, 6*) at maximum apparent pressures as high as 97,000 p.s.i.a. and maximum apparent temperatures up to 15,000° R.

EXPERIMENTAL APPROACH

The ballistic piston apparatus has been described in detail (*5, 6*). A cylinder, 3 inches in inside diameter and 11 feet long, surrounds a free piston. A space below the piston confines the sample, and a space above it contains the driving air. When a shear pin which restrains the piston is broken, the downward motion of the piston rapidly compresses the sample. The position of the piston as a function of time is measured with electrical contacts, four of which are located along the wall of the cylinder and four in the bottom face of the cylinder. After the sample reaches a minimum volume, the piston is accelerated upward, and the sample rapidly expands. The entire apparatus is constructed of low-carbon steel.

The sample was prepared by introducing the necessary amount of each component to the space below the piston. The initial composition was computed from temperature and pressure measurements obtained during the introduction. After compression and expansion, a sample of the product was withdrawn and its composition determined by mass spectrographic analysis. Samples were introduced and withdrawn using conventional high vacuum techniques. In the course of each test, the driving gas pressure, the sample pressure, and the position of the piston as a function of time were determined.

The experimental technique has been described (*5, 6*). It is believed that uncertainties in the analyses did not contribute significant errors in interpretation of the results. The volumetric compression ratio was known with an uncertainty of approximately 0.2%, and the position-time relationship of the piston was established within 0.002 inch and 2 microseconds.

From the basic experimental measurements, the maximum apparent pressure and maximum apparent temperature in the sample were determined, assuming that the gas was compressed isentropically from its initial volume to its minimum volume, returning then to a standard isentropic state. The influence of variation in composition of the system with time was not taken into account in calculating apparent pressure and apparent temperature. Some significant deviation of the apparent values of pressure and temperature from those actually realized is to be expected, particularly in cases in which appreciable