

ACKNOWLEDGMENT

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NOTATION

- c = polymer concentration, kg/m^3
 M = polymer molecular weight
 R = universal gas constant, $8.314 \text{ J}/\text{mole}\cdot\text{K}$
 S = numerical factor, dependent on solvent power
 T = absolute temperature, $^\circ\text{K}$
 h = root-mean-square end to end distance of polymer molecule, m
 η = solution viscosity, $\text{Pa}\cdot\text{s}$ or $\text{N}\cdot\text{s}/\text{m}^2$
 η_s = solvent viscosity, $\text{Pa}\cdot\text{s}$ or $\text{N}\cdot\text{s}/\text{m}^2$
 Θ = relaxation time, s
 κ = numerical factor, dependent on solvent power

LITERATURE CITED

- Balakrishnan, C., and R.J. Gordon, "Influence of Molecular Conformation and Intermolecular Interactions on Turbulent Drag Reduction," *J. Appl. Polymer Sci.*, **19**, 909 (1975)
Chiou, C.S., and R.J. Gordon, "Vena Contracta Suppression in Dilute Polymer Solutions," *ibid.*, **21**, 1359 (1977).
Ferry, J.D., *Viscoelastic Properties of Polymers*, 2 ed., Wiley, New York (1970).
Flory, P.J., *Statistical Mechanics of Chain Molecules*, Interscience, New York (1969).
Hinch, E.J., and C. Elata, "A New Model for the Flow of Freshly Prepared Dilute Macromolecular Solutions," paper presented at AIChE 86th National Meeting, Houston, Tex. (1979).
Zimm, B.H., and D.M. Crothers, "Simplified Rotating Cylindrical Viscometer for DNA," *Proc. N. Aca. of Sciences*, **48**, 905 (1962).

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Multiplicity and Pollutant Formation for the Combustion of Hexane in a Refractory Tube

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This paper presents the results of a continuing study of the process of combustion in a refractory tube. Chen and Churchill (1972a) first demonstrated experimentally that flames of premixed propane vapor and air could be stabilized over a wide range of operating conditions. As contrasted with combustion stabilized by diffusion or backmixing, stabilization in the refractory tube by wall to wall radiation, and thermal conduction in the wall was found to minimize backmixing, to avoid oscillations and to yield a very thin, very stable and nearly invisible flame front. Chen and Churchill (1972b) also developed and solved numerically a theoretical model for the turbulent regime which yielded predictions of the wall temperature distribution and the limits of stable flow in good agreement with their experimental measurements. However, owing to the intervening irreversible modification of the experimental apparatus, they were unable to test the prediction by this model of the existence of six additional stationary states for the same external conditions.

Bernstein and Churchill (1976) constructed an essentially identical combustion chamber and experimentally confirmed the existence of many multiple stationary states. They also discovered that the NO_x concentrations from this process of combustion were only 5 to 40 ppm, depending on operating conditions.

Choi and Churchill (1978) demonstrated that flames from the evaporation and combustion of hexane droplets could also be stabilized in a refractory tube. The same combustion chamber was used as in the prior investigations, but an extended inlet section was added to provide sufficient distance for the evaporation. Very low concentrations of NO_x were again observed. Choi and Churchill (1979) improved the method of solution of the theoretical model of Chen and Churchill (1972b) and extended

the model to include droplets as well as premixed gaseous fuel. Their solutions predicted the existence of at least two stationary states. Additional stationary states may have been eliminated by the approximation required to obtain convergence of the numerical calculations.

The objective of the current investigation was to investigate the possible existence and consequences of multiple stationary states for the evaporation and combustion of liquid droplets. To provide the necessary control and precision, the prior apparatus was completely rebuilt and recalibrated, and a system for on-line chemical analysis was added.

EXPERIMENTAL APPARATUS AND PROCEDURE

The investigation utilized an apparatus similar to that of Choi and Churchill (1978). The combustion chamber consisted of a round channel 9.7 mm in diameter and 864 mm long. The first 623 mm was a high purity aluminum oxide tube. The final 241 mm comprised the central hole in a cylindrical block of aluminum oxide, 75.5 mm in diameter. The central hole was surrounded by six identical outer holes which were used as guard heaters. The block was made from RTC-60 precision castable alumina ceramic. (The previous combustion chambers used by Churchill and co-workers were formed by cementing together pieces of channelled Wulff furnace elements.) The temperature distribution along the central hole and elsewhere in the cylindrical block was measured with platinum/platinum-10% rhodium thermocouples. The ceramic tube and block were both well insulated.

A single chain of uniformly sized and uniformly spaced droplets was generated by passing reagent grade hexane through 0.1143 mm ID (32 gauge) hypodermic tubing, vibrated at a controlled frequency of 543 Hz by the cone of a radio speaker. The observation that one droplet formed per oscillation permitted calculation of the droplet volume and, assuming a sphere, the droplet diameter from the rate of flow of hexane and the frequency. The droplet spacing was computed from a semitheoretical correlation of Choi and Churchill (1978). The inlet air stream was preheated sufficiently to assure complete evaporation of the droplets

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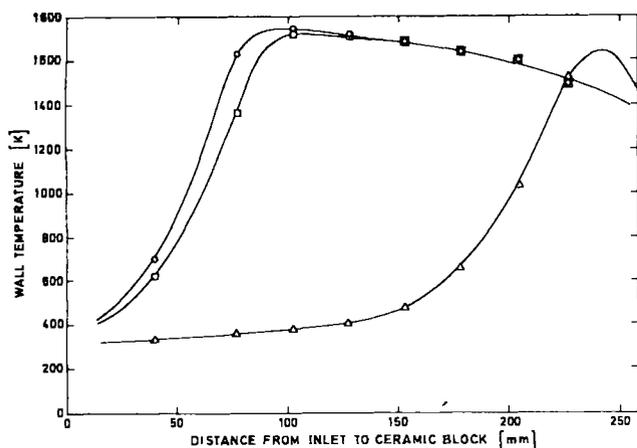


Figure 1. Wall temperature profiles for $w_a = 0.353$ g/s, $D = 462$ μm and $l_D = 5.06$ mm: \circ -I, \square -II, \triangle -III.

ahead of the flame front. Propane vapor and air were metered, mixed and distributed through the six outer holes in the ceramic block.

In the prior work, gas samples were collected in Teflon bags for subsequent analysis. For the work described herein, samples of the exit gas were quenched, dried and analyzed on-line. NO_x and NO concentrations were measured by chemiluminescence with a Thermo Electron Corp: model 10AR, CO and CO_2 by nondispersive infrared with two Horiba Instrument, Inc., model PIR-200 analyzers and O_2 by electrochemical measurement with a Beckman Instrument, Inc., model 7003 Oxygen Monitor and a model 639905 Oxygen Sensor Kit. These instruments were calibrated before each run with samples of known composition.

A sample was pulled from the gas stream leaving the combustor through a 1 or 2 mm fused-quartz tube with a Thomas Industries model 107-ca3 diaphragm pump. The gas was cooled and the bulk of the water removed in passage through a water cooled condenser. Two methods were tested for further removal of water: adsorption on Drierite (anhydrous calcium sulfate) and condensation in a pair of cold traps with ice water at 273°K and dry ice/trichloroethylene at 195°K. The tests revealed that the Drierite reduced the NO_2 content by 0.4 ppm, the CO content by 0.002% and the CO_2 by 0.3% by adsorption, whereas the cold traps reduced these three components by 0.05 ppm, 0.001% and 0.10%, respectively, by solution in the condensate. Cold traps were therefore utilized. However, it is concluded that the errors from the use of Drierite are not sufficient to invalidate the work of Bernstein and Churchill (1976) and Choi and Churchill (1978). All tubing was Teflon, glass or quartz, and all fittings were stainless steel or spring loaded, glass and quartz hall and socket joints to minimize losses by adsorption.

After a quasistationary state was established, the flow rate of the premixed propane and air was adjusted until the flame front locations in the propane-air holes were at the same level as in the hexane-air hole as indicated by equal radial wall temperatures. Multiple stationary states were sought by sharply increasing or decreasing the flow rate of air to the central hole, thus moving the flame front location a significant distance. The flow rate of air was then reset at its former value, and the return or nonreturn of the flame to its former location was observed. The propane-air flame fronts were subsequently adjusted to the same longitudinal location by trial and error.

Further details concerning the equipment and experimental procedures are given by Goepp (1978).

RESULTS

The primary experimental measurements consisted of the inlet air temperature, the wall temperature profile along the hexane-air combustion tube and the exit gas composition as a function of the flow rate of air for a fixed hexane to air mass ratio of 0.0533, corresponding to 23% excess air.

Gas temperatures were not measured, but values computed from the model of Choi and Churchill (1979) indicate that the maximum temperature is a few degrees higher than the adiabatic flame temperature and that the exit temperature only a few degrees lower than this maximum. Hence, a nearly isothermal zone exists from the flame front to the exit.

Typical wall temperature profiles are plotted in Figures 1 to 3. The runs in Figure 1 are for a single flow rate and for nearly the

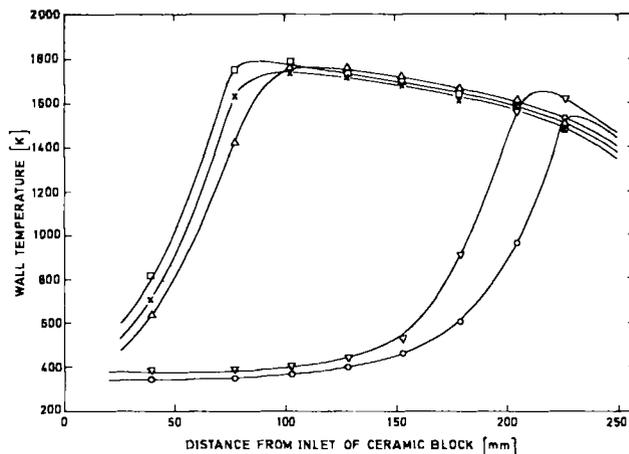


Figure 2. Wall temperature profiles for $w_a = 0.422$ g/s, $D = 491$ μm and $l_D = 6.05$ mm: \square -IV, \circ -V, \triangle -VI, ∇ -VII, \times -VIII.

same inlet temperature, and similarly in Figure 2 for another flow rate. The five runs in Figure 3 are for three different flow rates, of which run VII represents the highest flow rate for which a stationary state could be established. Except for run VII, the widely separated profiles in all three figures certainly represent multiple stationary states. The other curves at the same nominal conditions may represent additional stationary states or minor differences in preheating and external conditions.

Multiplicity is shown even more clearly in Figure 4, in which the flame front location (here defined as the point of maximum gradient in the wall temperature) is plotted vs. the air flow rate. As noted above, the slightly displaced locations at air flow rates of 0.353 and 0.422 g/s may or may not be additional stationary states.

Runs were attempted at 0.48 and 0.55 g/s, but a stationary state could not be established. This result and the curve of Figure 5 suggest that blowoff occurs with the flame near the center of the tube rather than at the exit.

As indicated in Figure 4, the results for hexane droplets are in excellent agreement with the experimental values of Bernstein and Churchill (1976) and the theoretical prediction of the locus of stationary states by Choi and Churchill (1979) for premixed propane-vapor and air, despite the lower adiabatic flame temperatures for hexane and air and the lower thermal conductivity of the cast block. The experimental results (not shown) of Choi and Churchill (1978) are in qualitative agreement but are not directly comparable because of higher hexane to air ratios, much smaller droplet diameters and greatly reduced droplet spacing.

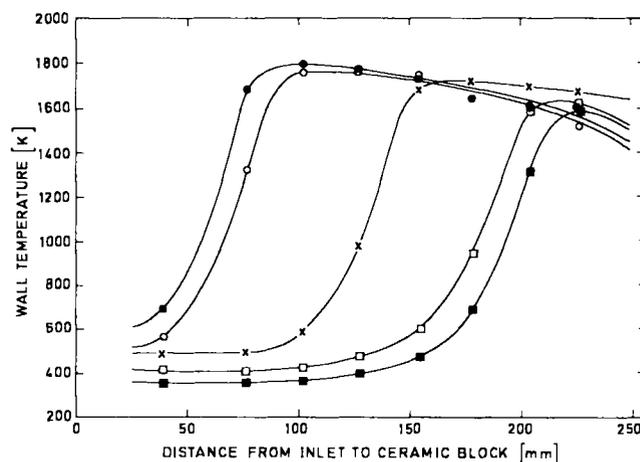


Figure 3. Wall temperature profiles for $w_a = 0.400, 0.450$ and 0.470 g/s: \times -X, \bullet -XI: 0.400 g/s, $D = 482$ μm , $l_D = 5.73$ mm, \square -VIII, \circ -IX: 0.4509 g/s, $D = 502$ μm , $l_D = 6.44$ mm, \times -VII: 0.470 g/s, $D = 509$ μm , $l_D = 6.72$ mm

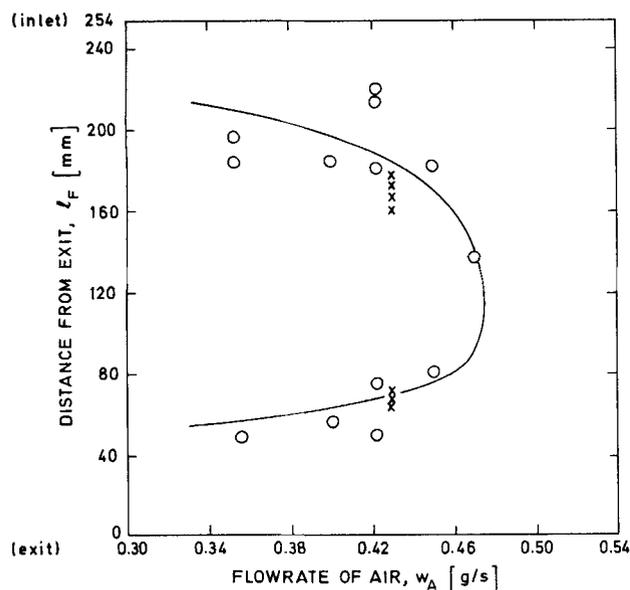


Figure 4. Flame front locations: \circ this study: hexane droplets and air, X Bernstein and Churchill (1976): propane-vapor and air, — Choi and Churchill (1979): propane-vapor and air, theoretical.

The measured concentrations of NO_x and NO are plotted in Figure 5 vs. the nominal residence time in the high temperature, post flame zone. The quantitative version given by Seinfeld (1975) for the Zel'dovich model for thermal NO production indicates that this quantity should be proportional to the residence time following the flame front, owing to the essentially constant concentrations of N_2 , O_2 and H_2O and hence of N , O , H and OH . At least-squares line through the measured values of NO yields a production rate of $\sim 6.2 \times 10^{-3}$ mole/mole s or ~ 0.035 mole/ m^3 s as compared to a prediction of ~ 0.016 mole/ m^3 s based on the Zel'dovich model. The least-squares line

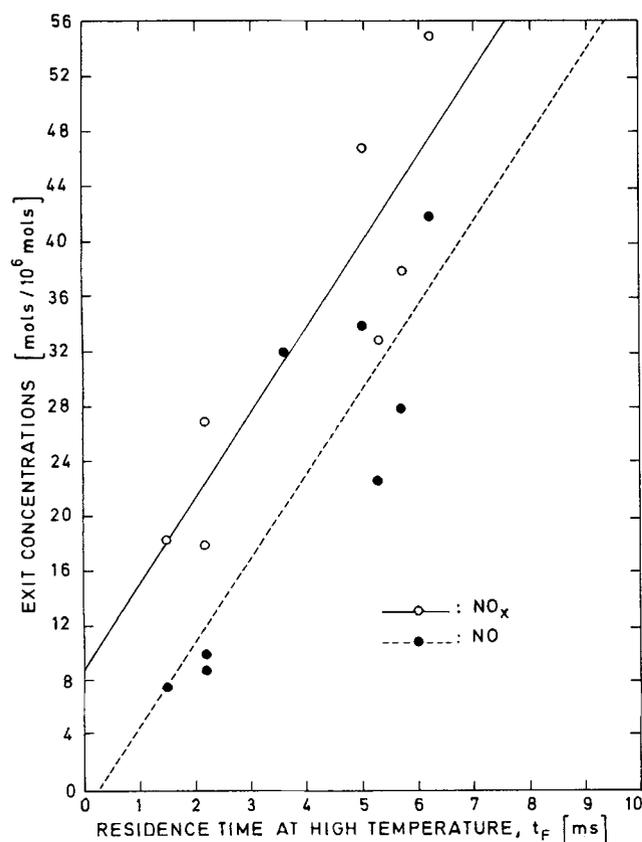


Figure 5. Exit concentrations of NO and NO_x .

extrapolates to the origin within its uncertainty, indicating negligible production of prompt NO in the flame itself. The scatter in the measured values of NO is presumed to be due in part to slightly different gas temperatures for the different runs, to varying degrees of conversion to NO_2 in the sampling and analytical train (as discussed below) as well as to inherent inaccuracies in analysis at this very low level of concentration.

The least-squares line through the NO_x values in Figure 5 indicates the same level of production as for NO but an initial value of 9 ppm (or 11 ppm greater than the NO concentration). One interpretation could be that 9 to 11 ppm of NO_{2+} are formed in the flame itself. A more likely explanation is that the rate of quenching is insufficient and that most or all of this NO_{2+} is formed in the sampling tube. This latter interpretation is supported on two grounds. First, both kinetic models and equilibrium calculations indicate that negligible NO_{2+} would be expected. Second, Johnson et al. (1979) showed from laser resonance fluorescence measurements that concentrations of NO_2 determined from samples of gas from a flame can be accounted for almost wholly by oxidation of NO at the intermediate temperatures in the sampling tube. This suggests interpretation of our measured values of NO_x as actual values of NO . The indicated local rate of production of NO is not changed, since the slopes of the lines in Figure 5 are the same. However, the production of 9 to 11 ppm of prompt NO in the flame front is implied.

CONCLUSIONS

From this investigation, it is concluded that the process of combustion of a liquid fuel inside a refractory tube is essentially the same as for a gaseous fuel premixed with air if the droplets are completely evaporated ahead of the flame front. Just as for premixed propane vapor and air, multiple stationary states, blowoff within the tube and exceptionally low concentrations of thermal NO_x were achieved. These low concentrations of NO_x were attained despite the use of 23% excess air and despite high flame and post flame temperatures, presumably because this unique process of combustion avoids backmixing and oscillations.

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NOTATION

- D = diameter of droplet, μm
 l_D = center to center axial spacing between droplets, mm
 l_F = nominal distance of flame from exit (location of maximum gradient in wall temperature), mm
 t_F = nominal residence time at adiabatic flame temperature, ms
 w_a = rate of flow of air, g/s

LITERATURE CITED

- Bernstein, M. H., and S. W. Churchill, "Multiple Stationary States and NO_x Production for Turbulent Flames in Refractory Tubes," *Sixteenth Symposium (International) on Combustion*, p. 1737, The Combustion Institute, Pittsburgh, Pa. (1977).
 Chen, J. L.-P., and S. W. Churchill, "Stabilization of Flames in Refractory Tubes," *Combustion and Flame*, 18, 37 (1972a).
 ———, "A Theoretical Model for Stable Combustion Inside a Refractory Tube," *ibid.*, 27 (1972b).
 Choi, B., and S. W. Churchill, "Evaporation and Combustion of Uniformly Sized Hexane Droplets in a Refractory Tube," *Advances in Chemistry Series, No. 166, Evaporation-Combustion of Fuels*, J. T. Zung, ed., p. 83, Amer. Chem. Soc., Washington, D.C. (1978).
 ———, "A Model for Combustion of Gaseous and Liquid Fuels in a Refractory Tube," *Seventeenth Symposium (International) on*

Combustion, p. 917, The Combustion Institute, Pittsburgh, Pa. (1979).

Goepp, J. W., "An Experimental Investigation of Multiplicity and Pollutant Levels for the Combustion of Hexane Inside a Refractory Tube," M.S. thesis, Univ. Pa., Philadelphia (1978).

Johnson, G. M., M. Y. Smith and M. F. R. Mulcahy, "The Presence of NO₂ in Premixed Flames," *Seventeenth Symposium (International)*

on Combustion, p. 647, The Combustion Institute, Pittsburgh, Pa. (1979).

Seinfeld, J. H., *Air Pollution-Physical and Chemical Fundamentals*, p. 373, McGraw-Hill, New York (1975).

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Correlation of Second Virial Coefficients of Polar Gases by Redlich-Kwong Equation of State

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In order to describe and accurately predict phase equilibria at superatmospheric pressures, it is usually necessary to take vapor phase nonideality into account. Nonidealities of vapor phase are pictured by the fugacity coefficients. The virial equation of state truncated after the second virial coefficient provides reliable estimates of the fugacity coefficients for conditions up to moderate densities. It is written as an expansion of the inverse powers of volume

$$Z = \frac{Pv}{RT} = 1 + \frac{B}{v} \quad (1)$$

The second virial coefficient B can be determined from experimental data mostly compiled by Dymond and Smith (1968) or calculated with a suitable correlation. It is well known that accurate procedures are required for the calculation of second virial coefficient of gases. However, it is difficult to establish corresponding correlations for this property of polar gases. Approximate estimations are based on the various approaches (Black, 1958; O'Connell and Prausnitz, 1967; Kreglevski, 1969; Halm and Stiel, 1971; Polak and Lu, 1972; Nothnagel et al., 1973; Tsonopoulos, 1974, 1975; Hayden and O'Connell, 1975; Tarakad and Danner, 1977; Lin and Stiel, 1977; Tsonopoulos, 1978). One of the proposals of the correlations used to compute the second virial coefficient is that based on semiempirical equations. When theoretical approaches are tedious, this semiempirical estimation has the major advantage. The Berthelot and the original and modified Redlich-Kwong (RK) equations have been used (Black, 1958; de Santis et al., 1974; Simonet and Behar, 1976) to calculate the second virial coefficients of some nonpolar and polar gases. Since the original RK equation (Redlich and Kwong, 1949) has only two constants, it is not able, generally speaking, to give a highly accurate representation of the second virial coefficients. The note presented here provides a reasonable method for making the best estimates.

In our previous papers (Djordjević et al., 1977; Mihajlov-Duduković et al., 1978; Djordjević et al., 1979) we have demonstrated the capability of the RK equation to correlate and predict the thermodynamic properties of some nonpolar, slightly polar and polar substances using the optimal values of constants for each available

isotherm. The objective of this study is to extend the same method to the correlation of second virial coefficient of polar gases. From extensive comparisons with other more frequently used analytical methods for predicting values of second virial coefficients of polar gases, the present method was found to be superior.

RESULTS AND DISCUSSION

The RK equation of state is given by

$$Z = \frac{v}{v-b} - \frac{a}{RT^{1.5}(v+b)} \quad (2)$$

The constants a and b can be related to the critical properties by

$$a = \Omega_a \frac{R^2 T_c^{2.5}}{P_c} \quad (3)$$

$$b = \Omega_b \frac{RT_c}{P_c} \quad (4)$$

The numerical values $\Omega_a = 0.4275$ and $\Omega_b = 0.0867$, as universal constants valid for all temperature and pressures, were found by applying $(\partial P/\partial v)_{T_c} = (\partial^2 P/\partial v^2)_{T_c} = 0$ at the critical point.

The method used in this investigation is already described (Djordjević et al., 1977) as follows. The parameters Ω_a and Ω_b have been determined from experimental P - v - T data of polar gases at each available isotherm. For each temperature, the optimal values of Ω_a and Ω_b were found by Newton-Raphson method (Rosenbrock and Storey, 1966). The objective function is given by

$$\sum_1^N (Z_{\text{exp}} - Z_{\text{cal}}) \rightarrow \min \quad (5)$$

Z_{cal} is calculated from Equation (2). As shown in our cited work, in all cases the proposed method is preferred to the results of other applied modifications of the RK equation.

The second virial coefficient B is defined by

$$B = \lim_{\substack{P \rightarrow 0 \\ v \rightarrow \infty}} (Z-1)v \quad (6)$$

Prediction of the second virial coefficient B_{RK} is obtained when Equation (6) is applied to the RK equation

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