Heat Transfer in the Nitrogen Dioxide-Nitrogen Tetroxide System

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Local heat transfer coefficients were carefully measured for the nitrogen dioxide-nitrogen tetroxide system in well-developed turbulent flow in an electrically heated, 0.194-in. I.D. tube. The average probable error determined from reproducibility tests was less than 2%.

The modification of the Deissler analogy presented earlier (*8*) was found to predict coefficients which agreed well (0 to 19% deviation) with the observed results. Some of this deviation may be due to uncertainties in the viscosity data. Brokaw's viscosity information (*1*) gives results that were higher than the experimental values, but that of Thievon et al. (*11*) would have given low values.

The data were also compared with a simpler Colburn type of analogy in which a heat transfer coefficient based upon enthalpy was employed. The deviations here were larger.

Heat transfer in homogeneous, reacting fluids is of interest because the contribution due to diffusion and reaction may overshadow the conventional contribution due to a temperature gradient. The nitrogen dioxide-nitrogen tetroxide reacting system is favorable for investigating this phenomenon because the diffusion contribution, which depends in general upon the heat and rate of reaction and temperature level, is large at normal laboratory conditions. Furthermore the rate of dissociation is so rapid (*2*) that chemical equilibrium may be assumed at any point (any temperature) in the gas.

Irving and Smith (*8*) proposed a means of predicting the total heat transfer coefficient in the nitrogen dioxide-nitrogen tetroxide system by modifying the Deissler analogy (*5*) developed for inert fluids. In order to evaluate the method experimental data are needed at conditions where the temperature variations are a minimum and are well established, because the magnitude of the diffusion contribution is sensitive to small changes in temperature. For heat transfer to the reacting fluid flowing in a tube this means that local heat transfer coefficients, applicable at a particular axial position, should be measured. This eliminates the uncertainty of taking into account the axial variations in properties and coefficients which occur over a finite heat exchange area. Hence the purpose of the present study was to measure local coefficients for nitrogen dioxide-nitrogen tetroxide mixtures in turbulent flow in a straight tube and compare the results with prediction methods.

Since the study was initiated two experimental investigations for the same system have been reported. The work of Thievon, Sterbutzel, and Beal (*11*) led to local coefficients, but the results were stated to include entrance effects. The investigation of Krieve and Mason (*9*) was concerned with overall heat transfer coefficients over a finite length of tube.

SCOPE OF DATA

The measurements were made in a 0.194 in. I.D. tube over the following range of conditions:

Reynolds number, N_{Re_0}
 5,600 to 68,200
Wall temperature
 110° to 350°F
Bulk temperature
 95° to 190°F.
Heat flux, B.t.u./(hr.sq.ft.)
 650 to 27,000
Pressure, lb./sq. in. abs. (inlet mixing chamber)
 14.3 to 25.0

EXPERIMENTAL WORK

The apparatus consisted of a heat transfer loop with suitable instrumentation and power supply as shown in Figure 1. Since nitrogen tetroxide is toxic, polyethylene film, stretched over a steel frame and equipped with an exhaust fan, was used to enclose the apparatus.

The test section was a 35.7 in. long section of the ¼ in. O.D. Inconel tubing with wall thickness of 0.028 in. On each end were installed mixing chambers containing copper-constantan thermocouples imbedded in the tips of 3-mm. glass tubing, as shown in Figure 2. These thermocouples determined the temperatures of the gas mixture entering and leaving the test section. For wall temperature measurements 30 B. and S. gauge copper-constantan thermocouples were silver soldered to the outer wall of the test section at intervals of 2 in. The thermocouples were calibrated

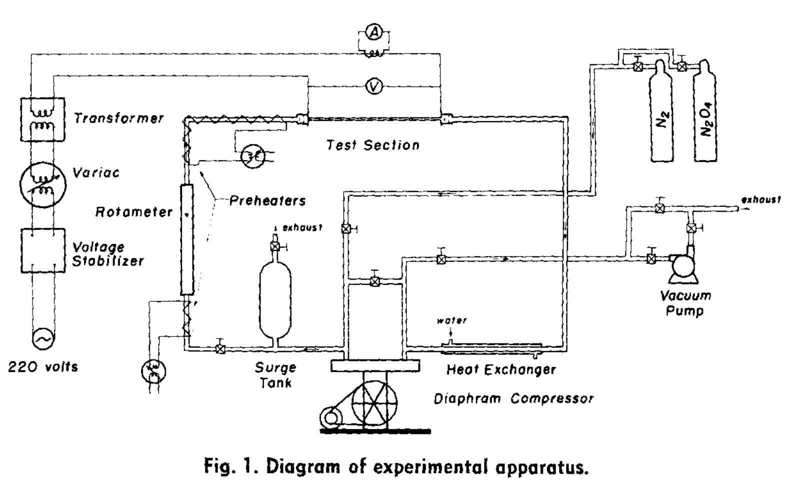

Fig. 1. Diagram of experimental apparatus.

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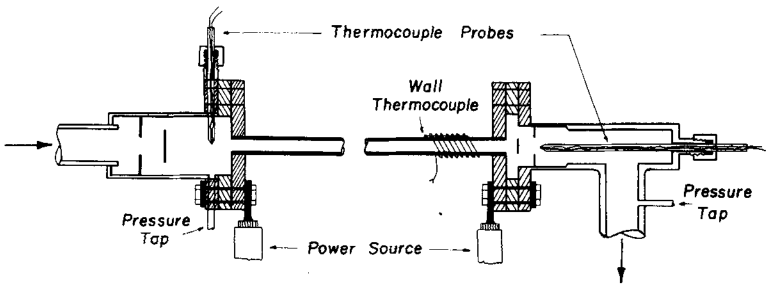

Fig. 2. Test section.

at the ice point, at the boiling point of water, and at the dehydration temperature of $Na_2SO_4 \cdot 5H_2O$.

The flowing gas was heated by passing electric current through the wall of the Inconel tube. The 230 v. A.C. power supply was first stabilized, then the current passed through a Variac and step-down transformer, and finally to the flanges of the test section as shown in Figures 1 and 2. Voltage and current readings at the test section were made with a calibrated voltmeter and ammeter, each with an accuracy of 0.5% of the instantaneous reading.

The gas was circulated through the system with a diaphragm compressor. To reduce the pressure fluctuations induced by the compressor a 1.3 cu. ft. surge tank and a globe valve were installed in the discharge line. This combination provided adequate dampening of the pulsations except at very low flow rates.

Details of the apparatus and operating procedure, including sizes of equipment, thermocouple construction, and instruments used are given elsewhere (*6*). While the gas in the system was not analyzed, the purity of the nitrogen dioxide—nitrogen tetroxide was specified by the manufacturers to be

$N_2O_4(NO_2—N_2O_4)$	99.5 wt. %, minimum
H_2O equivalent	0.1 wt. %, maximum
Cl, as NOCl	0.08 wt. %, maximum
nonvolatile (ash)	0.01 wt. %, maximum

ACCURACY OF DATA

In filling the apparatus the equipment was evacuated, filled with gas, evacuated again, and refilled.

A series of no-flow tests were conducted to determine approximately the heat losses from the insulated test section. During the operation of the equipment the highest energy input was 67.8 B.t.u./min., and at these conditions the average wall temperature was about 200°F. The no-flow tests showed a heat loss of 0.3 B.t.u./min. or 0.5% at this wall temperature. At the lowest energy input the heat loss was about 2%. From the slopes of the wall-temperature vs. tube-length curves at the end points it is estimated that 10% of the total heat loss occurred by axial conduction from the ends of the tube.

From the enthalpy-pressure-temperature data (see next section) for equilibrium mixtures of nitrogen dioxide and nitrogen tetroxide and the measured flow rate and temperatures, an energy absorption could be evaluated for comparison with the electrical energy input. In nearly all the runs the agreement was within 5% and included both positive and negative deviations. The absolute, average deviation was about 3%.

The precision of the heat transfer coefficients computed from the experimental data was estimated by a determination of the probable error from a set of four runs at the same conditions but carried out on different days. The temperature profiles and experimental heat transfer coefficients (h' values) are shown in Figure 3. The temperature data are included for only one run because it would not be possible to distinguish between the individual points on the scale of the figure. The average, probable error (that is an error such that one half of the errors of individual measurements are larger and one half smaller than the probable error) was 8 B.t.u./(hr.)(sq.ft.)(°F.) or less than 2%.

CALCULATION OF RESULTS

Two heat transfer coefficients were evaluated from the data, one based upon the temperature difference between the wall t_o and the bulk stream t_b and the other based upon the enthalpy difference:

$$q = h' (t_o - t_b) \quad (1)$$

$$q = h'' (H_o - H_b) \quad (2)$$

Inconel was chosen as the tube material because its electrical resistance does not vary significantly with temperature. Accordingly the heat flux, calculated from the measured voltage and current, was assumed constant along the tube length.

The bulk temperature at any tube length was evaluated from a heat balance over that length and the measured, entrance bulk temperature. The

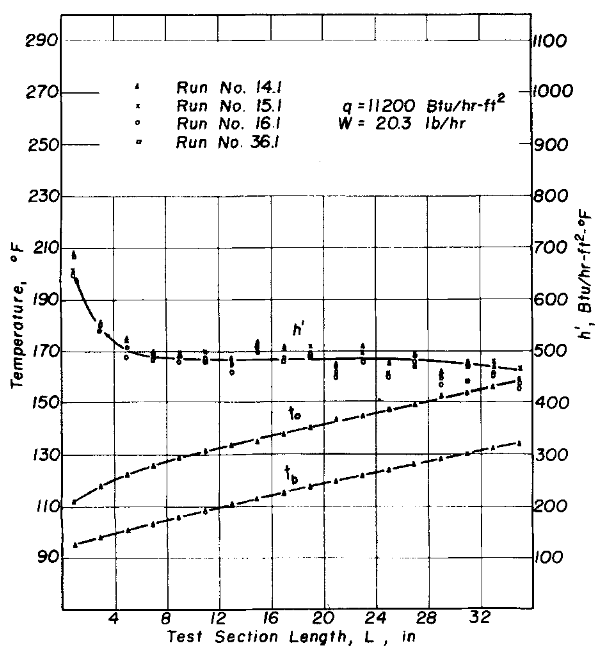

Fig. 3. Data reproducibility.

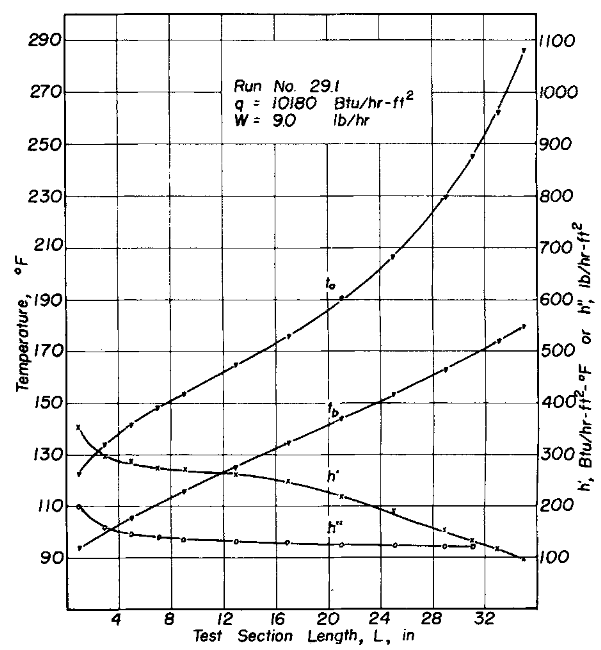

Fig. 4. Temperature and heat transfer coefficient profiles.

electrical energy input was assumed directly proportional to the tube length. This required a knowledge of the equilibrium enthalpy of the nitrogen dioxide-nitrogen tetroxide system as a function of temperature and pressure. Such information was obtained from thermodynamic property charts prepared for this system (7). The pressure drop across the test section was measured for each run and varied from 1 to 6 lb./sq. in. abs. Calculations indicated that about 20% of the drop occurred as entrance losses with the remainder assumed to be linear with distance. In this way the pressure at any tube length was calculated and used along with the enthalpy to determine the bulk temperature.

The inside wall temperature was evaluated from the measured outside wall temperature by means of the conduction equation in an annulus:

$$t_o = t_w + \frac{q r_w}{2k_s} \left[\frac{1 - (r_o/r_w)^2 + \ln (r_o/r_w)^2}{1 - (r_o/r_w)^2} \right] \qquad (3)$$

The difference between t_o and t_w was of the order of 1°F. in comparison with $t_o - t_b$ values from 10° to 30°F.

From these calculations it was possible to prepare plots of t_o, t_b, h', and h'' vs. tube length for each run. Figure 3 is typical of the results when the wall temperature is below 160°F. The h' values after the entrance and before the exit regions are very nearly constant. When the wall temperature is increased above 160°F., as illustrated in Figure 4, the value of h' decreases. Since the bulk temperature is below the wall value by 20° to 30°F., it is clear that the heat transfer coefficient

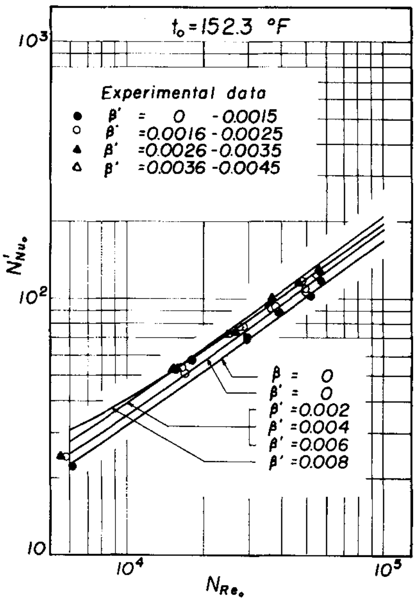

Fig. 6. Deissler analogy correlation.

becomes a function of temperature level in the region of 150°F. The effective heat capacity of the equilibrium system (7) goes through a maximum value at from 130°F. at 12 lb./sq. in. abs. to 160°F. at 30 lb./sq. in. abs. The effective thermal conductivity likewise shows a maximum at about this temperature level (1, 4). Thus the decrease in effective specific heat and thermal conductivity appears to be the cause of the decrease in h' above 160°F. wall temperature. The heat transfer coefficient, based upon enthalpy difference, includes the effect of specific heat variations. It is noted from Figure 4 that these values are nearly the same at any wall temperature.

The prediction methods, which are compared with the experimental coefficients in the following sections, apply for well-developed turbulent flow. As indicated in Figures 3 and 4 entrance and exit effects were significant for the first 6 to 8 in. of tube length and the last 2 in. In the comparisons only experimental data in the central section, where entrance and exit effects were not noticeable, were employed.

MODIFIED DEISSLER ANALOGY

To be able to predict the effect of property variations on heat transfer in reacting systems Deissler's analogy (5) was modified by the use of effective heat capacities and thermal conductivities. These quantities take into account the heat transfer due to diffusion and reaction and may be considered the equivalent quantities that an inert system must possess to give the same heat transfer characteristics as the reacting system. The formulation of these quantities and the prediction of heat transfer coefficients by this method are described in detail by Irving and Smith (8).

The effect of physical property variation is considered in the Deissler analogy through the use of a dimensionless quantity β' which depends upon the wall temperature and heat flux as follows:

$$\beta' = \frac{q\sqrt{\tau_o/\rho_o}}{C'_{p_o}\, g\, \tau_o\, T_o} \qquad (4)$$

With the procedures already presented (8), heat transfer coefficients and Nusselt numbers were predicted for three wall temperatures and several values of β'. The method involved obtaining dimensionless temperature and velocity profiles as a function of β', and the computations were performed on an IBM-650 computer. The results, in the form of solid curves of Nusselt vs. Reynolds number (both evaluated at wall temperature conditions), are shown in Figures 5 to 7. It is apparent that the method predicts correctly the effect of temperature level on the heat transfer coefficient. At low wall temperatures Figure 7 shows that the value of β' does not have a large effect on h', particularly at the lower Reynolds numbers. This corresponds to the experimental situation shown in Figure 3 where h' is nearly constant for all wall temperatures. On the other hand, at t_o = 206°F. (Figure 5) the Nusselt number is a strong function of β in agreement with the experimental data shown in Figure 4. For a more quantitative comparison the experimental data are also shown in Figures 5 to 7.

To determine β' from Equation (4) it was necessary to know the velocity profile and thereby evaluate the wall shear stress τ_o. The measured pressure drop, which included end losses, was

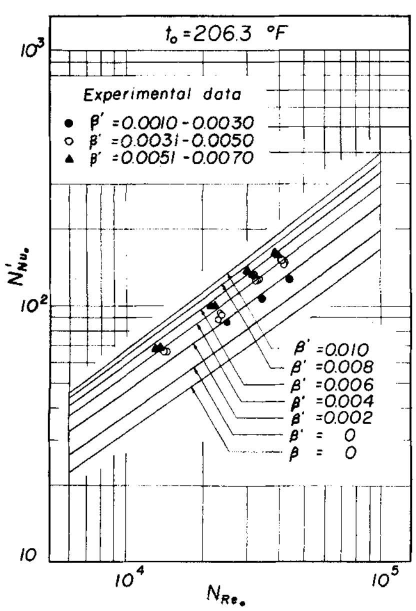

Fig. 5. Deissler analogy correlation.

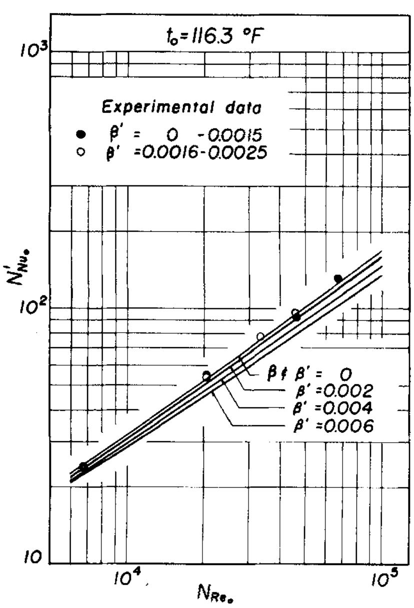

Fig. 7. Deissler analogy correlation.

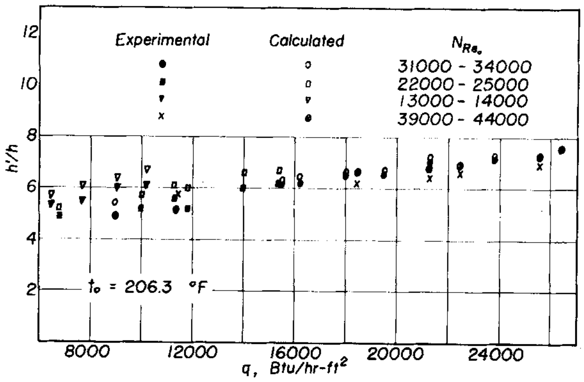

Fig. 8. Effect of reaction on the heat transfer coefficient.

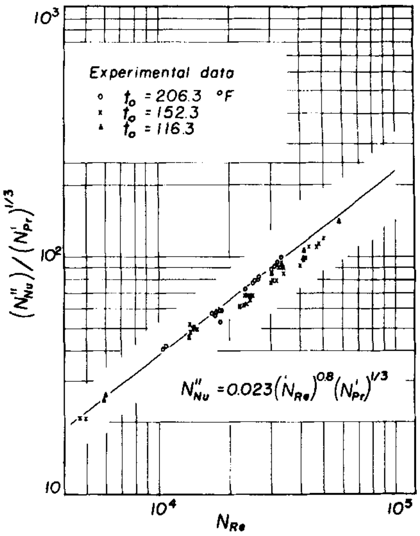

Fig. 10. Colburn analogy correlation.

not known accurately enough to do this. Hence the velocity profiles predicted by the Deissler analogy were employed. The agreement between the experimental and computed results (Figures 5, 6, 7) is good. At a wall temperature of 206°F. the predicted values were an average of 4% higher than the experimental coefficients, with a maximum difference of 13%. At 152°F. the predictions averaged 7% high, with a maximum deviation of 19%. At the lowest wall temperature 116°F., the predicted results were an average of 2% low with a maximum of 6%.

The large contribution of the diffusion and reaction term to the total heat transfer may be observed if one considers the ratio of the heat transfer coefficients for the reactive system and an inert system with the same physical properties. This ratio h'/h is illustrated in Figure 8 for a wall temperature of 206°F. The ratio increases from 6 to 7.5 over the range of heat flux studied. At lower wall temperatures the ratio is higher, that is about 10 at t_o = 116°F. It is interesting to note that at the higher wall temperature h'/h increases with q, while at t_o = 116°F. this ratio is essentially constant. This is the same effect shown by the prediction method in Figures 5 to 7 where the Nusselt number is dependent more on β' at high wall temperatures than at low ones. Predicted values of the ratio are also shown on Figure 8. The inert heat transfer coefficient was obtained from the Deissler analogy at $\beta = 0$.

The calculations based upon the Deissler analogy employed the viscosity results of Brokaw (*1*). These values were computed from molecular force constants. Later Thievon, Sterbutzel, and Beal (*11*) published experimentally determined viscosity data which were about 20% larger than the computed results at 116°F. and 80% larger at 206°F. If the experimental viscosity data had been used in the Deissler analogy, it is estimated that the predicted heat transfer coefficients would have decreased about 17% at a wall temperature of 206°F. and 7% at 116°F. This would change the direction of the deviation between predicted and experimental heat transfer coefficients. Rather than an average of 4% high at 206°F. the predicted results would have been 13% low, and at 116°F. the predicted coefficients would have been 9% low.

REFERENCE ENTHALPY METHOD

Several proposals have been made to use a form of the Colburn heat transfer correlation

$$N_{Nu} = a(N_{Re})^b\,(N_{Pr})^c \qquad (5)$$

for reacting systems. The difficulty in this approach arises in the choice of physical properties to be used in formulating the dimensionless groups. When the effective heat capacity and thermal conductivity pass through a maximum in proceeding from the bulk to wall temperatures the average temperature concept used for inert systems breaks down. Brokaw (*1*) used a reference enthalpy method, among others, to solve this problem. Mason and co-workers (*10*) carried the analysis further and showed that if the Lewis number is unity the following

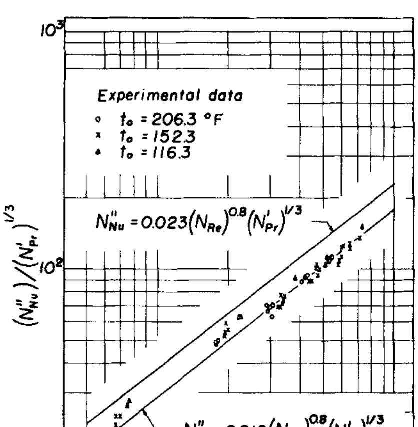

Fig. 9. Colburn analogy correlation.

form of Equation (5) might apply to a reacting system:

$$\frac{h''\,d}{k'/C_p'} = N''_{Nu} = 0.023\,(N_{Re})^{0.8}\,(N'_{Pr})^{1/3} \qquad (6)$$

In this expression the heat transfer coefficient h'' is defined by Equation (2), and the properties are evaluated at a temperature where the enthalpy is equal to the arithmetic average of the enthalpies at the wall and bulk conditions. The Lewis number is unity only at the temperature where the Schmidt and Prandtl numbers are equal. However at other temperatures the deviation from unity is less than ± 0.4 for the nitrogen dioxide-nitrogen tetroxide system.

The comparison between Equation (6) and the experimental data is shown in Figure 9. The prediction curve is about 10% high at low Reynolds numbers and 30% high at high values of N_{Re}. A much better fit can be obtained by changing the coefficient in Equation (6) to 0.018, as illustrated on the figure. Krieve and Mason (9) proposed this numerical coefficient to correlate their overall heat transfer coefficients. However they used N'_{Nu} rather than N''_{Nu}, and there was considerable scatter in the results. Figure 9 was prepared with the viscosity data of Brokaw (*1*). The original Equation (6) agrees better with the experimental results if the viscosities measured by Thievon et al. (*11*) are employed, as illustrated in Figure 10. Examination of this figure shows that the largest deviations, about 20%, occur at a wall temperature of 152°F. at the higher Reynolds numbers. For these runs the temperature variation is such that the effective heat capacity and thermal conductivity pass through a maximum between the bulk stream and the wall.

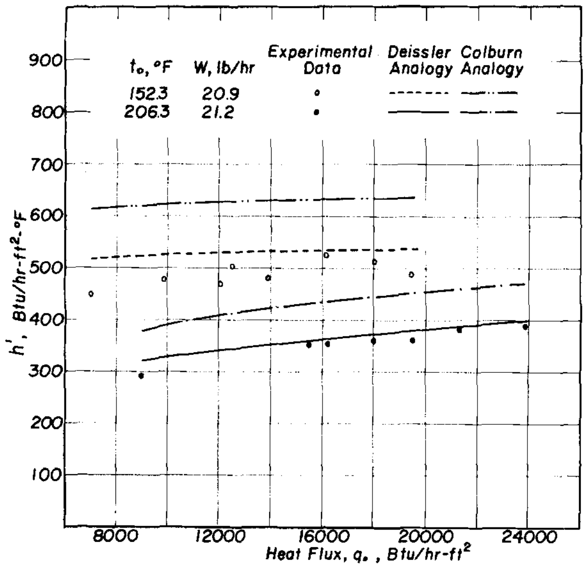

Fig. 11. Comparison of Deissler and Colburn analogies.

A more direct comparison between the data and the Deissler and Colburn prediction methods is given in Figure 11 at wall temperatures of 152° and 206°F. The h'' values from Equation (6) were converted to h' quantities by equating Equations (1) and (2). The Colburn results are 20 to 30% higher than the data, while the Deissler results are about 7% higher at t_o = 152°F. and 4% higher at t_o = 206°F. Both sets of predictions are based upon the viscosity data of Brokaw (*1*).

Figures 5 to 8 and 11 show that the modified Deissler analogy predicts local heat transfer coefficients for this system very well and close to the accuracy of the experimental data. The Colburn analogy which uses an enthalpy-based coefficient is less accurate.

OTHER EXPERIMENTAL DATA

None of the previous investigations reported local coefficients for well-developed turbulent flow. However the data of Thievon, Sterbutzel, and Beal (*11*) approached these conditions, the deviation depending upon the extent of the entrance effects involved. They correlated their results with an equation similar to Equation (6) except that an empirical enthalpy ratio was included and the coefficient was 0.018. As indicated in Figure 9 the present data also are reasonably well represented by this equation.

The overall coefficients presented by Krieve and Mason (*9*) cannot be compared with the local values because the latter vary with tube length, particularly at temperatures above 160°F. This is shown on Figure 4 where the local h' is seen to decrease from about 300 to 100 B.t.u./(hr.)(sq.ft.)(°F.) along the tube, even excluding entrance and exit effects. As the wall and bulk temperatures continue to increase, the decrease in h' becomes sharper. Thus above 200°F. the system is nearly all nitrogen dioxide, and the heat transfer coefficient is the low value corresponding to an inert gas. The overall coefficient is an average of the local values. An accurate correlation of this overall value in terms of the properties of the system requires establishment of a temperature which correctly represents the extensive changes in properties in both the longitudinal and radial directions.

ACKNOWLEDGMENT

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NOTATION

a, b, c = constants in Equation (5)
C_p = heat capacity, B.t.u./(lb.)(°F.), C_p' designates effective heat capacity for the reacting system
D_{12} = molecular diffusivity in binary system of components 1 and 2, sq.ft./hr.
d = tube diameter, ft.
G = mass flow rate, lb/(sq. ft.)(hr.)
g = acceleration of gravity, ft./hr.^{2}
H = enthalpy of reacting mixture, B.t.u./lb.
h = heat transfer coefficient in inert system. B.t.u./(hr.)(sq. ft.)(°F.)
h' = heat transfer coefficient in reacting system, B.t.u./(hr.)(sq. ft.)(°F.)
h'' = heat transfer coefficient in reacting system based upon enthalpy driving force, lb./(hr.)(sq. ft.)
k = thermal conductivity of inert system, B.t.u./(hr.)(ft.)(°F.)
k' = thermal conductivity of reacting system, B.t.u./(hr.)(ft.)(°F.)
k_s = thermal conductivity of Inconel, B.t.u./(hr.)(ft.)(°F.)
L = tube length, in.
q = heat flux at the wall, B.t.u./(hr.)(sq. ft.)
r = radial distance from center of tube, ft.; r_w is radius of outside wall of tube, r_o is radius of inside wall
T = temperature, °R.
t = temperature, °F.
W = mass flow rate, lb./hr.
μ = viscosity, lb./(hr.)(ft.)
ρ = density, lb./cu. ft.
τ = shear stress in fluid, lb./(hr.^{2})(ft.)

Dimensionless groups

N_{Nu} = Nusselt number, hd/k
N_{Nu}' = $h'd/k'$
N_{Nu}'' = $h''d/k'$
N_{Le} = Lewis number, $C_p \rho D_{12}/k$
N_{Pr} = Prandtl number, $C_p \mu/k$
N_{Pr}' = $C_p'\mu/k'$
N_{Re} = Reynolds number, dG/μ
β' = heat transfer parameter for reacting system, $\dfrac{q_o\sqrt{\tau_o/\rho_o}}{C'_{p_o}\, g\, \tau_o\, T_o}$

Subscripts

b = bulk conditions
o = inside tube wall condition
w = outside tube wall condition

Superscripts

$'$ = reacting system at chemical equilibrium
$''$ = heat transfer coefficient based upon enthalpy difference

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