THE UNIVERSITY OF MICHIGAN
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MATHEMATICAL SIMULATION OF A FIXED BED TUBULAR REACTOR DURING PERIODS OF TRANSIENT OPERATION

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Introduction

The present work considers a mathematical model for the fixed bed tubular reactor (hereafter referred to as FBTR) and the physical data required to test the validity of the solutions of the equations which represent this model. In order to compare this model with the experimental measurements, the heat transfer characteristics of the catalytic bed must be known. Unfortunately the correlations of the effective thermal conductivity of packed beds given in the literature are not in close agreement with one another.

It was necessary then to select heat transfer parameters for insertion into the finite difference solution of the transient equations for a FBTR which would make the solution match with experimental data. Since a thorough study of a catalytic reaction was not within the scope of this work, the catalytic decomposition of nitrous oxide on manganese sesquioxide was used in the experimental check of the mathematical models. Reliable rate data are available in the literature for this reaction[1]. The reactor was operated under unstable conditions so as to observe the formation of a hot spot within the catalyst bed. Using the selected heat transfer parameters, the feasibility of predicting the transient behavior of the catalytic bed when chemical reaction is occurring was investigated.

Theory

The equations for the FBTR are presented below without the derivations which may be found in several texts[2] treating the problem of heat and mass transfer in packed beds. For the single irreversible reaction to be considered in the work only one mass transfer equation is needed to describe the system.

There are three pertinent equations: one for heat transfer within the solid phase, another for heat transfer through the gas phase, and a third for mass transfer in the gas phase. Cylindrical coordinates are used and angular symmetry is assumed.

The equation for heat transfer through the solid is

$$k_a' \frac{\delta^2 TC}{\delta^2 z^2} + k_e' \left[\frac{1}{r}\frac{\delta TC}{\delta r} + \frac{\delta^2 TC}{\delta r^2}\right] + R\rho' (1-\epsilon)\,\Delta H$$

$$- h A (TC-T) = (1-\epsilon)\,\rho'\, C_p' \frac{\delta TC}{\delta \Theta}$$

where

k_a' (k_e') = axial (radial) thermal conductivity of the catalyst bed

TC = catalyst temperature

T = gas temperature

$$R = -\frac{dP_{N_2O}}{d\Theta} = \frac{b_1 P_{N_2O}\, k_o \exp(-E/R_g T)}{1 + b_1 P_{N_2O} + b_3^{1/2} P_{O_2}^{1/2}}$$

R = reaction rate

ΔH = - 19,400 cal/gm mol = heat of reaction

ρ' = 107 lb/ft^3 = apparent density of catalyst pellets

C_p' = 0.174 Btu/lb °F = heat capacity of catalyst

The first term on the left represents axial heat flow, and the second term describes the radial heat transfer. The third term defines the heat released by an exothermic chemical reaction at the surface of the catalyst, where the reaction rate R is expressed as lb mols reacted/lb catalyst hour, and the heat of reaction ΔH is expressed as cal/gm mol . The fourth term represents the heat transferred from the catalyst to the gas. The sum of these terms is equated to the rate of heat accumulation in the catalyst per unit reactor volume.

The equation for heat transfer through the gas is

$$- GC_p \frac{\delta T}{\delta z} + k_a \frac{\delta^2 T}{\delta z^2} + k_e \left[\frac{1}{r}\frac{\delta T}{\delta r} + \frac{\delta^2 T}{\delta r^2}\right] + h\,A\,(TC-T) = \epsilon \rho C_p \frac{\delta T}{\delta \theta}$$

where

G = superficial mass flow rate of gas, lb/hr ft^2

$k_a(k_e)$ = axial (radial) thermal conductivity of the gas

ρ = density of the gas

C_p = heat capacity of the gas

ϵ = 0.40 = void fraction of bed

A = 462 ft^2/ft^3 = heat transfer area between solid and gas

The terms are similar to those defined in the heat transfer equation for the solid, except that the first term on the left now represents the heat carried by the flowing gas, having a superficial mass velocity of G lb/hr ft^2 .

The equation for mass transfer through the gas is most conveniently written in terms of the conversion, X . This equation then is

$$+\frac{D_a}{U}\frac{\delta^2 X}{\delta z^2} - \frac{\delta X}{\delta z} - \frac{D_e}{U}\left[\frac{1}{r}\frac{\delta X}{\delta r} + \frac{\delta^2 X}{\delta r^2}\right] - \frac{R\rho'(1-\epsilon)}{C_o U_o} = -\frac{\epsilon}{U}\frac{\delta X}{\delta \theta}$$

where

$D_a(D_e)$ = axial (radial) eddy diffusivity of gas

$U(U_o)$ = gas velocity (at reactor inlet)

$X = \frac{C_o U_o - CU}{C_o U_o}$ = reactant conversion

$C(C_o)$ = gas concentration (at reactor inlet)

$D_e/U = d_p/Pe_m$

Pe_m = 11 = radial mass transfer Peclet number

$D_a/U = d_p/Pe_m'$

Pe_m' = 2 = axial mass transfer Peclet number

$d_p = \frac{1}{8}''$ = partical diameter

Since turbulent diffusion normally controls the mass transfer rate, the equation is written with a coefficient of D_e/U , which is assumed to be invariant with radius and temperature. The terms in the mass transfer equation are then analogous to the terms in the heat transfer equations.

The mathematical model for a FBTR defined by these equations has been solved numerically in a closed form on an IBM 709 digital computer. The axial heat transfer has been investigated by Carberry and Bretton[3], but it has no significant influence on the computed results obtained in this work as long as large temperature peaks were avoided.

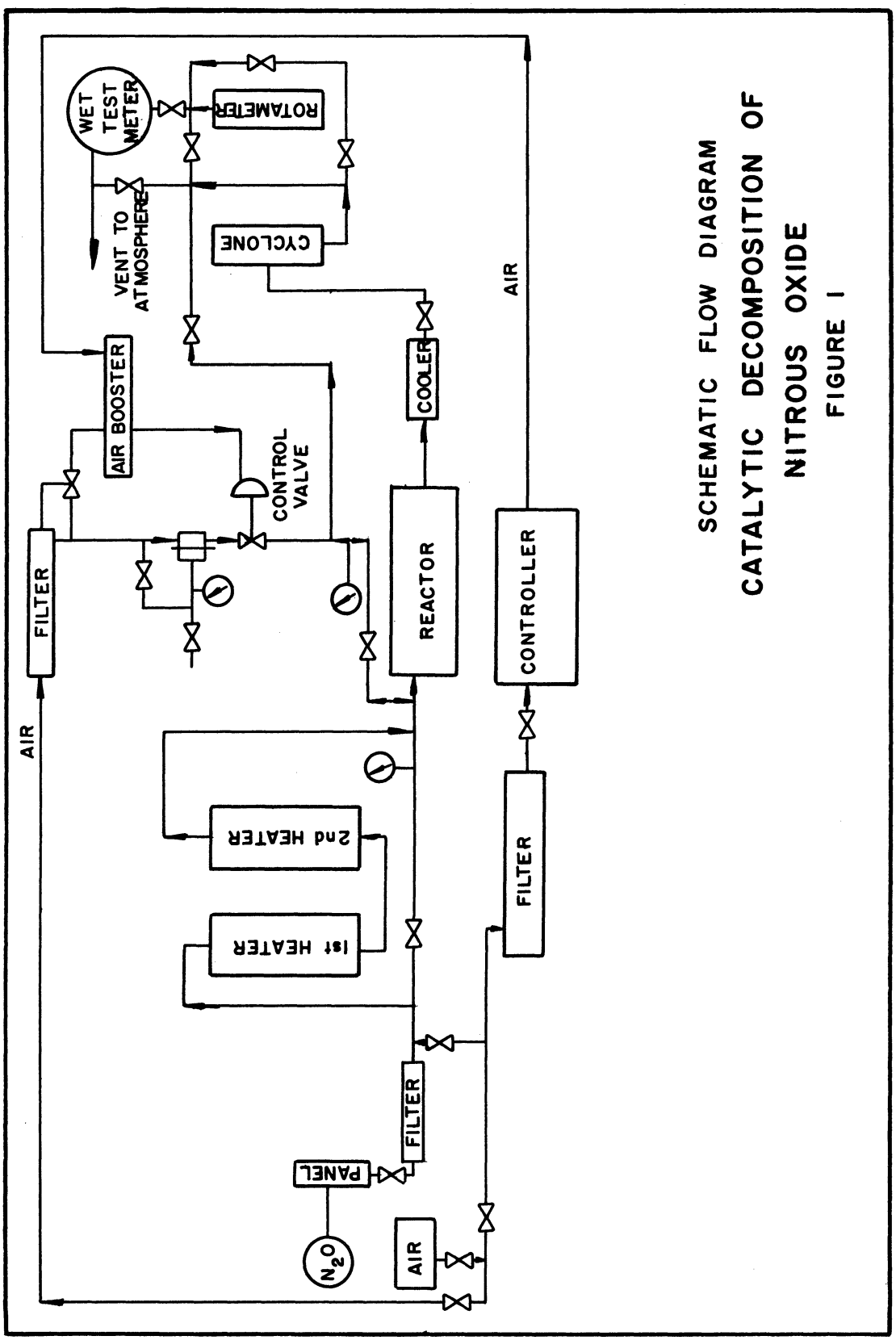
An extensive literature survey indicated that there was considerable diagreement concerning the appropriate values for the thermal conductivities and interphase heat transfer coefficients which must be used in these equations. Since the predictions from the computer solution are sensitive to small changes in these conductivities, it was decided to select empirically the values which could be used to match the predicted behavior of the FBTR with the experimentally observed behavior and compare these results with the literature.

Experimental

A FBTR was constructed and operated, and experimental data were obtained for the purposes of making the comparison with the behavior of the reactor as predicted on the basis of the mathematical model.

The equipment shown in Figure 1 was designed so that air or nitrous oxide could be fed through a gas heating system and into the reactor. The catalytic decomposition of N_2O over Mn_2O_3 was chosen for the investigation since data are available. Except for the need to activate the catalyst there apperared to be few anomalies associated with this reaction which would impede the extrapolation of the data over a moderate temperature range.

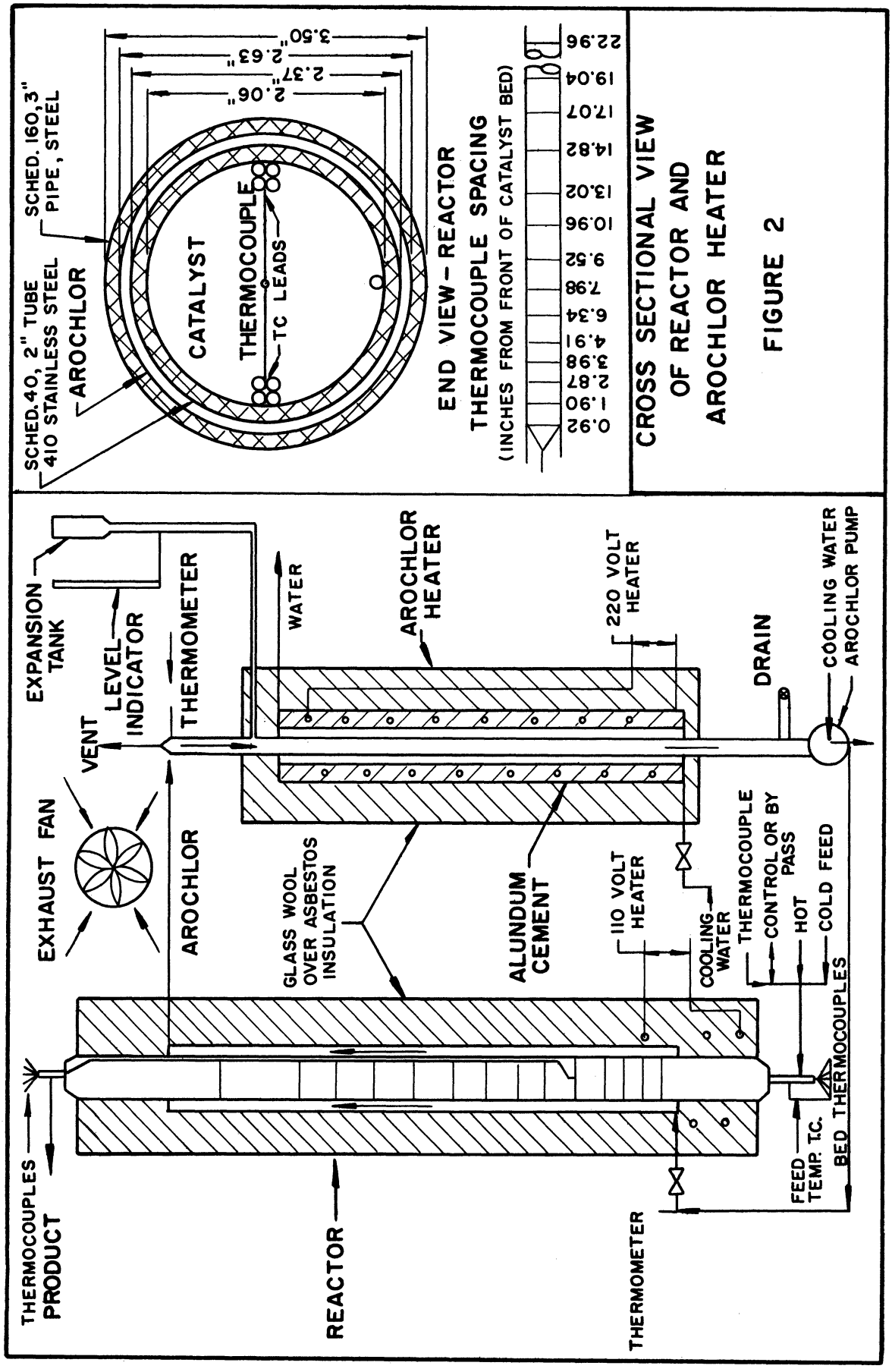
The reactor shown in Figure 2 was made from SAE 410 stainless steel, 2.375" ID and 36" long. This steel is substantially free of Ni, since NiO is a catalyst for the decomposition of the nitrous oxide. A jacket was constructed around the reactor tube and can be maintained at constant temperature with circulating chlorinated byphenyl.



SCHEMATIC FLOW DIAGRAM

CATALYTIC DECOMPOSITION OF NITROUS OXIDE

FIGURE I


SCHED. 160, 3" PIPE, STEEL
SCHED. 40, 2" TUBE 410 STAINLESS STEEL
AROCHLOR
CATALYST
THERMOCOUPLE
TC LEADS
3.50"
2.63"
2.37"
2.06"
END VIEW - REACTOR
THERMOCOUPLE SPACING
(INCHES FROM FRONT OF CATALYST BED)
0.92
1.90
3.98
4.91
6.34
7.98
9.52
10.96
13.02
14.82
17.07
19.04
22.96
CROSS SECTIONAL VIEW
OF REACTOR AND
AROCHLOR HEATER
FIGURE 2
EXPANSION TANK
LEVEL INDICATOR
THERMOMETER
VENT
WATER
AROCHLOR HEATER
220 VOLT HEATER
DRAIN
COOLING WATER
AROCHLOR PUMP
EXHAUST FAN
AROCHLOR
GLASS WOOL OVER ASBESTOS INSULATION
ALUNDUM CEMENT
110 VOLT HEATER
COOLING WATER
THERMOCOUPLE
CONTROL OR BY PASS
HOT
COLD FEED
THERMOCOUPLES
PRODUCT
REACTOR
THERMOMETER
FEED TEMP. T.C.
BED THERMOCOUPLES

The reactor centerline temperature was measured using the circuit shown in Figure 3 by 14 chromel-alumel thermocouples placed along the centerline of the catalyst bed. The thermocouple leads were connected to the gold plated contacts of a rotating switch, which sent the thermocouple outputs sequentially to the vertical scale of an oscilloscope. The oscilloscope traces were photographed and the data transcribed by enlarging the photographs and converting the millivolt readings to temperatures with a nomographic scale.

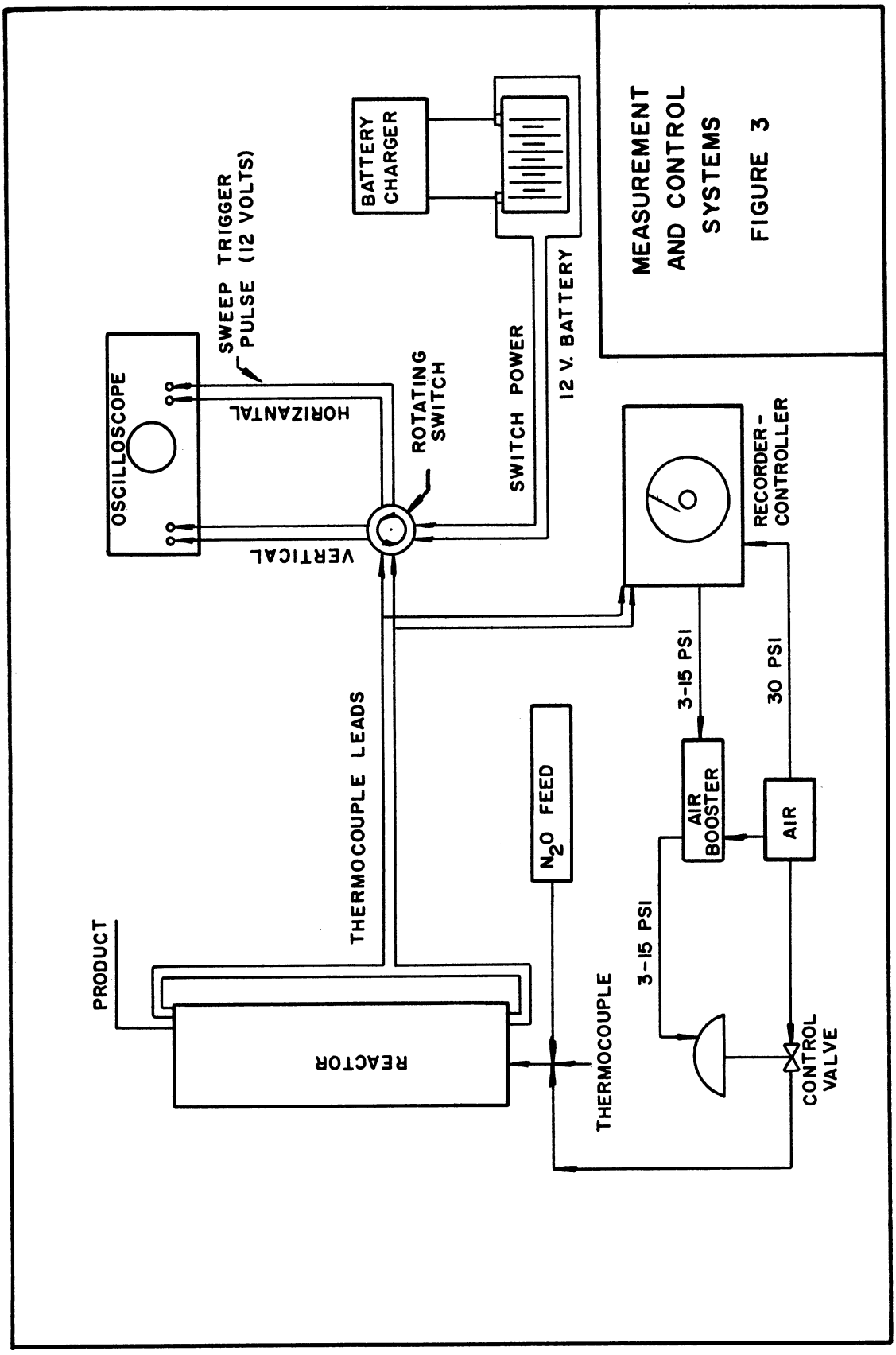
The catalyst was prepared from $MnCO_3$, oxidized to Mn_2O_3 and formed into pellets 1/8" dia. x 1/8" long. The reactor was packed to a length of two feet with catalyst pellets.

A total of 14 runs were made under various conditions of gas flow rate, reactor wall temperature, and reactor inlet temperature.

Correlation of Results

The various mechanisms which contribute to the radial heat transfer were identified and information from the literature was used insofar as possible to evaluate the various components. In the fluid phase, the various radial heat transfer mechanisms are:

1. Molecular conduction in the fluid.
2. Turbulent diffusion in the fluid.
3. Radiation between neighboring voids.
4. Gross radial flow of fluid.
5. Large scale fluid convection.


MEASUREMENT AND CONTROL SYSTEMS
FIGURE 3
BATTERY CHARGER
SWEEP TRIGGER PULSE (12 VOLTS)
OSCILLOSCOPE
HORIZANTAL
VERTICAL
ROTATING SWITCH
SWITCH POWER
12 V. BATTERY
RECORDER-CONTROLLER
3-15 PSI
30 PSI
AIR BOOSTER
AIR
N_2O FEED
THERMOCOUPLE LEADS
PRODUCT
REACTOR
THERMOCOUPLE
3-15 PSI
CONTROL VALVE

In the solid, the various heat transfer mechanisms are:

6. Radiation between pellets.
7. Conduction through points of contact of the pellets.
8. Solid-fluid-solid series conduction through points of contact of the pellets.
9. Solid-fluid-solid series heat transfer by convection between adjacent pellets.

Under the conditions of operation in this work, mechanisms 3, 5, 7 and 9 are believed to be insignificant. Therefore, for the solid phase

$$k_e' = k_r + k_p + k_{series}$$

where the radiation component of heat transfer is given by

$$k_r = 0.00173 \cdot 4\, d_p \epsilon \left(\frac{\delta}{2-\delta}\right)\left(\frac{1.8\, T_{avg}}{100}\right)^3$$

d_p = 1/8" = particle diameter

ϵ = void fraction

δ = 0.90 = emissivity of the pellets

$T_{avg} = (T_{wall} + T_{bed})/2$, °K

and is attribute to Damkoehler, as reported by Smith[2]. Conduction through points of contact has been considered by Wilhelm et al.[4] and this correlation is

$$\log_{10} k_p = -1.76 + 0.0129\, k_s/\epsilon$$

k_s = 0.50 Btu/hr ft °F = thermal conductivity of the pellets

The last term, k_{series}, had to be estimated from the empirical fit of the data, using a first approximation following Churchill and Gorring(5).

For the fluid phase

$$k_e = \epsilon k_c + k_{td}$$

where

k_c = the molecular thermal conductivity of the fluid

$k_{td} = G\, C_p\, d_p/Pe_h$

The Peclet number for heat transfer, Pe_h, was determined from the empirical fit of the experimental data.

The interphase heat transfer coefficient, h , was obtained from the Colburn equation

$$h = h_o\, C_p(\mu/d_p)^{0.4}\, G^{0.6}/(N_{Pr})^{2/3}$$

where the coefficient h_o was determined from the empirical fit of of the experimental data.

The empirical fit of the data was best when

k_{series} = 0.16 Btu/hr ft °F

Pe_h = 11

h_o = 0.15 Btu/hr ft^2 °F

The operating conditions for the 14 experimental runs are shown in the table along with the absolute average error between the predicted temperatures and the measured temperatures. One representative run, No. 23, is shown in more detail in Figure 4.

Discussion

The absolute average error over all runs was 7.7°C temperature difference between a predicted temperature and a data point. In view of the manner in which the data were taken, the present state of knowledge about heat transfer in packed beds, and the inherent limitations of the mathematical model, the empirical fit of the data with these parameters is adequate.

The empirical parameters obtained from this work can be used for extrapolation to other systems only with extreme caution. The static bed thermal conductivity probably could be extrapolated most satisfactorily by using the model described by Churchill and Gorring[5] or Yagi and Kunii[6].

The value for the Peclet number for heat transfer, Pe_h, which was found is not unreasonable and a correlation by Singer and

TABLE OF EXPERIMENTAL CONDITIONS

RUN NUMBER	FEED TEMPERATURE CENTIGRADE		WALL TEMPERATURE CENTIGRADE	FLOW RATE LB/HR. FT. SQ.		GAS	ABSOLUTE AVERAGE ERROR
	INITIAL	FINAL		INITIAL	TRANSIENT		
23	349.	258.	278.	210.	198.	Air	5.6
24	492.	363.	320.	218.	218.	Air	9.1
26	274.	170.	104.	240.	214.	Air	9.0
27	160.	240.	104.	214.	214.	Air	7.2
28A	382.	273.	280.	256.	258.	Air	8.2
28B	261.	375.	291.	251.	232.	Air	5.9
30A	441.	280.	304.	220.	224.	Air	7.1
30B	274.	373.	313.	224.	220.	Air	7.1
31	314.	198.	186.	194.	220.	Air	10.1
32A	271.	168.	183.	225.	096.	Air	8.3
32B	168.	234.	196.	110.	225.	Air	5.5
33A	284.	312.	095.	137.	137.	Air	12.0
33C	254.	126.	094.	073.	202.	Air	5.1
40	393.	320.	305.	178.	370.	Air	12.8
42A	292.	385.	313.	270.	270.	N_2O	-
42B	388.	345.	310.	400.	123.	N_2O	-
43A	427.	439.	292.	168.	370.	N_2O	-
43B	423.	344.	352.	370.	053.	N_2O	-
44A	444.	500.	316.	213.	213.	N_2O	-
45	453.	300.	316.	213.	213.	N_2O	-

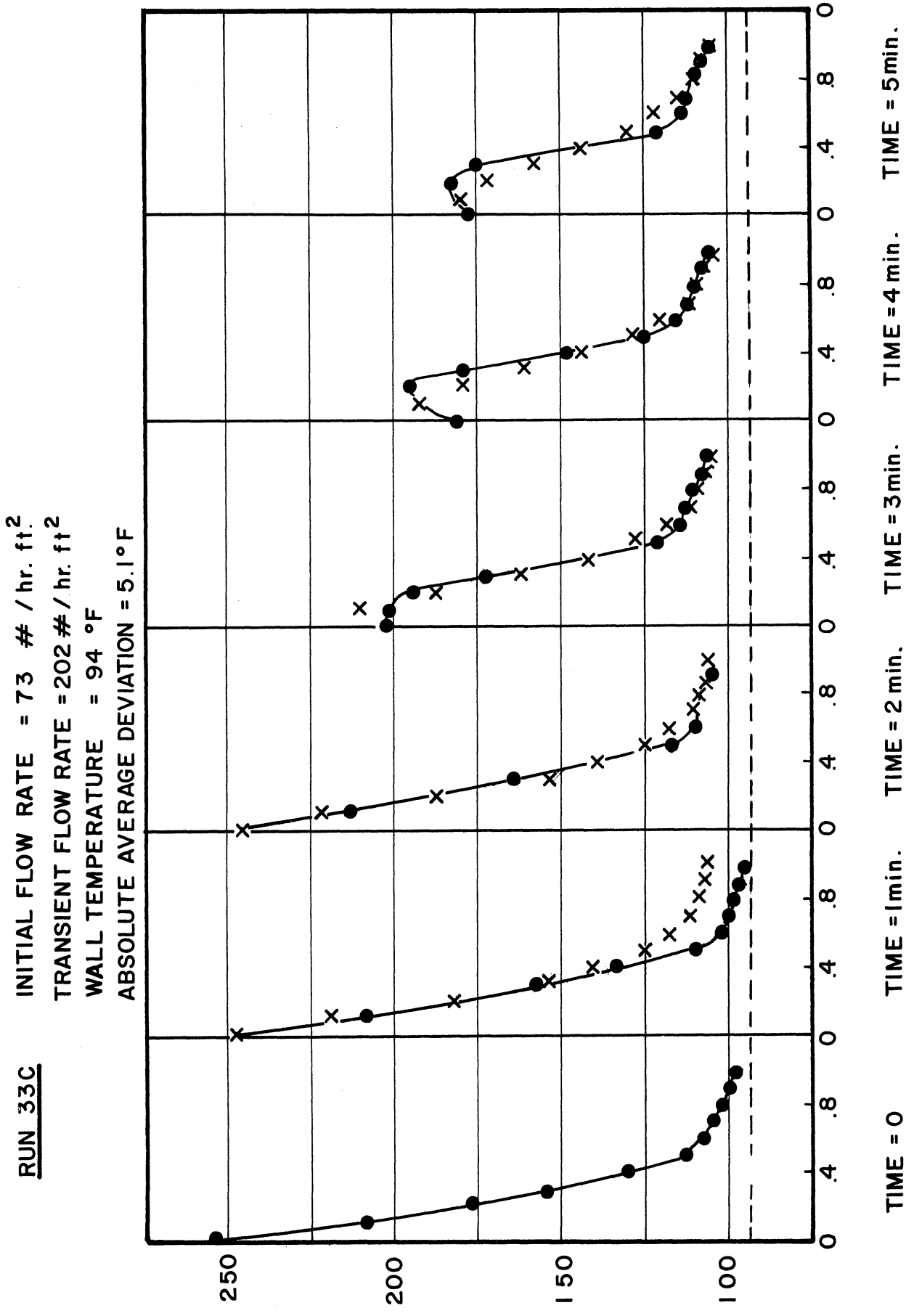

RUN 33C
INITIAL FLOW RATE = 73 # / hr. ft.²
TRANSIENT FLOW RATE = 202 # / hr. ft²
WALL TEMPERATURE = 94 °F
ABSOLUTE AVERAGE DEVIATION = 5.1° F
250
200
150
100
0
.4
.8
0
TIME = 0
TIME = 1 min.
TIME = 2 min.
TIME = 3 min.
TIME = 4 min.
TIME = 5 min.

FIGURE 4

Wilhelm[7] relating Pe_h to d_p/D_t and particle Reynolds number can be used.

The proportionality constant in the interphase heat transfer coefficient correlation should not be used in systems dissimilar to the one of this work, for which it was derived. However, Bowers and Reintjes[8] have presented a correlation for h_c as a function of d_p and temperature which predicts a value sufficiently close to that which was needed in this work to give support for using this correlation for making predictions for other systems.

These empirically derived constants were then used in this mathematical model to predict the behavior of the FBTR under conditions of run 44 wherein N_2O was being decomposed. The predictions followed the form of the experimental data, but not the position. On close examination, it was apparent that the reactor bed temperature was falling due to a slight drop in feed temperature in the first 0.2 feet, while the hot spot was developing at a point about 0.4 feet from the entrance. This combination is explainable only if the catalyst at the entrance of the bed is inactive.

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