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CHEMICAL REACTOR ANALYSIS PROGRAM (TCHREACT)

F. I. Honea, Development Division
and
T. R. Birch, Systems Division

DEVELOPMENT DIVISION

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CHEMICAL REACTOR ANALYSIS PROGRAM
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F. I. Honea, Development Division

and

T. R. Birch, Systems Division

The purpose of this activity is to develop a computer program for determining safe operating parameters for exothermic chemical reactions.

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CHEMICAL REACTOR ANALYSIS PROGRAM

(TCHREACT)

SUMMARY

The synthesis of many chemical compounds produces potentially dangerous exothermic reactions. The FORTRAN IV program described herein employs analytical techniques for the calculation of the batch temperature in a chemical reactor as a function of time. The program includes provisions for calculating (a) total batch and mass volume, (b) coolant and batch average thermodynamic properties, (c) heat transfer coefficients for the batch, wall, coolant, and the overall "U" value, and (d) reaction rates for zero through 3rd order reactions. The program is to be used for determining operating criteria (coolant flow rate, reactant feed rate, agitator speed, etc.) for maintaining batch temperatures at a safe level for processes with high exothermic heats of reaction or mixing.

1.0 PROGRAM DESCRIPTION

A chemical reactor is basically a vessel for mixing and retaining a mixture during a chemical reaction. Most of these vessels include (a) baffles and an agitator, and (b) an insulated jacket. The agitator is used to assure uniform reaction and to prevent concentrated local violent reactions, and the jacket is used to control the temperature of the reaction. The majority of reactor vessels are of the vertical model as shown in Fig. 1. For most modes of operation an exothermic reaction is carried out in batches with one or more reactants in solution poured into the reactor before another more potent reactant or catalyst is added to the batch in the reactor.

The mixing and chemical reactions of materials which generate an exothermic heat of reaction can create conditions of hazardous, high temperature operation known as thermal runaway. If the heat generated is sufficient, the reacting materials may, for example, vaporize and give off toxic fumes or explosive vapors which in turn may ignite. Because this dangerous potential exists, adequate controls must be provided and analyses must be made to assure that temperature rise is held to a safe level. In addition, the control of the temperature rise may be desirable to optimize the yield at nearly isothermal conditions.

The conditions for thermal runaway to exist can be controlled by means of any one of several parameters such as the reactant feed rate, the agitator shape and speed, the concentration of reactants, and the coolant flow rate and temperature. A computer program has been designed so that all of these parameters may be entered as input data for the calculation of the batch temperature as a function of time. A proper selection of operating parameters will lead to the desired control of the batch temperature and will effectively indicate safe operating conditions for the actual pilot-plant synthesis.

Fig. 1. Typical Chemical Reactor

2.0 METHOD OF SOLUTION

2.1 GENERAL

A computer program has been written in FORTRAN IV for implementation on the IBM 360/40. Conversion to other smaller computers and program languages is possible since storage requirements are minimal.

The basic program flow chart given in Fig. 2 indicates the major calculations and loops. The program begins with the summation of the batch mass and volume and the calculation of the average thermodynamic properties for the batch (2.2). The heat transfer coefficients are then calculated (2.3) if not given as input data. Following this, the program calculates reaction rates, if present, for zero or higher order reactions (2.4). The heat transfer coefficients and reaction rate (2.5) are used in computing the batch temperature. And, finally, the time is stepped up and calculations (2.3) through (2.5) are repeated for the next time interval. Added provisions are included for controlling the amount of temperature rise in a time interval and for setting different calculation and printout time intervals for each specified set of time limits.

2.2 CALCULATION OF BATCH MASS, VOLUME AND THERMODYNAMIC PROPERTIES

The masses and thermodynamic properties for up to five constituents in the batch and two constituents in the feed can be included in the input data (discussed in Section 3.0). The initial total mass is calculated by summing the number of specified batch constituent masses. The initial batch volume is also calculated by summing the mass of each constituent divided by its density.

Thermodynamic properties for the initial batch, such as thermal conductivity, viscosity, and specific heat, are determined by use of a mass-averaging technique for the initial batch constituents (Equation 1).

$$\text{Average Property} = \frac{\sum_{N=1}^N (\text{Mass} \times \text{Property})}{\text{Total Initial Mass}}, \quad N = \text{Number of Reactants} \quad (1)$$

The values obtained are not accurate for some solutions and reactions; however, this method of averaging provides estimates which quite often will be close to the actual values. The specific heat values for each constituent include two constants to provide a linear variation with temperature. The initial batch density is calculated separately by dividing the initial batch total mass by the total volume calculated previously. As the time increases and the amount of feed mass in the batch increases, the batch mass, volume and thermodynamic properties are recalculated by adding the mass-averaged values of the added feed constituents.

Fig. 2. Chemical Reactor Analysis (TCHREACT) Computer Flow Diagram

2.3 CALCULATION OF HEAT TRANSFER COEFFICIENTS

The program offers an option for calculation of the heat transfer coefficient for the batch, wall, and coolant and the resulting overall coefficient, U. If a value of U is unknown, an input value of U = 0.0 into the program will initiate the calculation routine. The equations for the batch and coolant coefficients have been described in a previous report [2].

2.3.1 Calculation of Batch Liquid Heat Transfer Coefficient

The equation for the heat transfer coefficient, h_b , for agitated vessels with an internal cooling coil or external cooling jacket is:

$$h_b = a \frac{k}{D_r} \left(\frac{D_a^2 N \rho}{\mu} \right)^{2/3} \left(\frac{C_p \mu}{k} \right)^{1/3} \left(\frac{\mu}{\mu_w} \right)^{0.14} \quad (2)$$

where

- a = agitator constant
- C_p = specific heat (batch)
- D_a = agitator diameter
- D_r = vessel internal diameter
- k = thermal conductivity (batch)
- N = agitator velocity
- ρ = density (batch)
- μ = batch viscosity
- μ_w = batch viscosity at the wall

The value of "a" has been determined [3] to be

- a = 0.87 paddle agitator
- a = 1.50 turbine agitator
- a = 0.83 propeller agitator

for internal cooling coils, and

- a = 0.36 paddle agitator
- a = 0.62 turbine agitator
- a = 0.54 propeller agitator
- a = 0.46 anchor agitator

for external cooling jackets.

The Sieder-Tate viscosity correction, $(\mu/\mu_w)^{0.14}$, in Equation 2 is not included in the program since the viscosity variation with temperature at the wall is not included. This correction factor is negligible in relation to the overall transfer coefficient, U, for many batches, especially for small temperature changes.

2.3.2 Wall Thermal Conductivity

The wall thermal conductivities and thicknesses for the most popular chemical reactors are listed in Table I. The data on wall thickness and some of the thermal conductivity data has been obtained from [3] and [4].

Table I Wall Thermal Conductivity

Material	Thickness (in)	Conductivity, k (Btu-in/sq ft- F-hr)	Total (k/X) (Btu/ F-hr)
Glass, Pyrex Tube	.09375	8.0	85.3
Glass-Lined Glass	.06	6.5	108
Steel	.688	30.0	523 89.5
Stainless Steel (100-Gallon Size) Type 316	.25	8.9	356

2.3.3 Coolant Heat Transfer Coefficient

For the coolant flow through the spiral tube heat exchanger or coolant jacket, the heat transfer coefficient can be estimated from the following equations:

$$h_c = 0.028 \frac{K}{D} \left(\frac{m}{\mu D} \right)^{.8} \left(\frac{C_p \mu}{k} \right)^{1/3} \left(\frac{\mu}{\mu_w} \right)^{.14} \left[1 + 3.54 \frac{D}{D_t} \right] \quad (3)$$

for $\frac{4m}{\pi \mu D} > 2100$ (turbulent flow)

or

$$h_c = 0.94 \left[\left(\frac{m}{\mu D} \right) \left(\frac{C_p \mu}{k} \right) \right]^{1/3} \left(\frac{\mu}{\mu_w} \right)^{.14} \quad (4)$$

for $\frac{4m}{\pi \mu D} < 2100$ and $\frac{L}{D} > 10$ (laminar flow)

where h_c = coolant heat transfer coefficient

L = flow length

m = mass flow rate

D = tube or hydraulic diameter

D_t = flow path turn diameter

C_p, μ, μ_w, k = coolant thermodynamic properties

Equation 3 is based on the Reynold's analogy for fully-developed, turbulent tube flow with the factor (.028) determined empirically. The ratio of $(\mu/\mu_w)^{.14}$ is the Sieder-Tate correction for wall viscosity and the ratio

$\left[1 + 3.54 \frac{D}{D_t} \right]$ is a correction for the spiral flow effect as introduced

by Jacob [5]. Equation 4 for laminar flow was theoretically derived by Graetz [6] with the constant determined empirically and with the Sieder-Tate correction for viscosity.

In the program, the Sieder-Tate correction for the coolant flow has again, as for the batch, been assumed to be equal to 1.0. However, Marshall and Yazdani [7] have utilized a Dittus-Boelter type change in the Prandtl number exponent of 0.3 for cooling and 0.4 for heating of the coolant. This change in exponent can correct for wall effects and may be incorporated into a later version of the program.

2.3.4 Calculation of Overall Heat Transfer Coefficient

The overall heat transfer coefficient is computed based on the series heat transfer resistance concept as

$$U = \frac{1}{\frac{1}{h_b} + \left(\frac{x}{k} \right)_w + \frac{1}{h_c}} \quad (5)$$

Table II Summary - Overall Heat Transfer Coefficients [2]

	Heat Transfer Area (Sq Ft)	Agitator Speed (rpm)	Coolant Reactant	Coolant Flow Rate (lb/hr)	Measured LMTD (Average) (F)	U - Coefficient (Btu/hr- F-Sq Ft)		
						Measured	Estimated	Literature
200-Liter Glass, (Corning)	7	Hollow Tube, 6" D. 188	None Ethyl-Alcohol	0	23	2.6 ^(c)		
			Water Water	3600	40	67 ± 6	69.3	
			Hot Water Water	3590	48	72 ± 7	70.2	
			Steam Water		91	72 ± 7	69.8	66.3 ^{(a)*}
100-Gallon, Glass-Lined Steel (Pfaudler)	30.27	Anchor, rpm Varied, not Significant	None Ethyl-Alcohol	0	23	0.53 ^(c)		
			Water Water		41	62 ± 6	57.3	50-60 ^(b)
			Steam Water		79.6	63 ± 8	74.3	66.5 ^(a)
200-Gallon, Glass-Lined Steel (Pfaudler)	39.35	Anchor, Varied rpm ~ 100	None Ethyl-Alcohol	0	23	0.53 ^(c)		
			Water Water	9620	66.2	55 ± 5	57.3	50-60 ^(b)
			Steam Water		131	58 ± 7	74.3	66.5 ^(a)
100-Gallon ** Stainless Steel (Pfaudler)	24.2	Turbine, Operating	Water Water			**	88	
			Steam Water			**	134	116 ^{(a)*}

(a) The Pfaudler Company, Bulletin 1023 [4]

(b) Perry, Chemical Engineers Handbook [5]

(c) [9]

* Corrected to new wall thickness

** No experimental data

Typical values for U as measured and as calculated from equation 2, 3, and 5 are shown in Table II. The calculated values of U are in good agreement with the measured values for all cases (with a maximum deviation of 12% from the quoted literature values).

2.4 REACTION RATE EQUATIONS

The program includes three reaction rate equations - zero order, Nth-order and second-order.

Zero-order rate:

$$\frac{\partial C}{\partial t} = K \cdot \exp [-\lambda t - E/(R \cdot TB)] \quad (6)$$

Nth-order rate:

$$\frac{\partial C}{\partial t} = K \cdot C^n \cdot \exp [-E/(R \cdot TB)] / V^{n-1} \quad (7)$$

Second-order rate:

$$\frac{\partial C}{\partial t} = K \cdot C_b \cdot C \cdot \exp [-E/(R \cdot TB)] / V \quad (8)$$

where

$\partial C / \partial t$ = reaction rate, (mass)
 C = concentration of feed (mass)
 C_b = concentration of batch reactant (mass)
 E = reaction energy
 n = order of reaction
 R = gas constant
 K = program constant (reaction)
 TB = batch temperature
 t = time
 V = batch volume
 λ = reaction rate constant

Equation 6 is automatically selected if the order is zero and Equation 8 is selected if the order is four. The constant, K, for Equations 6, 7, and 8 is dependent on the reaction rate constant or the feed rate and conversion factors. The reaction rate constant can be entered directly into Equation 6 for first-order reactions as λ or Equation 7 can be used with $n = 1$. The expression $\exp [-E/(R \cdot TB)]$ in the rate equations is an Arrhenius-type [8] correction factor for the reaction temperature.

To control the reaction, the concentration has been entered as a mass differential between the total feed mass and the total mass previously reacted. Controls have been introduced by designating (a.) a maximum feed mass which is the limit amount to be metered into the reactor and (b.) a reacted mass limit which cuts off the reaction after a stoichiometric amount of feed has been reacted. By this method, a larger feed than required for completion of the reaction can be introduced.

Most reactions for explosives synthesis are in solution with a bimolecular reaction such as $aA + bB \longrightarrow cC + dD$. For these reactions, $n = 2$, and a value for K can usually be estimated from data presented in the literature. Moelwyn - Hughes [8] lists a theoretical value of $A = 3.5165 \times 10^{13}$ cu. ft/lb-hr for many bimolecular reactions where $\lambda = A \exp \cdot [-E/(R TB)]$. For typical values of $E = 22,000$ cal/gm and $TB = 600$ R, the reaction rate constant becomes $\lambda = 58.9$ cu ft/(lb-mole·hr)--which can be input to the program with $E = 0$ as $K = 58.9/MW$ (MW = molecular weight of batch reactant). Either Equation 7 with order 2 or Equation 8 can be used for bimolecular reactions. However, Equation 8 should be more accurate for most cases since the feed reactant concentration and the batch concentration differ appreciably.

Equation 7 is useful when the feed reactant is very reactive; then the batch reactant concentration may not be critical. The reaction rate constant, λ , for the first-order reaction can be estimated as presented in Fig. 3, providing an approximate time is known for the completion of the reaction or for reaching the maximum batch temperature. The time for reaching the peak batch temperature will be close to the same time as that required for completion of the reaction if the heat of the reaction is directly related to the mass reacted.

If the feed reactant is extremely reactive, the feed rate may control the reaction rate. For this condition, a zero-order reaction may be used (Equation 6) with,

$$K = \text{feed rate} \quad (9)$$

2.5 BATCH TEMPERATURE

The energy balance for the batch reactor should include at least three equations: (1) heat transfer from or to the coolant from the batch, (2) heat transfer and energy storage in the vessel walls, and (3) energy transfer, reaction and storage in the batch. However, for the chemical reactors used at Pantex, the high coolant flow rates result in high film coefficients (~ 1300 Btu/hr. sq. ft. - F) and a small temperature rise (~ 5 F) in the coolant. Thus, the coolant temperature and coil or vessel wall is held essentially constant during the reaction. With use of an estimated constant average temperature for the coolant, the three energy equations can be reduced to one equation for the batch:

$$(C_{pm})_B \frac{\partial(TB)}{\partial t} = Q \frac{\partial C}{\partial t} - U \cdot SA \cdot (TB - TC) + (C_{pm})_f (TB - TF) \quad (10)$$

where $(C_{pm})_B$ = batch specific heat $\cdot$ mass
 $(C_{pm})_f$ = specific heat $\cdot$ rate (feed)
 $\frac{\partial(TB)}{\partial t}$ = temperature rate (batch)

Fig. 3. First-Order Reaction Rate Constant Estimate Curve

Q = chemical heat
 SA = heat transfer area
 TB = temperature (batch)
 TC = temperature (coolant)
 TF = temperature (feed)

For computational purposes, Equation 10 has been rearranged and converted to a linear, stepped-time equation:

$$TB_{N+1} = TB_N + \frac{\Delta t}{(mc_p)_B + (mc_p)_f} \cdot \left[Q \cdot \frac{\partial C}{\partial t} - U \cdot SA \cdot (TB_N - TC) - (C_p \dot{m})_f \cdot (TB_N - TF) \right] \quad (11)$$

where $(mc_p)_f$ = specific heat $\cdot$ mass of total added feed at time, t .

Δt = time increment

At the time when the reaction is completed and the feed is stopped, the reaction and feed cooling terms, $Q \cdot \frac{\partial C}{\partial t}$ and $(C_p \dot{m})_f \cdot (TB_N - TF)$, respectively, are eliminated and Equation 11 is replaced by a simple cooling equation:

$$TB_{N+1} = TB_N - \frac{\Delta t}{(mc_p)_B + (mc_p)_f} [U \cdot SA \cdot (TB_N - TC)] \quad (11)$$

Thus, the program can estimate the complete temperature profile for a reaction upward through the reaction, to a peak and downwards with cooling.

If, after any time step, the difference in two successive calculations of batch temperature exceeds the specified maximum, the step size is reduced in half, and the program backs up in time and repeats the calculation based on the new step size. Again, if the new batch temperature difference exceeds the specified maximum, the step size is reduced in half once more, and so on until the process is repeated up to a maximum of four times provided the specified maximum is exceeded each time. If at this point the batch temperature still exceeds maximum, the program will print a message and will halt.

3.0 INPUT INSTRUCTIONS

3.1 INPUT DATA

The input information required by the program has been arranged into six groups of data (see data form on next page). These groups include:

- (1) problem parameters, (2) feed data, (3) reactant data, (4) coolant data, (5) vessel and agitator data, and (6) miscellaneous data.

Although any consistent set of units can be utilized, all conversions within the present program are for use with engineering units-Btu, feet, pounds, hours, F. All program parameters except those specifically designated on the data form must be entered in these engineering units. Note, also, parameters with an asterisk require integer values that must be entered at the extreme right of each entry field. Here the abbreviation "cc" will be used to refer to card column.

3.1.1 Card 1, Problem Identification

Eighty columns of identification information such as problem title, date, name, etc. are provided.

3.1.2 Card 2, Problem Parameters

Type of Reaction (ITYPE) - Enter into cc 10 the type, or in most instances, the order of the reaction as below.

<u>ITYPE</u>	<u>Rate Equation</u>	<u>Order</u>
0	(6)	0
1, 2, or 3	(7)	1, 2, or 3
4	(8)	2
5 and up	Unacceptable	_____

Feed Constituents (NOF) - Enter the number of feed constituents in cc 20. A maximum of two may be used (such as a feed reactant and a solvent). This number determines the amount of feed data cards to be read in (see Paragraph 3.1.3).

CHEMICAL REACTOR ANALYSIS

PROG. NO. 406-001-130-000

PROBLEM IDENTIFICATION

Problem Parameters							
Type of Reaction*	No. of Feed Const.*	No. of Reactant Const.*	Max Batch Temp Diff	Initial Time	Finish Time	Print Time Factor	No. of Ranges
1	10	20	30	40	50	60	70
End of Range 1	Time Step	End of Range 2	Time Step	End of Range 3	Time Step	End of Range 4	Time Step
1	10	20	30	40	50	60	70
Temp. (°F)	Initial Mass	Maximum Mass	Feed Data				
1	10	20	30				
Feed Rate	Thermal Conductivity	Specific Gravity	Viscosity	SPECIFIC HEAT COEFFICIENTS			
				A	B		
1	10	20	30	40	50	60	
Temp. (°F)	Initial Mass	Maximum Mass	Reactant Data				
1	10	20	30				
Comp. Mass	Thermal Conductivity	Specific Gravity	Viscosity	SPECIFIC HEAT COEFFICIENTS			
				A	B		
1	10	20	30	40	50	60	
Coolant Data							
Temp (°F)	Flow Rate	Thermal Conductivity	Specific Gravity	Viscosity	Specific Heat	Dia. Tube	Spiral Dia of Tube
1	10	20	30	40	50	60	70
Vessel and Agitator Data							
Dia. Agitator	Dia. Vessel	Agitator RPM	Vessel Thermal Conductivity	Vessel Thickness	Initial HT Surface Area	Delta HT Surface Area	Paddle Constant
1	10	20	30	40	50	60	70
Miscellaneous Data							
Reaction Energy	Heat of Reaction	Reaction Rate Const.	Program Const.	Overall HT Const.			
1	10	20	30	40	50		

*Integer values (right justified in field)

Reactant Constituents (NOR) - Enter the number of reactant constituents in cc 30. A maximum of five batch constituents may be specified. For a second-order reaction using Equation 8, the reactant in the batch must be entered as the first batch constituent in the reactant data cards (see Paragraph 3.1.4).

Maximum Batch Temperature Difference (TMAX) - This entry sets the maximum allowable temperature increase for each time interval. It must be specified in cc 31 to 40. If the value is exceeded, the time interval will be halved and iteration repeated up to a maximum of four times.

Initial Time (IT) - Enter into cc 41-50 the initial or start time of the reaction in hours (usually 0.0).

Finish Time (FINTIM) - Enter into cc 51-60 the finish or end time for the reaction in hours.

Print Time Factor (RATIO) - Select the edit or printout time desired as a multiple of the calculation time step (1., 10., etc.). Enter this value in cc 61-70.

Number of Ranges (N) - Enter into cc 80 the number of desired values for the time step. This allows the selection of up to four time ranges during the reaction so that the calculation time step can be smaller during critical periods of the reaction.

Time Step and Range Card - Beginning sequentially, enter the end of the first time in hours and the corresponding time step in minutes for that range inclusive into cc 1-10 and cc 11-20, respectively. Proceed similarly with the second set of values into cc 21-30 and cc 31-40, and continue on until the number N has been satisfied.

3.1.3 Card 3, Feed Data

Temperature (TF) - Enter into cc 1-10 the temperature (F) of the feed constituents prior to feed. This value is constant for a run.

Initial Mass (MFT) - Enter into cc 11-20 the initial mass in pounds of feed for dumped or prior reacted feed (usually set as 0.0).

Cards 3A-3B

Feed Rate - Fill out as many cards as specified by NOF (see Paragraph 3.1.2). Enter the rate of feed of the one or two feed constituents (pounds/hour) into cc 1-10.

Thermal Conductivity, Specific Gravity, Viscosity, Specific Heat (A & B) - These thermodynamic properties for a feed constituent must be specified in cc 11-20, cc 21-30, cc 31-40, cc 41-50, and cc 51-60 in the order as listed above. All properties are in Btu, hours, pounds, feet, F except specific gravity (no units). The "A" value for specific heat is a constant; the "B" value may be used for linear variations in specific heat with temperature.

3.1.4 Card 4, Reactant Data

Temperature (TR) - Enter into cc 1-10 the temperature (F) of the reactant constituents, (batch) prior to the reaction.

Initial Mass (MR) - Enter into cc 11-20 the inclusion of added mass for the agitator and vessel walls (pounds).

Maximum Mass (MRMAX) - (pounds) This mass is the total mass of the feed which must react to achieve complete reaction with the batch reactant. This mass includes the stoichiometric mass amount of feed reactant plus the proportional amount of the other feed constituent (if any) in the total feed. Enter this value in cc 21-30.

Cards 4A-4E

Component Mass - Fill out as many cards as specified by NOR (see paragraph 3.1.2). Enter the amount of mass in pounds for a component in the batch in cc 1-10. No provision has been made at present for change-over of component masses during the reaction although the mass and heat capacity is continuously corrected for added feed mass. The batch reactant must be the first component.

Thermal Conductivity, Specific Gravity, Viscosity, and Specific Heat (A & B) - These thermodynamic properties for a batch component must be specified in cc 11-20, cc 21-30, cc 31-40, cc 41-50 and cc 51-60 in the order as listed above. All properties are in engineering units except specific gravity which is dimensionless. The specific heat includes provisions for a constant "A" and a linear coefficient of change "B" with temperature. For second order reactions using Equation 8 where ITYPE = 4, the first component must be the batch reactant.

3.1.5 Card 5, Coolant Data

Temperature (TC) - Enter the temperature (F) of the coolant into cc 1-10. This temperature represents an estimated average for the coolant (inlet to outlet plus time variation) for the total reaction run.

Flow Rate (RC) - Enter the flow rate of the coolant (pounds/hour) in cc 11-20.

Thermal Conductivity, Specific Gravity, Viscosity, Specific Heat -

Enter these thermodynamic properties of the coolant in engineering units into cc 21-30, 31-40, 41-50, and 51-60 in the order as listed above. The specific heat is just a single constant value. No properties are necessary if the overall heat transfer coefficient U is specified in cc 41-50 of the miscellaneous data card (see paragraph 3.1.7).

Tube Diameter - Enter the flow diameter (inches) for a coolant passage into cc 61-70. Use the hydraulic diameter if the cross section of the tube is not circular.

Spiral Diameter of Coil - Enter the spiral diameter (inches) for the coolant coils or for the jacket into cc 71-80. (Applies a correction factor for curvature to the heat transfer coefficient).

3.1.6 Card 6, Vessel and Agitator Data

Agitator Diameter - Enter the diameter (inches) of the agitator in cc 1-10.

Vessel Diameter - Enter the diameter (inches) of the vessel or reactor in cc 11-20. This value is the average internal diameter.

Agitator RPM - Enter the rotational speed of the agitator paddle (revolution/minutes) into cc 21-30.

Vessel Thermal Conductivity - Enter the thermal conductivity of the vessel wall (Btu/(hour-feet²- F) into cc 31-40.

Vessel Thickness - Enter the thickness of the vessel wall (inches) into cc 41-50. This value along with that of the thermal conductivity are used to calculate vessel heat transfer or cooling coil heat transfer. Substitute cooling coil conductivity and thickness if internal cooling coils are used for cooling. (See Table I for some values for typical vessels).

Initial HT Surface Area - Enter the initial heat transfer surface area (square feet) of the interior of the vessel in cc 51-60.

Delta HT Surface Area - Enter the incremental heat transfer area (feet²) factor to be added to the initial HT surface area into cc 61-70. The incremental factor is multiplied times the new batch volume at the end of each time step and is added to the previous calculation of surface area.

Paddle Constant - Enter into cc 71-80 a correction factor for the agitator blade shape used in the calculation of the batch heat transfer coefficient (see paragraph 2.3.1 for values of this constant).

3.1.7 Card 7, Miscellaneous Data

Reaction Energy - Enter into cc 1-10 the reaction energy for the Arrhenius-type temperature correction with units of Btu/(pound-mole).

Heat of Reaction - Enter into cc 11-20 the heat of reaction in terms of the feed reactant mass (Btu/pound). This concentration may include another constituent (usually a solvent).

Reaction Rate Constant - (hour^{-1}) - This is a reaction rate constant ($\lambda = \text{LAM}$) as used in the first-order reactions where

$$\frac{\partial c}{\partial t} = \lambda c_0 e^{-\lambda t}$$

Enter this value into cc 21-30.

Program Constant - This constant is used in the reaction rate equations for conversions and reaction rate constants. Enter this value into cc 31-40.

Overall HT Coefficient - Enter into cc 41-50 the value of the overall heat transfer coefficient (Btu/(square feet- F-hour)) (Some representative value may be found in Table II.) For an overall HT coefficient left blank or set to 0., the heat transfer coefficient and overall coefficient are calculated by the program.

3.2 PROGRAM OUTPUT

The printed output for the program includes (a) a summary form of all input variables and (b) a presentation of the computed results. The example printouts of the input variables and results is included in Section 5.0. The summary of input variables is arranged in a format which is similar to the Computer Data Input Form. All parameter values are labeled for identification.

The presentation of computed results begins with the initial values for the batch mass and volume. The results for each printout time are then presented in order on a line as follows: time, batch temperature, batch film coefficient, coolant film coefficient, overall heat transfer coefficient, total feed mass, total reacted feed mass and heat transfer surface area. At the end of the run, the relative maximum and minimum temperatures and their associated times are indicated. If the overall heat transfer coefficient is input ($U \neq 0$), then the batch and coolant film coefficients are not computed and are recorded as "0".

Although the time and batch temperature are the main objective results for the program, the other printout information is useful for checking the heat transfer and reaction rates.

4.0 PROGRAM INFORMATION

This section includes the flow charts, variable name glossary, and program source listing for the TCHREACT program.

4.1 TCHREACT Flow Chart

4.1 (Continued)

4.1 (Continued)

4.1 (Continued)

3

$KB = (P1 + MFT * KFT) / (MB + MFT)$
 $MUB = (P2 + MFT * MUFT) / (MB + MFT)$
 $RH0 = (MB + MFT) / (VB + [MFT / PFT])$
 $CPB = ART + BRT * TB$
 $CPR = (MB * CPB + MFT * CPF2) / (MB + MFT)$
 $HB = (C * KB / DV) * (DA * 2 * RPM * RH0 / MUB)^{2/3} \frac{CPR * MUB^{1/3}}{KB}$
 $RE = 4 * RC / (PI * MUC * DC)$

Yes $RE \leq 2100$

No

$HC = .028 * (RC / MUC * DC)^{.8} * (CPC * MUC / KC)^{1/3}$
 $(1. + 3.54 * DC / DSC) * (KC / DC)$

$HC = .94 * (RC * CPC / DC * KC)^{1/3} * (KC / DC)$

$U = \frac{1.}{1. / HB + XS / KS + 1. / HC}$

2

MR.LT.MRMAX

No

Yes

$TB = TB + (DELT [ISUB] * [-U * SA * (TB - TC)])$
 $/(MB * CPB + MFT * CPF2)$

3

No $ITYPE \geq 1$ Yes

$RATE = RC0N * e^{(-LAM * TIME - E / R / TB)}$

ITYPE EQ. 4

Yes

No

$RATE = \frac{RC0N * (MFT - MR) \frac{ITYPE}{e^{(-E / R / TB)}}}{(VB + \frac{MFT}{PFT})^{ITYPE - 1}}$

$RATE = \frac{RC0N * (MFT - MR) (M1 - M1MR / MRMAX)}{e^{(-E / R / TB)} / (VB + MFT / PFT)}$

4

4.1 (Continued)

4.1 (Continued)

4.1.1 Subroutine Minmax

4.2 PROGRAM DATA NAME GLOSSARY

<u>Data Name</u>	<u>Definition or Comment</u>
AF(I)	Specific heat (constant) for each feed constituent
AFT	Total feed specific heat (constant term)
AR(J)	Specific heat (constant) for each reactant component
ART	Total specific heat of batch (constant term)
BF(I)	Specific heat (linear term) for each feed constituent
BFT	Total feed specific heat (linear term)
BR(J)	Specific heat (linear term) for each reactant component
BRT	Total specific heat of batch (linear term)
C	Paddle constant
CPB	Partial specific heat of batch
CPC	Specific heat of coolant
CPF1	Average specific heat of feed
CPF2	Partial specific heat of batch from feed
CPR	Specific heat of batch
DA	Diameter of agitator
DC	Diameter of coolant coil
DELT(I)	Time step indicator
DELTO(I)	Original time step indicator
DSC	Spiral diameter of coolant coil
DV	Diameter of vessel
E	Reaction energy
FINTIM	Finish time of reaction
HB	Batch heat transfer coefficient
HC	Coolant heat transfer coefficient
ICARD(I)	Alphanumeric input information and problem description
ITYPE	Order of reaction
KB	Thermal conductivity of batch
KC	Thermal conductivity of coolant
KF(I)	Thermal conductivity for each feed constituent
KFT	Total feed thermal conductivity
KR(J)	Thermal conductivity of each reactant component
KS	Vessel thermal conductivity
L	Counter heat transfer coefficient
LAM	Reaction rate constant

4.2 PROGRAM DATA NAME GLOSSARY (continued)

<u>Data Name</u>	<u>Definition or Comment</u>
MB	Total mass of batch
MFT	Initial mass of feed
MFMAX	Maximum allowable mass of feed
M(J)	Mass of each reactant component
MR	Initial mass of reactant
MRMAX	Maximum allowable amount of feed to react
MUB	Viscosity of batch
MUC	Viscosity of coolant
MUF(I)	Viscosity of each feed constituent
MUFT	Total feed viscosity
MUR(J)	Viscosity of each reactant component
N	Number of different time step ranges
NOF	Number of feed constituents
NOR	Number of reactant components
P1	Total thermal conductivity of batch
P2	Total viscosity of batch
PB	Density of reactant
PC	Density of coolant
PF(I)	Density of each feed constituent
PFT	Total feed density
PINC	Print time increment
PR(J)	Density of each reactant component
PTIME	Print time
Q	Heat of reaction
R	Gas constant
RATE	Chemical reaction rate
RATIO	Print time factor
RC	Mass flow rate of coolant
RCON	Program constant
RE	Reynolds number
REND(I)	End of range for each different time step
RF(I)	Mass flow rate for each feed constituent
RFT	Total feed mass flow rate
RHO	Density of batch
RPM	Speed of agitator paddle
SA	Surface area of inside vessel
SAV	Delta surface area factor

4.2 PROGRAM DATA NAME GLOSSARY (continued)

<u>Data Name</u>	<u>Definition or Comment</u>
TB	Temperature of batch
TBF	Temperature of batch for printout (F)
TBLAST	Previous batch temperature calculated
TBMAX	Relative maximum of time-temperature profile
TBMIN	Relative minimum of time-temperature profile
TBNEW	New temperature of batch
TC	Temperature of coolant
TF	Temperature of feed
TI	Start time of reaction
TIME	Time of reaction
TIMIN	Time of relative minimum batch temperature
TIMAX	Time of relative maximum batch temperature
TMAX	Maximum allowable temperature increase of batch
TR	Temperature of reactant
U	Overall heat transfer coefficient
VB	Total volume of batch
V(J)	Volume of each reactant component
XS	Thickness of vessel wall

4.3 Source Listing

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DOS FORTRAN IV 360N-ED-479 3-3

MAINPGM

DATE 02/24/71

TIME

14.21.23

PAGE 0002

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4.3 Source Listing (Cont'd)

DD5 FORTRAN IV 360N-FD-479 3-3

MAINPGM

DATE 02/24/71

TIME

14.21.23

PAGE 0003

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0058      KFT=0.                                RACT 415
0059      MJFT=0.                              RACT 420
0060      PFT=0.                                RACT 425
0061      AFT=0.                                RACT 430
0062      RFT=0.                                RACT 435
0063      MB=0.                                RACT 440
0064      VB=0.                                RACT 445
0065      ART=0.                                RACT 450
0066      RRT=0.                                RACT 460
0067      P1=0.                                RACT 465
0068      P2=0.                                RACT 470
0069      HB=0.                                RACT 471
0070      HC=0.                                RACT 472
0071      L=0.                                 RACT 475
0072      ISUB=1                               RACT 480
0073      IPASS=0                               RACT
0074      PINC=RATIO*DELT(ISUB)                RACT 483
0075      PTIME=0.                             RACT 484
0076      TIME=TI                              RACT 485
0077      TIMIN=TIME                           RACT 490
0078      TIMAX=TIME                           RACT 491
0079      TB=TR                                RACT 495
0080      TBLAST=TB                            RACT 496
0081      TBMIN=TB                             RACT 497
0082      TBMAX=TB                             RACT 498
      C      SAVE STEPSIZE VECTOR
0083      DO 66 I=1,N                           RACT 499
0084      56 DELT(I)=DELT(I)                   RACT 500
      C      CALCULATE TOTALS FOR ALL FEED QUANTITIES
      C      NORMALIZE WITH RESPECT TO THE TOTAL MASS FEED RATE
0085      DO 70 I=1,NDF                         RACT 505
0086      70 RFT=RFT + RF(I)                   RACT 510
0087      DO 75 I=1,NDF                         RACT 515
0088      KFT=KFT + (F(I)*RF(I))               RACT 520
0089      MJFT=MJFT + MUF(I)*RF(I)            RACT 525
0090      AFT=AFT + AF(I)*RF(I)               RACT 530
0091      BFT=BFT + BF(I)*RF(I)              RACT 535
0092      75 PFT=PFT + PF(I)/RF(I)            RACT 540
0093      KFT=KFT/RFT                          RACT 545
0094      MJFT=MJFT/RFT                        RACT 550
0095      AFT=AFT/RFT                          RACT 555
0096      BFT=BFT/RFT                          RACT 560
0097      PFT=1./(PFT/RFT)                    RACT 565
      C      CALCULATE INITIAL BATCH PARAMETERS(FROM REACTANT DATA)
0098      DO 80 J=1,NDR                         RACT 570
0099      V(J)=M(J)/PR(J)                      RACT 575
0100      MB=MB + M(J)                         RACT 580
0101      80 VB=VB + V(J)                      RACT 585
0102      WRITE (IW,91) MB,VB                  RACT 586
0103      91 FORMAT (1H1,'BATCH MASS' =,F8.2/14,'BATCH VOLUME' =,F8.2/1H3,9XRACT 587
      1'BATCH',3X,'BATCH FILM',5X,'COOLANT FILM',3X,'OVERALL',4X,'TOTAL MRACT 588
      2ASS',3X,'REACTED',3X,'HT SURF'/1H,1X,'TIME',3X,'TEMP',3(4X,'COEFFRACT 589
      3ICIENT'),2(4X,'FEED'),' MASS',3X,'AREA'/) RACT 590
0104      PB=MB/VB                             RACT 591

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4.3 Source Listing (Cont'd)

DOS FORTRAN IV 350N-FO-479 3-3	MAINPGM	DATE 02/24/71	TIME 14.21.23	PAGE 0004
0105	DO 85 J=1,NDR			RACT 595
0106	ART=ART + AR(J)*M(J)			RACT 600
0107	BRT=BRT + BR(J)*M(J)			RACT 605
0108	P1=P1 + KR(J)*M(J)			RACT 610
0109	85 P2=P2 + MUR(J)*M(J)			RACT 615
0110	ART=ART/MB			RACT 620
0111	BRT=BRT/MB			RACT 625
	C CALCULATE SPECIFIC HEATS OF FEED			
0112	90 CPF1=AFT + BFT*((TF+TB)/2.)			RACT 630
0113	CPF2=AFT + BFT*TB			RACT 635
	C HAS OVERALL HEAT TRANSFER COEFFICIENT BEEN SPECIFIED AS INPUT			
0114	IF (U.NE. 0.) GO TO 105			RACT 640
	C CALCULATE BATCH THERMAL CONDUCTIVITY,VISCOSITY,DENSITY,SPECIFIC			
	C HEAT,AND FILM TRANSFER COEFFICIENT			
0115	KB=(P1+MFT*KFT)/(MB+MFT)			RACT 645
0116	MJB=(P2+MFT*MJFT)/(MB+MFT)			RACT 650
0117	RHD=(MB+MFT)/(VB+(MFT/PFT))			RACT 655
0118	CPR=ART + BRT*TB			RACT 660
0119	CPR=(MB*CPB + MFT*CPF2)/(MB+MFT)			RACT 665
0120	HB=(C*KB/DV)*(DA**2*RPM*RHO/MUB)**(2./3.)*(CPR*MUB/KB)**(1./3.)			RACT 670
	C CALCULATE REYNOLDS NO. TO CHECK FOR LAMINAR OR TURBULENT FLOW IN			
	C CALCULATION OF THE COOLANT FILM TRANSFER COEFFICIENT			
0121	RE=4.*RC/(PI*MUC*DC)			RACT 675
0122	IF (RE.LE. 2100.) GO TO 95			RACT 680
0123	HC=.028*(RC/MUC/DC)**.8*(CPC*MUC/KC)**(1./3.)*(1.+3.54*(DC/DSC))			RACT 685
	1 *(KC/DC)			RACT 686
0124	GO TO 100			RACT 690
0125	95 HC=.94*(RC*CPC/(DC*KC))**(.1./3.)*(KC/DC)			RACT 695
	C CALCULATE OVERALL HEAT TRANSFER COEFFICIENT			
0126	100 U=1./(1./HB + XS/KS + 1./HC)			RACT 700
0127	105 IF (MR.LT. MRMAX) GO TO 110			RACT 705
	C CALCULATE NEW BATCH TEMPERATURE			
0128	TBNEW=TB + (DELT(ISUB)*(-U*SA*(TB-TC)))/(MB*CPB+MFT*CPF2)			RACT 710
0129	GO TO 125			RACT 715
	C CHECK ORDER OR TYPE OF REACTION			
0130	110 IF (ITYPE.GE. 1) GO TO 114			RACT 720
0131	RATE=RCOV*EXP(-LAM*TIME-E/R/TB)			RACT 725
0132	GO TO 120			RACT 730
0133	114 IF (ITYPE.EQ. 4) GO TO 116			RACT 731
0134	115 RATE=(RCOV*(MFT-MR)**ITYPE*EXP(-E/R/TB))/(VB+(MFT/PFT))*(ITYPE-1)			RACT 735
0135	GO TO 120			RACT 737
0136	116 RATE=(RCOV*(MFT-MR)*(M(1)-M(1)*MR/MRMAX)*EXP(-E/R/TB))/(VB+(MFT/			RACT 738
	1PFT))			RACT 739
	C CALCULATE NEW BATCH TEMPERATURE			
0137	120 TBNEW=TB + (DELT(ISUB)*(Q*RATE-U*SA*(TB-TC)-CPF1*RFT*(TB-TF)))/(MB*CPB+MFT*CPF2)			RACT 740
	1*CPB+MFT*CPF2)			RACT 745
	C IF TEMPERATURE DIFFERENCE BETWEEN TWO SUCCESSIVE STEPSIZES IS			
	C GREATER THAN SPECIFIED MAXIMUM,REDUCE STEPSIZE IN HALF			
0138	125 IF (ABS(TBNEW-TB).LE. TMAX) GO TO 140			RACT 750
0139	L=L+1			RACT 755
0140	IF (L.LE. 4) GO TO 135			RACT 760
0141	WRITE (IW,130)			RACT 765
0142	130 FORMAT (1H0,'THE DIFFERENCE BETWEEN 2 SUCCESSIVE CALCULATIONS OF THE			TRACT 770
	BATCH TEMPERATURE EXCEEDS THE SPECIFIED LIMIT.')			RACT 775

4.3 Source Listing (Cont'd)

DOS	FORTRAN IV	350N-FO-479 3-3	MAINPGM	DATE	02/24/71	TIME	14.21.23	PAGE	0005
0143		CALL EXIT					RACT 780		
0144	135	DELT(ISUB)=DELT(ISUB)/2.					RACT 781		
0145		GO TO 105					RACT 782		
	C	INCREMENT TIME							
0146	140	TIME=TIME+DELT(ISUB)					RACT 784		
	C	HAS FINISH TIME BEEN EXCEEDED							
0147		IF (TIME .GT. FINTIM) GO TO 165					RACT 785		
	C	CHECK TO SEE IF STEPSIZE IS TO BE CHANGED							
0148		IF (TIME .LT. REWD(ISUB)) GO TO 145					RACT 786		
0149		ISUB=ISUB+1					RACT 790		
0150		PINC=RATIO*DELT(ISUB)					RACT 795		
	C	IS IT TIME TO PRINT OUT RESULTS							
0151	145	IF (TIME .LT. PTIME) GO TO 151					RACT 809		
0152		TBF=TB-460.					RACT 809		
0153		WRITE (IW,150) TIME,TBF,HB,4C,U,MFT,MR,SA					RACT 810		
0154	150	FORMAT (1H ,F5.3,3X,F5.1,4X,2(F8.3,7X),F8.3,2X,3(3X,F7.3))					RACT 815		
0155		PTIME=PTIME + PINC					RACT 816		
0156	151	L=0					RACT 820		
	C	RESTORE STEPSIZE TO ORIGINAL VALUE							
0157		DELT(ISUB)=DELT(ISUB)					RACT 825		
0158		IF (TBNEW .LE. 1500.) GO TO 160					RACT 830		
0159		WRITE (IW,155)					RACT 835		
0160	155	FORMAT (1H0,'BATCH TEMPERATURE EXCEEDS 1500 DEG R')					RACT 840		
0161		CALL EXIT					RACT 845		
	C	SET BATCH TEMPERATURE,TOTAL MASS FEED,TOTAL REACTANT FEED,AND							
	C	SURFACE TO NEW VALUES FOR THE NEXT ITERATION							
0162	160	TB=TBNEW					RACT 850		
0163		CALL MINMAX					RACT 855		
0164		MFT=MFT + RFT*DELT(ISUB)					RACT 860		
0165		MR=MR + RATE*DELT(ISUB)					RACT 865		
0166		SA=SA+SAV*(VB+(MFT/PFT))					RACT 866		
0167		IF (MR .GT. MFT) MR=MFT					RACT 867		
0168		IF (MR .GT. MRMAX) MR=MRMAX					RACT 868		
0169		IF (MFT .LE. MFMAX) GO TO 90					RACT 870		
0170		MFT=MFMAX					RACT 871		
0171		RFT=0.					RACT 872		
0172		GO TO 90					RACT 875		
0173	165	TBMIN=TBMIN-460.					RACT 880		
0174		TBMAX=TBMAX-460.					RACT 881		
0175		WRITE (IW,166) TBMIN,TIMIN,TBMAX,TIMAX					RACT 885		
0176	166	FORMAT (1H0/1H , 'RELATIVE MINIMUM BATCH TEMP OF ',F5.1, ' OCCURRED					RACT 890		
		1AT ',F5.3,' HRS.'/1H , 'RELATIVE MAXIMUM BATCH TEMP OF ',F5.1, ' OCCURRED					RACT 895		
		2URRED AT ',F5.3,' HRS.')					RACT 900		
0177		GO TO 1000					RACT 905		
0178	170	CALL EXIT					RACT 909		
0179		END					RACT 910		

4.3 Source Listing (Cont'd)

DOS FORTRAN IV 360N-FD-479 3-3 MINMAX DATE 02/24/71 TIME 14.22.37 PAGE 0001

MINMAX01
COMM 02
MINMAX03
MINMAX04
MINMAX05
MINMAX06
MINMAX07
MINMAX08
MINMAX09
MINMAX10
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MINMAX28
MINMAX29
MINMAX30
MINMAX31

SUBROUTINE MINMAX
COMMON IPASS,TIME,TIMIN,TIMAX,TBMIN,TBMAX,TBLAST,TB

IF (IPASS .GT. 1) GO TO 15
IPASS=IPASS+1
IF (IPASS .EQ. 1) GO TO 15
IMIN=0
IMAX=0
IF (TB-TBLAST) 6,5,10
5 IPASS=0
GO TO 50
6 ISIGN=0
GO TO 15
10 ISIGN=1
15 IF (TB-TBLAST) 20,50,22
20 IF (IMIN .EQ. 1) GO TO 50
IF (TB .GE. TBMIN) GO TO 21
TBMIN=TB
TIMIN=TIME
GO TO 25
21 IF (ISIGN .EQ. 0) GO TO 25
IMAX=1
GO TO 25
22 IF (IMAX .EQ. 1) GO TO 50
IF (TB .LE. TBMAX) GO TO 23
TBMAX=TB
TIMAX=TIME
GO TO 25
23 IF (ISIGN .EQ. 1) GO TO 25
IMIN=1
25 TBLAST=TB
50 RETURN
END

5.0 EXAMPLE PROBLEM

5.1 PROBLEM DESCRIPTION

As an example reaction to illustrate the use of the program, the phosphorous oxychloride (POCl_3) addition to pyridinium picrate to form picryl chloride (PiCL) has been selected. Actual measured and theoretical batch temperatures for this reaction have already been presented in previous report [1].

The synthesis of picryl chloride from picric acid includes two reactions:

- (1) The addition of pyridine to picric acid in a dimethyl formamide (DMF) solvent to form pyridinium picrate, and,
- (2) The addition of POCl_3 to form picryl chloride.

REACTION 1:

Picric Acid

Pyridine

REACTION 2:

Picryl Chloride

The input information for this second reaction has been entered into a computer input data form (Fig. 4) which is discussed further in the next paragraph.

CHEMICAL REACTOR ANALYSIS

PROG. NO. 406-001-130-000

PROBLEM IDENTIFICATION

PICRYL CHLORIDE SYNTHESIS - POCL3 ADDITION

Problem Parameters

Type of Reaction*	No. of Feed Const.*	No. of Reactant Const.*	Max Batch Temp Diff	Initial Time	Finish Time	Print Time Factor	No. of Ranges
4	1	3	2.0	0.0	1.0	1.0	1
End of Range 1	Time Step	End of Range 2	Time Step	End of Range 3	Time Step	End of Range 4	Time Step
1.0	0.1						
Temp. (°F)	Initial Mass	Maximum Mass	Feed Data				
72.0	0.0	13.5					
Feed Rate	Thermal Conductivity	Specific Gravity	Viscosity	SPECIFIC HEAT COEFFICIENTS			
36.9	0.100	1.675	1.500	A	B		
				0.210	0.0		
Reactant Data							
Temp. (°F)	Initial Mass	Maximum Mass					
84.0	0.0	4.170					
Comp. Mass	Thermal Conductivity	Specific Gravity	Viscosity	SPECIFIC HEAT COEFFICIENTS			
20.2	0.095	1.760	4.840	A	B		
116.8	0.104	0.945	1.476	0.338	0.0003		
7.0	0.097	0.982	1.597	0.254	0.0003		
Coolant Data							
Temp (°F)	Flow Rate	Thermal Conductivity	Specific Gravity	Viscosity	Specific Heat	Dia. Tube	Spiral Dia of Tube
72.3	360.0	0.344	1.00	2.36	1.00	0.69	12.9
Vessel and Agitator Data							
Dia. Agitator	Dia. Vessel	Agitator RPM	Vessel Thermal Conductivity	Vessel Thickness	Initial HT Surface Area	Delta HT Surface Area	Paddle Constant
6.0	28.0	18.8	0.667	0.094	7.00	0.0	0.87
Miscellaneous Data							
Reaction Energy	Heat of Reaction	Reaction Rate Const.	Program Const.	Overall HT Const.			
0.0	800.0	0.0		0.0			

*Integer values (right justified in field)

Fig. 4. Computer Data Input Form

5.2 PROGRAM INPUT DATA

The batch size chosen for the example reaction will yield a theoretical maximum yield of 22.05 lb (10 kg) of picryl chloride. Since the POCl_3 is known to react in a violent, highly exothermic manner, the POCl_3 is added into the pyridinium picrate - DMF solution at a slow, metered rate. Water cooling is used to maintain safe reaction temperatures in the batch.

5.2.1 Problem Identification

This input identifies the picryl chloride synthesis and the POCl_3 addition.

5.2.2 Problem Parameters

The type of reaction has been selected as a first order reaction (ITYPE = 1) since the POCl_3 feed reactant is very reactive and is metered slowly into the batch. Three-batch constituents have been entered in the data since the thermodynamic properties of picric acid and pyridine have been included in the data in place of the unknown properties of pyridinium picrate. The time input data and calculation interval are arbitrary based on the known or estimated reaction time.

5.2.3 Feed Data

The POCl_3 is the only feed constituent. The total feed will be 13.5 lb at room temperature (72 F). This feed mass is more than that required for the stoichiometric reaction so that the reaction is driven towards completion and good yield is obtained. The feed rate is metered slowly at 36.9 lb/hr. Thermodynamic properties for the POCl_3 are entered in engineering units.

5.2.4 Reactant Data

The pyridinium picrate reaction is exothermic and, as a result, the batch temperature is about 84 F when the POCl_3 addition is started. The maximum mass entered here is the stoichiometric mass for the POCl_3 of 4.170 lb. For the second order reaction, the picric acid is entered as the first component of the reactant batch. The masses and thermodynamic properties of the DMF and pyridine are also entered.

5.2.5 Coolant Data

Water has been used as a coolant in the reactor cooling coil with a flow rate of 3600 lb/hr. Average coolant temperature (inlet to outlet plus time variations) is 72.3 F. The thermodynamic properties for water have been entered for the coolant.

5.2.6 Vessel and Agitator Data

The reaction is carried out in a 200-liter Corning glass reactor with internal cooling coils. The type of agitator and heat transfer area for this reaction are indicated in Table II (paragraph 2.3.4). Also, the wall properties of the glass cooling coil are indicated in Table I (paragraph 2.3.2).

5.2.7 Miscellaneous Data

For the first order reaction, the reaction energy and reaction rate constant have been set as zero. The heat of reaction has been estimated at 800 Btu/lb- POCl_3 based on known values for bond-energy and heats of formation and also, on data from previous synthesis batches. The program constant has been estimated at $\lambda = 2.0$ from Fig. 8 (paragraph 2.4) with a reaction completion time estimated at 30 minutes. The overall HT coefficient has been entered as "0.0" as an indicator for the program to calculate this coefficient.

5.3 Program Output

The print-out of the input data is presented in Fig. 5, and of the results in Fig. 6. A plot of the calculated and measured temperature histories is given in Fig. 7. Data from a previous mathematical solution [1] is also included.

Although the calculated curve for batch temperature versus time is not completely similar to the measured curve, the results for peak temperature and the time at which this peak occurs are close. The peak temperatures are within 2 F and the corresponding times are within 0.005 hours. Differences in the shapes of the computed and measured temperature curves were attributed to differences between the actual and calculated heat transfer coefficients, heats of reaction, and reaction rate constants.

The calculated values for the heat transfer coefficients agree with values calculated and measured previously [2]. The measured values were slightly higher than the calculated values in that reference. However, in viewing the cool-down slopes in Fig. 7, the measured value of the overall film coefficient for this example is slightly lower than the calculated value since the batch temperature decreases more rapidly in the theoretical case than in the measured data.

PROG. NO. 6-300-1-4-BH-1

CHEMICAL REACTOR ANALYSIS

PICRYL CHLORIDE SYNTHESIS - POCL3 ADDITION 12-14-70 1ST ORDER

PROBLEM PARAMETERS

TYPE OF REACTION	NO. OF FEED CONSTITUENTS	NO. OF REACT CONSTITUENTS	MAX BATCH TEMP DIFF	INITIAL TIME	FINISH TIME	PRINT TIME FACTOR	NUMBER OF TIME RANGES
1	1	3	2.0	0.0	1.0	6.	1
TIME INTERVAL FROM TO		TIME STEP					
0.0 HR 1.00 HR		0.1 MIN					

FEED DATA

TEMP DEG F	INITIAL MASS	MAXIMUM MASS	FEED RATE	THERMAL CONDUCTIVITY	DENSITY	VISCOSITY	SPEC. HEAT COEF. A	COEF. B
72.	0.0	13.5	36.9	0.100	1.675	1.500	0.2100	0.0

REACTANT DATA

TEMP DEG F	INITIAL MASS	MAXIMUM MASS	COMP MASS	THERMAL CONDUCTIVITY	DENSITY	VISCOSITY	SPEC. HEAT COEF. A	COEF. B
34.	0.0	4.170	20.2	0.095	1.760	4.840	0.2500	0.0
			116.8	0.104	0.945	1.476	0.3380	0.0003
			7.0	0.097	0.982	1.597	0.2540	0.0003

COOLANT DATA

TEMP DEG F	FLOW RATE	THERMAL CONDUCTIVITY	DENSITY	VISCOSITY	SPECIFIC HEAT	DIAM TUBE	SPIRAL DIAM OF COIL
72.3	3500.	0.344	1.000	2.360	1.000	0.69 IN	12.00 IN

VESSEL AND AGITATOR DATA

DIAMETER AGITATOR	DIAMETER VESSEL	AGITATOR REV/MIN	VESSEL THERMAL CONDUCTIVITY	VESSEL THICKNESS	INITIAL HT SURF AREA	DELTA HT SURF AREA	PADDLE CONST.
5.00 IN	23.00 IN	188.	0.667	0.094 IN	7.00	0.0	0.870

MISCELLANEOUS DATA

REACTION ENERGY	HEAT OF REACTION	REACT. RATE CONSTANT	PROGRAM CONSTANT	OVERALL HT COEF.
0.0	800.0	0.0	2.000	0.0

Fig. 5. Input Data for Example Problem

TIME	BATCH TEMP	BATCH FILM COEFFICIENT	COOLANT FILM COEFFICIENT	OVERALL COEFFICIENT	TOTAL MASS FEED	REACTIONED FEED MASS	MT SJRF AREA
0.002	84.0	159.162	1325.179	53.332	0.0	0.0	7.000
0.012	83.4	159.162	1325.179	53.332	0.369	0.303	7.000
0.022	82.9	159.162	1325.179	53.332	0.738	0.313	7.000
0.032	82.5	159.162	1325.179	53.332	1.107	0.331	7.000
0.042	82.2	159.162	1325.179	53.332	1.477	0.355	7.000
0.052	82.0	159.162	1325.179	53.332	1.846	0.387	7.000
0.062	81.9	159.162	1325.179	53.332	2.215	0.424	7.000
0.070	81.9	159.162	1325.179	53.332	2.523	0.461	7.000
0.080	81.9	159.162	1325.179	53.332	2.892	0.511	7.000
0.090	82.1	159.162	1325.179	53.332	3.261	0.567	7.000
0.100	82.2	159.162	1325.179	53.332	3.630	0.630	7.000
0.110	82.5	159.162	1325.179	53.332	4.000	0.698	7.000
0.120	82.3	159.162	1325.179	53.332	4.369	0.773	7.000
0.130	83.2	159.162	1325.179	53.332	4.738	0.853	7.000
0.140	83.5	159.162	1325.179	53.332	5.107	0.939	7.000
0.150	84.0	159.162	1325.179	53.332	5.476	0.931	7.000
0.160	84.5	159.162	1325.179	53.332	5.845	0.928	7.000
0.170	85.0	159.162	1325.179	53.332	6.215	0.931	7.000
0.180	85.5	159.162	1325.179	53.332	6.584	1.038	7.000
0.190	86.1	159.162	1325.179	53.332	6.953	1.152	7.000
0.200	86.7	159.162	1325.179	53.332	7.322	1.270	7.000
0.210	87.4	159.162	1325.179	53.332	7.692	1.393	7.000
0.220	88.0	159.162	1325.179	53.332	8.061	1.521	7.000
0.230	88.7	159.162	1325.179	53.332	8.430	1.654	7.000
0.240	89.4	159.162	1325.179	53.332	8.799	1.791	7.000
0.250	90.1	159.162	1325.179	53.332	9.168	1.933	7.000
0.260	90.3	159.162	1325.179	53.332	9.538	2.080	7.000
0.270	91.5	159.162	1325.179	53.332	9.907	2.231	7.000
0.280	92.2	159.162	1325.179	53.332	10.276	2.386	7.000
0.290	93.0	159.162	1325.179	53.332	10.645	2.545	7.000
0.300	93.7	159.162	1325.179	53.332	11.014	2.709	7.000
0.310	94.5	159.162	1325.179	53.332	11.384	2.877	7.000
0.320	95.2	159.162	1325.179	53.332	11.753	3.049	7.000
0.330	96.0	159.162	1325.179	53.332	12.122	3.224	7.000
0.340	96.3	159.162	1325.179	53.332	12.491	3.404	7.000
0.350	97.5	159.162	1325.179	53.332	12.860	3.587	7.000
0.360	98.3	159.162	1325.179	53.332	13.230	3.774	7.000
0.370	99.0	159.162	1325.179	53.332	13.599	3.965	7.000
0.380	99.3	159.162	1325.179	53.332	13.968	4.155	7.000
0.390	98.7	159.162	1325.179	53.332	13.535	4.170	7.000
0.400	97.3	159.162	1325.179	53.332	13.535	4.170	7.000
0.410	95.9	159.162	1325.179	53.332	13.535	4.170	7.000
0.420	94.7	159.162	1325.179	53.332	13.535	4.170	7.000
0.430	93.5	159.162	1325.179	53.332	13.535	4.170	7.000
0.440	92.4	159.162	1325.179	53.332	13.535	4.170	7.000
0.450	91.3	159.162	1325.179	53.332	13.535	4.170	7.000
0.460	90.3	159.162	1325.179	53.332	13.535	4.170	7.000
0.470	89.3	159.162	1325.179	53.332	13.535	4.170	7.000
0.480	88.4	159.162	1325.179	53.332	13.535	4.170	7.000
0.490	87.5	159.162	1325.179	53.332	13.535	4.170	7.000
0.500	86.3	159.162	1325.179	53.332	13.535	4.170	7.000
0.510	85.0	159.162	1325.179	53.332	13.535	4.170	7.000
0.520	85.3	159.162	1325.179	53.332	13.535	4.170	7.000
0.530	84.6	159.162	1325.179	53.332	13.535	4.170	7.000
0.540	83.9	159.162	1325.179	53.332	13.535	4.170	7.000
0.550	83.3	159.162	1325.179	53.332	13.535	4.170	7.000
0.560	82.7	159.162	1325.179	53.332	13.535	4.170	7.000
0.570	82.2	159.162	1325.179	53.332	13.535	4.170	7.000
0.580	81.5	159.162	1325.179	53.332	13.535	4.170	7.000
0.590	81.1	159.162	1325.179	53.332	13.535	4.170	7.000
0.600	80.7	159.162	1325.179	53.332	13.535	4.170	7.000
0.610	80.2	159.162	1325.179	53.332	13.535	4.170	7.000
0.620	79.3	159.162	1325.179	53.332	13.535	4.170	7.000
0.630	79.4	159.162	1325.179	53.332	13.535	4.170	7.000
0.640	79.0	159.162	1325.179	53.332	13.535	4.170	7.000
0.650	78.7	159.162	1325.179	53.332	13.535	4.170	7.000
0.660	78.3	159.162	1325.179	53.332	13.535	4.170	7.000
0.670	78.0	159.162	1325.179	53.332	13.535	4.170	7.000
0.680	77.7	159.162	1325.179	53.332	13.535	4.170	7.000
0.690	77.4	159.162	1325.179	53.332	13.535	4.170	7.000
0.700	77.1	159.162	1325.179	53.332	13.535	4.170	7.000
0.710	76.9	159.162	1325.179	53.332	13.535	4.170	7.000
0.720	76.5	159.162	1325.179	53.332	13.535	4.170	7.000
0.730	76.4	159.162	1325.179	53.332	13.535	4.170	7.000
0.740	76.2	159.162	1325.179	53.332	13.535	4.170	7.000
0.750	76.0	159.162	1325.179	53.332	13.535	4.170	7.000
0.760	75.3	159.162	1325.179	53.332	13.535	4.170	7.000
0.770	75.5	159.162	1325.179	53.332	13.535	4.170	7.000
0.780	75.4	159.162	1325.179	53.332	13.535	4.170	7.000
0.790	75.3	159.162	1325.179	53.332	13.535	4.170	7.000
0.800	75.1	159.162	1325.179	53.332	13.535	4.170	7.000
0.810	74.9	159.162	1325.179	53.332	13.535	4.170	7.000
0.820	74.3	159.162	1325.179	53.332	13.535	4.170	7.000
0.830	74.7	159.162	1325.179	53.332	13.535	4.170	7.000
0.840	74.5	159.162	1325.179	53.332	13.535	4.170	7.000
0.850	74.4	159.162	1325.179	53.332	13.535	4.170	7.000
0.860	74.3	159.162	1325.179	53.332	13.535	4.170	7.000
0.870	74.2	159.162	1325.179	53.332	13.535	4.170	7.000
0.880	74.1	159.162	1325.179	53.332	13.535	4.170	7.000
0.890	74.0	159.162	1325.179	53.332	13.535	4.170	7.000
0.900	73.9	159.162	1325.179	53.332	13.535	4.170	7.000
0.910	73.3	159.162	1325.179	53.332	13.535	4.170	7.000
0.920	73.7	159.162	1325.179	53.332	13.535	4.170	7.000
0.930	73.7	159.162	1325.179	53.332	13.535	4.170	7.000
0.940	73.5	159.162	1325.179	53.332	13.535	4.170	7.000
0.950	73.5	159.162	1325.179	53.332	13.535	4.170	7.000
0.960	73.5	159.162	1325.179	53.332	13.535	4.170	7.000
0.970	73.4	159.162	1325.179	53.332	13.535	4.170	7.000
0.980	73.3	159.162	1325.179	53.332	13.535	4.170	7.000
0.990	73.3	159.162	1325.179	53.332	13.535	4.170	7.000
1.000	73.2	159.162	1325.179	53.332	13.535	4.170	7.000

RELATIVE MINIMUM BATCH TEMP OF 81.9 OCCURRED AT 0.067 HRS.
RELATIVE MAXIMUM BATCH TEMP OF 99.9 OCCURRED AT 0.380 HRS.

Fig. 6. Results for Example Problem

Fig. 7. Theoretical and Measured Batch Temperatures vs. Time
Picryl Chloride Synthesis, POCl_3 Addition Reaction

6.0 CONCLUSIONS

TCHREACT has been verified for a limited number of representative reactions by comparison of program results with measured data. Additional experience may disclose limitations in the program and will undoubtedly lead to requirements for revisions.

The selection of the proper order of the reaction and the determination of the heat-of-reaction and reaction rate constant values for use in the program is difficult for many reactions where much of this data is not available. The order of the reaction can be determined from the literature or past experience. The heat-of-reaction can be estimated from bond-energies and known heats of formation, but the resulting value is subject to significant error. Also, the reaction rate constant can be estimated from distribution functions for bimolecular reactions or from integration of the rate equation with known values of temperature or concentration at a point in time. In addition, all of these reaction parameters (the order of the reaction, heat-of-reactions, and reaction rate constant) can be determined experimentally from laboratory measurements of concentration and temperature versus reaction time.

At the present, latter experimental approach in the laboratory appears to be the most trustworthy method of obtaining reliable parameters for the program which will yield the accurate estimates of the temperature rise during a large batch reaction. These computed results must be fairly accurate if the program is to be of value in predicting high temperature, dangerous operating conditions. In the near future, a follow-on effort is planned to develop one or two additional computer programs for analytically determining the heat-of-reaction and the reaction rate constant.

7.0 REFERENCES

1. F. I. Honea, Chemical Reactor Analyses - Exothermic Reaction, Mason & Hanger - Silas Mason Co., Inc., Acct. No. 22-2-44-00-221 (July 1970).
2. F. I. Honea and D. V. Hayes, Heat Transfer Coefficients for Chemical Reactors, Mason & Hanger - Silas Mason Co., Inc., Acct. No. 22-2-44-04-3-1 (August 1970).
3. John H. Perry, Chemical Engineer's Handbook, 4th Edition, McGraw-Hill (1963).
4. The Pfaudler Company, Bulletin 1029.
5. Max Jacob, Heat Transfer, Volume I, John Wiley and Sons (1949).
6. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, Transport Phenomena, John Wiley and Sons (1960).
7. V. C. Marshall and N. Yazdani, "Design of Agitated, Coil-in-Tank Coolers," Chemical and Process Engineering (April 1970).
8. E. A. Moelwyn-Hughes, The Kinetics of Reactions in Solutions, Oxford at the Clarendon Press, 2nd Ed. (1947).
9. D. V. Hayes and F. I. Honea, Synthesis of Picryl Hydrazine, Mason & Hanger - Silas Mason Co., Inc., P.O. 93-1840, (August 1970).