



The following article introduces a new feature series by Chemical Engineering Education in cooperation with the CACHE (Computer Aides for Chemical Engineering Education) Committee. Proven computer-based homework problems suitable for undergraduate or first year graduate chemical engineering courses will be published on a regular basis.

The current problem, together with listings and documentation, is too long for full publication so the following article presents the problem and outlines the computer program developed to solve it. Complete documentation of the problem and program may be obtained for the cost of reproduction by writing the problem author.

Problems submitted for publication should be documented according to the published "Standards for CACHE Computer Programs" (September 1971). That document is available now through the CACHE representative in your department or from the CACHE Computer Problems Editor. Because of space limitations, problems should normally be limited to twelve pages total; either typed double-space pages or actual computer listings. A problem exceeding this limit will be considered. For such a problem

the article will have to be extracted from the complete problem description. The exact procedure to distribute the total documentation is evolving and may involve distribution at the cost of reproduction by the author, as we are doing with the current problem.

Before a problem is accepted for publication it will pass through the following review steps

- 1) selection from among all contributions an interesting problem by the CACHE Computer Problem Advisory Board
- 2) documentation review (with revisions if necessary) to guarantee adherence to the "Standards for CACHE Computer Programs".
- 3) program testing by running it on a minimum of three different computer systems.

It is hoped these problems will indeed be an aid in teaching computing and engineering to our students.

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Non-Isothermal Tubular Reactor Program

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THIS COMPUTER PROGRAM is a numerical integration procedure for solving complex plug-flow reactor problems. The program will handle up to ten simultaneous reactions and ten different chemical compounds. The program is designed to handle a constant heat flux per unit area, but by proper choice of input data, isothermal or adiabatic (zero heat input) cases may be treated. With minor modification, the program has been used to calculate the heat flux, based on radiant heat transfer to the tubes with an internal film coefficient evaluated by the Dittus-Boelter equation.

The specific problem considered here is problem number 29, page 899, *Chemical Process Principles, Vol. III*, O. A. Hougen and K. M. Watson, John Wiley and Sons, Inc., New York, 1947. The discussion of the program refers specifically to this problem.

PROBLEM STATEMENT

IT IS DESIRED TO DESIGN a tubular heater and reactor for the pyrolysis of propane to produce a mixture of ethylene and propylene. Substantially pure propane is to be charged through a preheater which delivers it at a

temperature of 600°F and an absolute pressure not in excess of 60 lb per sq. in. to the inlet of the reactor-heater. In order to avoid secondary and reverse reactions the absolute pressure at the outlet of the reactor is maintained at 20 lb per sq in. The gases from the reactor are compressed and fractionated to recover the desired products and substantially pure propane which is recycled to the heater and reactor. The design is to be based on a total propane feed to the reactor of 7000 lb per hr and a conversion per pass of 80 per cent, corresponding to a net fresh charge of 5600 lb per hr.

A trial design is to be prepared on the basis of passing the entire heater and reactor charge in a single stream through a series of uniformly sized tubes each 30 feet long and connected together with 180° return bends. Each return bend has a volume equal to $3.1d^3$ where d is the inside diameter of the tube. The equivalent length of a return bend is 60 diameters of straight pipe, and the heated length of each tube is 28.0 feet. Tubes are available with inside diameters varying by $\frac{1}{2}$ -in. increments from 1 in. Since the maximum operating temperature permitted by the tube material is 1400°F, the heater will be designed to raise the charge to this temperature with a uniform heat input rate of 8000 Btu/(hr)(sq ft) based on the actually heated internal tube area. In order to obtain favorable heat-transfer conditions the tube diameter should be as small as possible without exceeding the allowable inlet pressure. In the

reactor section a constant temperature of 1400°F will be maintained by varying the heat-input rate.

It is required to determine the diameter and numbers of tubes for the specified service and also the temperature, pressure, conversion, product distribution, and heat-input-rate distribution curves throughout the heater and reactor, using the following kinetic data.

REACTION RATE DATA

r = rate of reaction, lb mole/(cu. ft.) (hr)

π = total pressure, atm.

$k = A \exp(-E/RT)$

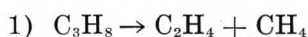
E = Cal./g-mole

T = temperature, °K

N = mole fraction

$K = \exp(-\Delta H^\circ/RT + \Delta S^\circ/R)$

Reaction



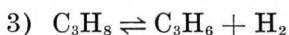
$$r = k\pi N_{C_3H_8} \quad \text{lb moles } C_3H_8$$

$$A = 3.0158 \times 10^{14}; E = 66500.$$



$$r = k\pi N_{C_3H_8} \quad \text{lb moles } C_3H_8$$

$$A = 3.6745 \times 10^{13}; E = 65000.$$

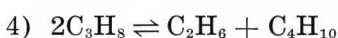


$$r = k\pi [N_{C_3H_8} - (N_{C_3H_6})(N_{H_2})(\pi/K)]$$

$$A = 9.989 \times 10^{12}; E = 60000.$$

$$\Delta H^\circ = 30505.; \quad \Delta S^\circ = 32.85$$

(the values for ΔH° and ΔS° are at 1300°F; it may be assumed K does not vary with temperature)



$$r = k\pi [N_{C_3H_8} - (N_{C_2H_6})(N_{C_4H_{10}})/K]$$

$$A = 2.490 \times 10^{10}; E = 54000.$$

$K = 1.30$ (substantially independent of temperature)

METHOD OF SOLUTION

The material balance across a differential increment of a tubular (plug-flow) reactor is:

$$F dX = r dV_r$$

where

F = feed rate, mass units/hr.

X = moles of reactants converted/
unit mass of feed

r = reaction rate, lb moles/(hr)
(cu. ft.)

V_r = reactor volume, cu. ft.

The rate of reaction is a function of temperature, pressure and composition which vary along the length of the reactor, and which are all inter-related. There are four competing reactions and thus composition is a function of the four reactions rates. Thus:

$$r = r(T, \pi, X)$$

$$T = T(X)$$

$$\pi = \pi(X, T, \pi)$$

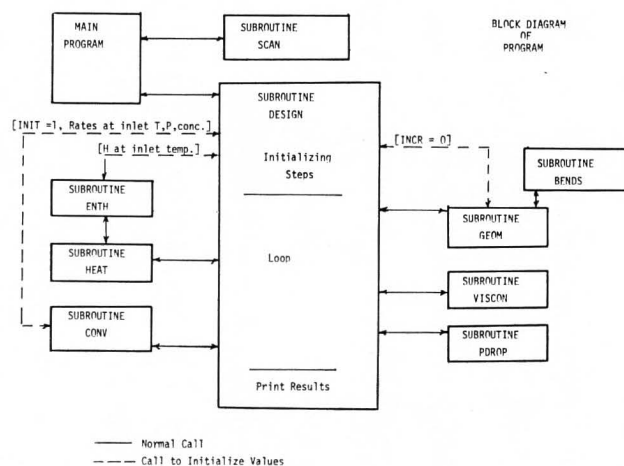
$$X = X(r)$$

Solution of this problem is a numerical integration of the four simultaneous material balance equations for the four reactions expressed in a difference form. The particular method of solution used in this program is based upon choosing a tube increment sufficiently small that the change in conversion can be calculated from the arithmetic average of the rates of reaction. That is:

$$\Delta X_i = \bar{r}_i \Delta V_r / F$$

where \bar{r}_i is the arithmetic average of the rates of reaction at the beginning and end of the increment for the i th reaction. Successive increments of volume ΔV_r are added until the total conversion, $\sum \Delta X$ of propane, reaches the desired level.

The detailed calculation procedure is described in the section *Subroutine DESIGN*.



Program Details

A discussion of each subroutine follows. Their inter-relationship is shown in the block diagram of the program. Subroutine DESIGN, the most important, is listed first, then the main program, and the other subroutines in alphabetical order.

Subroutine DESIGN

This subroutine is the executive subroutine,

providing the logic for the solution as well as initializing the variables and printing the results. Its operation is best described in tabular form. Reference is made to the various subroutines in the program. The letters A and B are affixed to each variable to designate respectively values at the beginning of an increment (known values, as TA) and values at the end of the increment (values to be calculated, as TB).

- 1) Convert feed data to lb. moles/hr and mole fraction
- 2) Initialize all variables for conditions at inlet to reactor
 - a) Establish heat transfer area, volume, and equivalent length for each tube increment and return bend (SUBROUTINES GEOM [INCR = 0] and BENDS).
 - b) Initialize enthalpy, HA (Subroutine ENTH)
 - c) Initialize rates of reaction, RA_i (Subroutine CONV [INIT = 1])
 - d) Set assumed conversions, $DDN_i = 0.0$
- 3) For each increment, establish area, volume and equivalent length. (SUBROUTINE GEOM [INCR])
- 4) Calculate heat input to increment and enthalpy at end of increment, HB. For assumed composition, calculate outlet temperature TB by Newton-Raphson secant procedure. (SUBROUTINES HEAT and ENTH). If exit temperature exceeds maximum value, TMAX, set $TB = TMAX$
- 5) Calculate viscosity of mixture at average temperature of increment (SUBROUTINE VISCON).
- 6) Calculate pressure drop across increment. (SUBROUTINE PDROP). If pressure falls below minimum set value; stop; print out results, and start over, using next size tube.
- 7) Calculate rates of reaction and conversion, DN_i for each reaction and compute changes in number of moles of each component. (SUBROUTINE CONV [INIT = 2])
- 8) Check if calculated conversions DN_i agree with assumed values, DDN_i within prescribed tolerance. If not, set $DDN_i = DN_i$, and repeat steps 3 through 8. If no convergent is obtained in 15 passes through loop (KRX), stop.
- 9) When satisfactory agreement between calculated and assigned conversions is obtained, proceed to next increment; store the results in array OUT if the end of a tube has been reached.

Calculate the changes in temperature, (e.g. $TDEL = TB - TA$), conversion, and composition of each component. Set the calculated values at end of this increment equal to the values at beginning of next increment. Set trial values of variables at end of next increment equal to values at beginning of increment plus changes in these variables occurring during this increment. For example:

$$\begin{aligned} (TA)_{n+1} &= (TB)_n \\ TDEL &= (TB)_n - (TA)_n; \\ \text{but if } (TB)_n &= (TA)_n, \text{ do not reset TDEL} \\ (TB)_{n+1} \text{ (trial)} &= (TA)_{n+1} + TDEL \end{aligned}$$

Return to Step 2 and proceed.

- 10) When conversion of key component (C_3H_8) reaches desired value, stop and print out results. Depending on input data, program will stop if a satisfactory solution is obtained, or will continue through a specified range of tube sizes.

The output array OUT has provision for 75 tubes; if more are needed, the program prints a warning and stops.

Main Program, REACT

The main program merely sets the logical unit numbers of the card reader (INP) and the printer (IOUT); then CALLs SCAN (to read in the data) and DESIGN (to perform the calculation).

Subroutine BENDS (FLBEND, VBEND, ABEND, DI)

This subroutine contains the constants for the return bends. For the specific problem listed, the following data is given:

Volume of return bend, $VBEND = 3.1 d_i^3$
 Equivalent length of straight pipe for pressure drop calculations, $FLBEND = 60 d_i$
 where d_i = internal diameter of tube, inches.
 $ABEND$ = heat transfer area of return bend.
 For specific problem given here, the return bends are not heated, thus $ABEND = 0$.

The constants in this subroutine must be changed by the user, if the return bends are heated, or if return bends with different volume and friction loss characteristics are used.

Subroutine CONV (PB, TB, VOL)

This subroutine calculates the rate of reaction, RB, for each reaction at the temperature TB, pressure PB, and assumed composition at the exit of the increment.

The conversion for each reaction is calculated from:

$$\begin{aligned} DN(K) &= 0.5 * (RA(K) + RB(K)) * VOL/FEED \\ DN(K) &= \text{conversion for the kth reaction, moles/mole feed} \\ RA(K) &= \text{rate at entrance of increment} \\ RB(K) &= \text{rate at exit if increment as calculated above} \\ VOL &= \text{volume of increment, cu. ft.} \\ FEED &= \text{feed rate, lb. moles/hr.} \end{aligned}$$

The number of moles of each component is then determined from the overall material balances.

The rate equations and material balances listed in this subroutine are for the four reactions given in the specific problem statement. For other problems, this subroutine must be rewritten.

Subroutine ENTH(HTOTAL, TEMP)

This subroutine calculates the enthalpy of the

reaction mixture at a temperature = TEMP (°R). Enthalpies are defined with respect to the elements at a base temperature of 77°F. Thus:

$$(H_i)_{77}^T = (\Delta H_{fi})_{77} + H_o^T - H_o^{77}$$

and $HTOTAL = \sum (XX_i) (WTMOL_i) (H_i)_{77}^T$,
Btu/lb. mole mixture

where: $(H_i)_{77}^T$ = enthalpy of component i at temperature T, above 77°F, Btu/lb.

$(\Delta H_{fi})_{77}$ = heat of formation at 77°F, Btu/lb.

H_o^T = enthalpy of component i at temperature T with respect to liquid at -200°F.

H_o^{77} = enthalpy of component i at 77°F with respect to liquid at -200°F.

XX_i = mole fraction of component

$WTMOL_i$ = molecular weight of component i

The total enthalpy change across the increment is:

$$\Delta H = (BMOLS * HB - AMOLS * HA) * FEED$$

where BMOLS and AMOLS are total moles/mole of feed.

Thus ΔH , as defined here, includes the heat of reaction as a function of temperature.

The peculiar set of base temperatures in the first equation is necessary to use the data in the *API Technical Data Book*—gaseous enthalpies based on liquid at -200°F and heats of formation at 77°F. The API book gives the following equation for H_o^T :

$$H_o^T = A(T/100) + B(T/100)^2 + C(T/100)^3 + D(100/T) + E$$

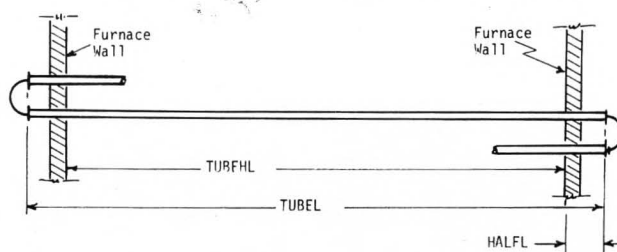
where A, B, C, D, E are constants for each component, Btu/lb., T = °R.

Any set of data may be used, as long as the enthalpies are referred to the elements. *The API Technical Data Book* provides a convenient set of data for an enthalpy equation, rather than a heat capacity equation.

Subroutine GEOM (INCR)

The initial call to GEOM [INCR = 0] triggers a call to BENDS to set the area, volume and length parameters for the return bends. Thereafter, this subroutine assigns to each specific increment the proper values of heat transfer area, volume, and equivalent length of straight pipe for pressure drop calculation.

The complexities of the subroutine are required to handle the case of furnace tubes whose ends and return bends are not heated and to allow the use of various sizes of increments in the integration. A diagram of the furnace is below:



The program identifies three different increments:

- 1) The normal increment—the entire portion of the increment is heated (if three or more increments per tube are used).
- 2) Cold increments—the increment at the beginning and end of each tube. The cold increments may include some heat transfer area if the increment size is greater than HALFL.
- 3) The return bends—in this problem the bends are cold and so ABEND (Subroutine BENDS) is set to zero. If the return bends are heated, ABEND should be set equal to the external surface area of the bend. Note that regardless of the number of increments used per tube, the return bend is treated separately.

For a furnace in which the whole tube is heated, the input data values of TUBEL and TUBEHL (see SCAN) should be identical.

Subroutine HEAT (HA, HB, TA, TB)

The enthalpy balance and exit temperature are calculated in this subroutine. The exit enthalpy is calculated by:

$$Q = FLUX * AREAX$$

$$HBD = (FEED * AMOLS * HA + Q) / (FEED * BMOLS)$$

Where

- Q = heat added, Btu/hr
- FLUX = specified flux
- AREAX = heat transfer area of increment (as set in GEOM)
- AMOLS = total moles entering/mole feed
- BMOLS = ditto for exit
- HA = enthalpy at beginning of increment, at temperature TA, Btu/lb mo'e of mixture
- HBRD = ditto at exit temperature TB; double precision
- FEED = feed rate, lb moles/hr.

The exit temperature TB is then calculated by a Newton-Raphson secant iteration based on TA

(Continued on page 102.)

ChE book reviews

Chemical Kinetics and Reactor Design, A. R. Cooper and G. V. Jeffreys, Prentice Hall (1972). Reviewed by Dan Luss, University of Houston.

This is an undergraduate text on the analysis and design of chemical reactors. The approach is elementary with emphasis on the underlying concepts and techniques as is most proper for the first exposure to this subject. The coverage of several chapters is very good and the chapters on gas liquid and liquid-liquid reactors contain more material than most other texts. On the other hand, several other chapters, such as that on gas solid reactors, are rather superficial and leave much to be desired. In several cases, the authors make errors which indicate lack of knowledge of the literature. For example, they state on page 167 that for a system of first order reactions, "the reaction paths will not be straight lines," or that "the slope condition is sufficient for stability" even though both statements are not true in general. Similarly, the example on p. 133 applies a numerical solution for a problem for which an analytical solution was published already in 1962. Several definitions are rather unclear and that on catalysis fails to point out its important effect on selectivity. It is not clear why a modern text should apply the old height of reactor unit concept for design of packed bed reactors.

The book contains an appropriate number of suitable examples. It is, however, surprising to note that several of them have been taken, with only slight changes in the numerical values, from other texts without giving any proper credit to this fact. The example on butane decomposition is based on a 1939 kinetic investigation. In view of the many improved and more accurate recent studies, application of a more modern rate expression would have been desired. The text contains a rather large number of disturbing printing errors. For example, there is a consistent error in the sign for the rate expression developed on page 112. The captions for some figures are missing and in others there is no marking on the ordinate leaving the reader guessing.

The first chapter treats chemical reactor thermodynamics and applies them to some important processes such as methanol, SO_3 and NH_3 synthesis. Most of this material is covered in the U. S. in the thermodynamic course. The second

chapter discusses the kinetics of chemical reactions and the influence of concentration, temperature and changes in volume. This is followed by a discussion of rate expression for complex reactions, chain reactions, and heterogeneous catalysis. Several examples demonstrate techniques for the determination of rate constants from experimental data.

The third chapter contains a discussion of the batch and semi batch reactor for both isothermal and non-isothermal single reactions. A rather comprehensive chapter on the continuous stirred tank reactor follows. It includes a discussion of several optimization problems as well as of the stability and control. A description of plug flow and laminar flow tubular reactors is contained in the next chapter and it covers isothermal and non-isothermal operation, optimal operating temperature profile and the effect of laminar velocity on conversion.

The chapter on flow characteristics and their effects on the performance of continuous reactors presents an analysis of residence time distribution and dispersion models and their application to design for reactions with linear kinetics. A rather brief chapter is devoted to heterogeneous reactors. It describes briefly solid gas kinetics, the effect of diffusion on a first order isothermal reaction and non-isothermal operation. The last two chapters discuss gas liquid and liquid-liquid reactors, and several design examples demonstrate the effect of the chemical reaction on the mass transfer rate.

CACHE Computer Problem

(Continued from page 93.)

and TDEL, the assumed temperature change across the increment.

The subroutine checks if the calculated TB is greater than the specified maximum temperature, TMAXO ($^{\circ}\text{R}$). If so, TB is set equal to TMAXO and the enthalpy at TMAXO is calculated.

Subroutine PDROP

The pressure drop equation for a gas phase system at high velocities may be simplified to:*

*Hougen, O. A. and K. M. Watson, *Chem Process Principles III*, p. 869, John Wiley & Sons Inc., New York (1947).

$$\Delta P / \Delta L = \frac{0.0235}{D_1} \left(\frac{W}{1000} \right)^{1.8} \left(\frac{\mu^{0.2}}{\rho} \right) \quad [1]$$

where $\Delta P / \Delta L$ = pressure drop, psi/foot of pipe

D_1 = i.d. of tube, inches
 W = flow rate of gases, lbs./hr.
 μ = viscosity, micropoises
 ρ = density, lb./cu. ft.

This equation may be solved for ΔP by an iterative method; however, this can be avoided by defining ρ as:

$$\rho = \frac{W}{\bar{V}} = \frac{W}{\bar{N}_t R T * FEED / \bar{\Pi}} \quad [2]$$

where $\bar{\Pi}$ = average pressure = $(PA + PB) / 2$
 \bar{N}_t = average number of moles/mole of feed
 \bar{T} = average temperature, $(TA + TB) / 2$
 \bar{V} = average specific volume
 $FEED$ = flow rate, lb. moles/hr.

Substituting [1] into [2] and grouping constant values

$$\Delta P = \frac{CONST * \bar{N}_t R \bar{T}}{\bar{\Pi}} * \Delta L = \frac{CONST 1}{\bar{\Pi}}$$

$$PA - PB = \frac{CONST 1}{(0.5 * (PA + PB))}$$

$$PA^2 - PB^2 = 2 * CONST 1$$

or

$$PB = \sqrt{PA^2 - 2 * CONST 1}$$

This is the final working equation for this subroutine. A flag, KPOP, is set to 2 if the group $(PA^2 - 2 * CONST 1) \leq 0.0$. In this case, calculations are stopped, and results to this point are printed out. The program then stops or if the data so provide, the tube size is incremented and the calculations are started anew.

Subroutine SCAN

This subroutine reads in the data, checks that the physical property cards are in the right order and that there are sufficient cards to agree with the specified number of components. The data is then printed out according to the input format.

The documentation accompanying the program

listing contains detailed descriptions of the input variables, and the data card specifications.

Subroutine VISCON (T)

Calculates viscosity according to equation proposed by Chapman-Cowling, *Mathematical Theory of Non-Uniform Gases*, Cambridge Univ. Press, Cambridge (1952) as given in *API Technical Data Book*, p. 11-47.

$$\mu_i = 0.001989 \frac{\sqrt{M_i T}}{\sigma^2 \Omega_v}$$

where μ_i = viscosity, cp.

M_i = molecular weight

T = temperature, °R

σ = Lennard Jones collision diameter, Å

Ω_v = collision integral = function $T/\epsilon / K$

ϵ / K = Lennard Jones potential parameter, °R

Ω_v is given by an empirical equation as a function of $(T/\epsilon / K)$ between TK/ϵ of 0.3 and 400 with an accuracy of $\pm 0.15\%$.

(See the program listing for the actual equation.)

The mixture viscosity is calculated according to

$$\mu_{mix} = (\sum y_i \mu_i \sqrt{M_i}) \div (\sum y_i \sqrt{M_i})$$

where y_i = mole fraction of component i.

This equation was suggested by Hering and Zipperer, *Gas Wasser-foch*, 79, 49 (1936) as reported in the *API Technical Data Book*, p. 11-51.

Values of ϵ / K (in °K) and T are listed in Reid and Sherwood, and many other sources. The group $T/(\epsilon / K)$ must be dimensionless.

REFERENCES

- Hougen, O. A., and K. M. Watson, *Chemical Process Principles, Vol. III*, John Wiley and Sons, New York (1947).
 Smith, J. M., *Chemical Engineering Kinetics, 2nd ed.*, pp. 214-223. McGraw-Hill Book Co., New York (1970).
 Amer. Petroleum Inst., *Technical Data Book-Petroleum Refining*, New York (1966).
 Reid, R. C. and T. K. Sherwood, *Properties of Gases and Liquids*, 2nd ed., McGraw-Hill Book Co., New York (1966).

DATA

The API Technical Data Book is a particularly convenient source of consistent data and tested methods of correlation. However, the required physical and thermal properties of compounds are readily available elsewhere.