COMPUTER MODEL FOR REACTOR DESIGN OF AN ETHANE CRACKING UNIT

by

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ABSTRACT

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The purpose of this thesis is to develop a Fortran Computer Program to model the radiation section of a pyrolysis tube reactor designed for cracking 100 percent ethane feed. The model calculates the length of the tubular reactor required to obtain a specified ethane conversion or the ethane conversion for a specified reactor length. The resulting solution yields a conversion profile, a temperature profile, and the reactor residence time as a function of tube length. From this data it can be determined if the design is adequate and lies within the reactor model's constraints.

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CHAPTER I

THEORY BEHIND TUBULAR REACTORS

Tubular furnaces for the synthesis of ethylene are the simplest and most common ones in use today. Tubular furnaces consist of a convection section and a radiation section, heated by natural gas fired burners in the furnace itself.

The tubular reactor is relatively simple and easy to operate, however, it does have a number of limitaions. First, pyrolysis of ethane gives rise to some carbon formation. This condition is aggravated by very high temperatures, long residence time at these temperatures, and the presence of any liquid hydrocarbon phase. With this in mind, tubular cracking units should be designed for use on completely vaporized feedstocks and for short residence times at high temperatures. The latter requirement calls for high heat flux furnaces so designed that the preheated feed can be rapidly brought to the desired cracking temperature.

The use of steam with the ethane feed is a method of limiting the carbon or coke formation in the tubes. Steam serves a four-fold purpose in such an application:

1. It reduces the partial pressure of the ethane and permits complete vaporization of ethane before the highest temperatures are reached.

2. In reducing the partial pressure of hydrocarbon higher conversion of feed is obtained.
3. The residence time of the hydrocarbon in the high temperature pyrolysis zone is lowered.
4. Steam assists in keeping the furnace tubes clean, having a scavenger action due to reaction of steam with carbon to form carbon monoxide and hydrogen.

The steam to ethane weight ratio is usually 0.2 - 0.4 lb. steam per lb. ethane feed. (ref. no. 13)

Pyrolysis of ethane is an endothermic reaction and, in addition, the sensible plus vaporization heat loads are high. In the tubular cracking furnace the reactant temperature rises continuously from inlet to outlet of the reactor coil. The temperature gradient is greater at the inlet, where the charge is being heated to the temperature level at which the reaction rate is substantial, and is less rapid towards the tube exit due to the endothermic nature of the reactions. Convection and radiation sections are incorporated in the furnace design to steepen the temperature gradient and bring the ethane up to the desired reaction temperature rapidly.

The convection section serves to handle vaporization and preheating, while the radiation section, in the furnace proper, contributes the remaining sensible heat plus the heat of reaction.

Two reactions of importance in the cracking of ethane are:

$$C_2H_6 \xrightarrow{k_1} C_2H_4 + H_2 \qquad (1)$$

ethane ethylene hydrogen

$$C_2H_6 \xrightarrow{k_2} 1/2\ C_2H_4 + CH_4 \qquad (2)$$

ethane ethylene methane

The dependence of the reaction rate constants on temperature is obtained by the Arrhenius equation:

$$k = Ae^{\frac{-E}{RT}}$$

k = reaction rate constant (sec.$^{-1}$)

A = frequency factor (sec.$^{-1}$)

E = activation energy (BTU/lb. mole or cal./g. mole)

T = absolute temperature (^{o}R or ^{o}K)[1]

R = gas constant (1.987 BTU/lb. mole-^{o}R or 1.987 cal./g. mole-^{o}K)

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[1] Units chosen must be consistent to obtain a dimensionless exponential term.

The necessary parameters for the reactions are:

Reaction	1	2
A	1.535×10^{14} sec^{-1}	2.58×10^{16} sec^{-1}
E cal/g. mole	70,200[2]	86,000[3]

Neglecting the reversible kinetics of reactions (1) and (2) is possible and can give reasonable results up to a conversion of 75 percent. This method has the effect of absorbing the equilibrium effects into the first order forward reaction rate constants. To go beyond conversions of 75 percent it is necessary to include the reverse reaction kinetics. This model as presented does not include the reversible kinetics necessary to allow ethane conversions above 75 percent and hence must be applied only to the design of systems with less than 75 percent conversion. A discussion of the reversible kinetics is presented in Chapter V. Normal commercial practice is to crack ethane at a level of 55-60 percent conversion per pass. Ethane feedstock has the advantage of high ethylene yield with minimum production of by-products other than hydrogen and methane.(ref. no. 6)

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2. Schutt, H.C., Chem. Eng. Prog., vol. 55, p.68, January, 1959

3. Davis, H. G., 5th World Petroleum Congress, New York, 1959

CHAPTER II

APPROACH AND EQUATIONS USED IN DEVELOPING THE MODEL

The purpose of the model[4] is to calculate the length of reactor tube required to obtain a certain ethane conversion or calculate the ethane conversion for a fixed reactor length under specified reactor conditions. The model simulates only the radiation section of the fired reactor, since it is here that the chemical reactions take place, rather than in the convection section of the furnace.

The tubular reactor is assumed to be plug-flow, with no radial concentration gradients or axial dispersion. This is quite realistic, since Reynolds numbers in a practical design are in the range of 300,000 to 600,000. The ideal gas law is used in the calculations, which is also a good assumption in the range of 2-6 atmospheres encountered in practical designs.

The model itself is broken up into three parts, (1) input and calculation of constants, (2) iterative procedure to calculate conversion vs. reactor length, and (3) output.

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4. The basic approach and equations used in developing this model were obtained from "Design Case Study 6, Ethylene Plant Design and Economics" by W.L.Bolles & B.D.Smith, Washington University, St. Louis, Missouri.

INPUT & CALCULATION OF CONSTANTS

To completely specify the system, six process variables and five reactor variables must be specified, they are:

(1) Process

- A. The desired ethane conversion (wt. percent) or the desired reactor length (ft.).
- B. The steam to ethane ratio (lb. steam per lb. ethane).
- C. The inlet pressure to the radiation section (atm.).
- D. The inlet temperature to the radiation section (^oF).
- E. The radiating flue gas temperature (^oF).
- F. The feed mass velocity (lb./hr.-ft.^{2}).

(2) Reactor

- A. Inside tube diameter (inches).
- B. Length at center line of one tube plus return bend (ft.).
- C. The number of tube rows per bank.
- D. The thermal conductivity of the tubing.
- E. Tube surface emissivity.

The input data sheet for submitting the above variables is found in Appendix I

The first step is to calculate those quantities that will remain constant throughout the simulation, such as the tube pitch, the tube wall thickness, the factor for added resistance of return bends, and the production rate in pounds per hour.

Calculations

After all the constants have been defined, the program begins the iterative calculation procedure of determining the degree of reaction through the reactor. Since the reaction is a linear process, the reactor equations are solved numerically by considering small incremental lengths of reactor tubing. The calculation steps are as follows:

1. Gas Parameters

Molecular weight:

$$MWf = 1/\sum \frac{(Xi)}{(Mi)}$$

where, MWf = molecular weight of gas mixture

Mi = molecular weight of component

Xi = weight fraction of component

Density:

$$\rho = \frac{(P)(MWf)}{(R)(T)}$$

where, ρ = density, lb./ft.^{3}

P = pressure, atm.

T = temperature gas, ^{o}R

R = gas constant, 0.73 atm.-ft.^{3}/lb.mole ^{o}R

Specific heat:

$$Ci = A + BT + CT^2$$

where, Ci = component specific heat, BTU/lb. mole °R

T = temperature, °K

This method for calculating component specific heat is accurate over the range of 77°F to 2200°F.

Enthalpy:

$$Hi = Hi^{o} + \int_{Tr}^{T} Ci \, dT$$

where, Hi = component enthalpy, BTU/lb. mole

Hi^{o} = heat of formation, BTU/lb. mole at 537°R

Ci = specific heat, BTU/lb. mole °R

Tr = reference temperature, 537°R

T = current temperature, °R

Viscosity:[5]

$$\mu i = \frac{(.0027)(MW)^{1/2}(T)^{3/2}}{(VB)^{2/3}\,((1.47\ TB) + T)}$$

where, μi = viscosity, centipoise

VB = volume constant, cc/g. mole

TB = temperature constant, °K

T = current temperature, °K

MW = molecular weight component

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[5] Perry, J.H., Chemical Engineers Handbook, 4th. Ed., 1963, p. 3-230.

Thermal conductivity:[6]

$$K_i = .605\,\mu_i(\,4C_i + 10)$$

where, K_i = thermal conductivity, BTU/hr.- ft^2-°F

The values of specific heat, enthalpy, viscosity, and thermal conductivity of the individual components are then all combined using Kay's rule to obtain the values for the gas mixture. For example, in the case of enthalpy,

$$H_f = \Sigma\, Y_i\, H_i$$

where, H_f = gas enthalpy

Y_i = mole fraction component

H_i = component enthalpy

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[6] Perry, J. H., Chemical Engineers Handbook, 4th. Ed., 1963, p. 3-224

2. Reactor Parameters

Reynolds Number

$$N_{re} = \frac{D\,V\,\rho}{\mu}$$

where, D = inside tube diameter, ft.

Nre = Reynolds Number, dimensionless

Prandtl Number

$$N_{pr} = \frac{C_f\,\mu}{K}$$

where, Npr = Prandtl number, dimensionless

Cf = specific heat gas, BTU/lb. mole °F.

Velocity

$$V = \frac{F}{\rho A} \times \frac{1}{3600}$$

where, V = velocity, ft./sec.

F = production rate, lb./hr. per pass

ρ = density gas, lb./ft.^{3}

A = cross sectional area tube, ft.^{2}

Sonic Velocity

$$V_s = 223 \left[\frac{\gamma\,T}{MW}\right]^{1/2}$$

where, γ = heat capacity, ratio, dimensionless

Vs = sonic velocity, ft./sec.

Mach Number

$$M_a = \frac{V}{V_s}$$

where, Ma = Mach number, dimensionless

The Mach number is an indication of how close the velocity of the gas is to the speed of sound, a Mach number of 1.0 being equal to the speed of sound.

3. Kinetic Constants

$$k = Ae^{-E/RT}$$

where, k = reaction rate constant
A = frequency factor
E = activation energy

4. Heat Flux

The heat flux across the tube wall is calculated using the following procedure:

A. A heat flux (dq/dAo) of 5000 BTU/hr.-ft^2 is assumed based on the outside tube area.

B. The inside tube surface temperature is calculated by convection.

$$dq/dAo = hi\ (Di/Do)\ (Ti-Tg)$$

where, hi = heat transfer film coefficient, BTU/ft^2- $^{\circ}$F
Di, Do = inside and outside tube diameter, ft.
Ti = inside tube surface temperature, $^{\circ}$F
Tg = temperature of gas, $^{\circ}$F

C. The outside tube surface temperature is calculated by conduction.

$$dq/dAo = (Kt/Th)(To - Ti)$$

where, Kt = thermal conductivity tube, BTU/hr.-ft^2-$^\circ$F

Th = tube wall thickness, ft.

To = tube outside temperature, $^\circ$F

D. A new value of heat flux is calculated from the radiation equation.

$$dq/dAo = \sigma \phi (Tf^4 - To^4)$$

where, σ = Stefan-Boltzman constant, 1.713×10^{-9} BTU/ft^2-hr.-($^\circ$R)^4

ϕ = tube bank geometry - emissivity factor

Tf = furnace temperature, $^\circ$R

To = outside tube surface temperature, $^\circ$R

E. Steps A through D are repeated until the value obtained for the heat flux remains constant for two successive iterations.

5. Friction Factors

Fluid friction:[7]

$$f = .0035 + .264\,(Nre)^{-.42}$$

where, f = fluid friction factor

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[7] Wilson, R.E., McAdams, W.H., Selzer, M., Ind. Eng. Chem., 14, (1922), p. 105.

Equivalent length:

$$Lr = (Kr)(Di)/4f$$

where, Lr = equivalent length of return bends, ft.

Kr = factor for added resistance of return bends

Ratio of equivalent length to straight length:

$$\wedge = (Lr + Ls)/Ls$$

where, Ls = length at center line of one tube plus return bend, ft.

6. Gradients, Change in Gas Conditions with Length

Concentration:

$$\frac{dC_2H_6}{dL} = -(1/V)\ (k_1 + k_2)\ X1$$

$$\frac{dC_2H_4}{dL} = (1/V)\ (MC_2H_4/MC_2H_6)\ (k_1 + k_2/2)\ X1$$

$$\frac{dCH_4}{dL} = (1/V)\ (MCH_4/MC_2H_6)\ (k_2)\ X1$$

$$\frac{dH_2}{dL} = (1/V)\ (MH_2/MC_2H_6)\ (k_1)\ X1$$

$$\frac{dH_2O}{dL} = 0$$

where, k = reaction constants, $sec.^{-1}$

where $C_2H_6 \xrightarrow{k_1} C_2H_4 + H_2$

$C_2H_6 \xrightarrow{k_2} 1/2\ C_2H_4 + CH_4$

M = molecular weight

V = velocity, ft./sec.

$X1$ = weight fraction ethane

Molecular weight:

$$dM/dL = -MW^2 \Sigma (1/Mi)(dXi/dL)$$

where, Mi = molecular weight of individual component

MW = average molecular weight of the gas mixture

Heat transfer:

$$dq/dL = (3.14)(Do)(dq/dAo)$$

Temperature and pressure:

The temperature and pressure gradients **are** obtained by solving the mechanical energy balance and the total energy balance simultaneously. The mechanical balance:

$$\left(\frac{\rho V^2}{gT}\right) \frac{dT}{dL} + \left(1 - \frac{\rho V^2}{gP}\right) \frac{dP}{dL} + \left(\frac{4\Lambda f\rho V^2}{2gDi} - \frac{V^2}{gM}\right) \frac{dM}{dL} = 0$$

The energy balance:

$$\left(Cp + \frac{V^2}{JgT}\right) \frac{dT}{dL} + \left(\frac{-V^2}{JgP}\right) \frac{dP}{dL} +$$

$$\left(\Sigma Hi \frac{dXi}{dL} - \frac{V^2}{JgM} \frac{dM}{dL} - \frac{1}{F} \frac{dq}{dL}\right) = 0$$

where, J = dimensional constant, 778 ft.-lb./BTU

g = dimensional constant, 32.2 ft./sec.^{2}

The above represent two linear equations in two unknowns, of the form:

$$A_1X + B_1Y + C_1 = 0$$

$$A_2X + B_2Y + C_2 = 0$$

where, $X = dT/dL$, the temperature change per foot of incremental reactor length

$Y = dP/dL$, the pressure change per foot of incremental reactor length

solving,

$$X = \frac{(B_1/B_2)\ C_2 - C_1}{A_1 - (B_1/B_2)\ A_2} = {}^{o}F./ft.$$

$$Y = \frac{(A_1/A_2)\ C_2 - C_1}{B_1 - (A_1/A_2)\ B_2} = lb.\ force/ft.^2\text{-}ft.$$

7. Increments and New Values of Variables

Tubular reactor design consists of the use of Euler's method of numerical integration with tube length as the independent variable. Thus, the change in Y, any dependent variable, is:

$\triangle Yi = (dY/dL)i\ \Delta Li$, where L is tube length

$Y = Yo + \Delta Y$, where Yo is the previous value of the dependent variable.

The new values of molecular weight, temperature, pressure, and conversion are calculated in this manner, and the overall program loop repeated until the desired conversion or reactor length is obtained.

Output

The computer printout offers all the necessary information for the design of the radiation section of the furnace. **The pro**cess and reactor data are printed and act as a check on the input data. A conversion profile is presented, which correlates conversion to ethylene, methane, and hydrogen as a function of reactor length, temperature, and tube residence time. The outlet tube velocity, the production rate, the physical properties, and the Mach number are also included for the designers information.

A sample of the printout is included with the examples in Chapter IV

CHAPTER III

REACTOR MODEL CONSTRAINTS

The reactor model has certain constraints which are dependent on processing and physical design of the furnace and reactor. The important constraints associated with the derived model are:

1. Process Velocity

   The Mach number (velocity of gas/sonic velocity) of the gas flowing through the tubes must be kept below 1.0. This is necessary to keep the gas velocity below the speed of sound.

2. Process Pressure

   The process pressure must be kept above 1.0 atmospheres to prevent leakage of air into the process. Air in the process side will cause oxidation and carbonization of the tubes.

3. Material Temperatures

   The following are the temperature limits for the materials of construction in the reactor and furnace.

A. Incoloy tubes	$<1800^{\circ}F$ at 30 psig.
B. Incoloy tube hangers	$<2100^{\circ}F$
C. K-23 refractory brick	$<2100^{\circ}F$
D. Mild steel stack	$<1000^{\circ}F$

4. Conversion

The converssion of ethane to form ethylene and by-products is limited to 75 percent in this model. The reversible kinetics of reactions (1) and (2) presented in Chapter I must be included before the model's stability can be extended beyond 75 percent ethane conversion.

CHAPTER IV

EXAMPLE PROBLEMS

This chapter contains three example problems chosen to show the methods used in applying the computer model to design of the radiation section of a pyrolysis tube reactor for cracking ethane.

Example no. 1 is a conversion based problem, in which the model develops a reactor design for a specified set of conditions and a desired ethane conversion per pass.

Example no. 2 is a length based problem, in which the model develops a reactor design for the conditions of example no. 1 and a specified tubular reactor length.

Example no. 3 shows the importance of selecting a suitable incremental length for use in the model's calculations. A large incremental length is found to produce instability in the reactor model.

A. Example No. 1 - Reactor length required for specified ethane conversion.

The purpose of this example is to determine the reactor length required to obtain a specified ethane conversion. The necessary data and input are found below.

(1) Select the reactor geometry

(a) Tube material - Incoloy

Most ethane cracking units employ Incoloy as the tube material. Incoloy tubes do however have some temperature limitations, and must be kept below 1800°F. Specification of the tube material also specifies the tube surface emissivity and tube thermal conductivity which are .90 and 12.5 respectively for Incoloy.

(b) Tube inside diameter - 4 inches

The tube inside diameters selected are usually between 3 and 5 inches. The tube wall thickness (D/16) and the tube pitch (2D) are then calculated from the diameter.

(c) Number of tube rows per bank - 1
This can be 1 or 2, depending on the case in study. The tube pitch is equal to (2D) for the one tube row case, and (3D) for the two tube row case.

(d) Tube length including return bend - 15 ft.
Usual design lengths are between 12 and 20 ft.

(2) Select the operating conditions

(a) Feed compostion - 100 percent ethane
The model is designed for 100 percent ethane feed.

(b) Feed pressure - 5.5 atm. absolute
Inlet pressures are in the range of 4-6 atm.

(c) Steam ratio - .2 lb. steam/lb. hydrocarbon
The steam ratio is usually in the range of .2-.4 lb.steam/lb. hydrocarbon feed.

(d) Mass velocity - 82,800 lb./hr.-ft.^{2}
This is the mass velocity of the gas including steam. Mass velocities in the range of 50,000 to 90,000 lb./hr.-ft.^{2} are common.

(e) Flue gas equilibrium temperature - 1900°F.

The flue gas temperature, equivalent to the furnace temperature, is usually between 1800 and 2000 °F. during ethane pyrolysis.

(f) Feed temperature - 250 °F.

Since the model is designed to include only single phase flow, it is important that the feed temperature is kept above the dew point of the inlet steam in order to avoid two phase flow. Feed temperatures are in the range of 200 - 300 °F., depending on the inlet steam ratio and total pressure of the gas.

(g) Ethane conversion - 55 percent

From the above conditions the necessary data are inserted into the model. The results show that for an ethane conversion of 55 percent the reactor length required is 600 feet and the ethylene yield is 48 percent of the ethane fed (see attached printout). The temperature of the gas at the reactor outlet has increased to 1526°F. and the pressure decreased to 1.33 atm., both within the reactor model's constraints. The pressure, however, is approaching atmospheric and extension of this case beyond 55 percent conversion may cause problems of excessive pressure drop and violation of model constraints. To extend this case beyond 55 percent conversion it would be necessary to study the effects of increasing the tube diameter, which would in turn reduce the velocity in the tube and accordingly also the pressure drop. Another important value obtained from the results is the total heat duty required in the radiation section of the furnace. This number is necessary to assist in design of the furnace heating system.

A number of cases must be tried to define the optimum conversion and reactor length to satisfy a given problem. Consideration must be given to the residence time of the gas in the reactor which if too long can contribute to the decomposition of ethylene into by-products (ref. no. 2) and to the total heat duty which can affect furnace sizing and thus capital investment. When all the reactor variables have been optimized it is possible to define the furnace heating requirements and the size of the convection section.

EXAMPLE NO. 1 RESULTS

```
     INPUT DATA CHECK
                          PROCESS  DATA

     THE MASS FLOW RATE IS   82800.0 LB/HR-FT2

     INLET TEMPERATURE TO RADIATION SECTION IS   250.00 F.

     INLET PRESSURE TO RADIATION SECTION IS  5.5 ATM

     TEMPERATURE IN THE RADIATION SECTION IS  1900.00 F.

     THE STEAM TO HYDROCARBON RATIO IS  .20

     THE SPECIFIED ETHANE CONVERSION IS  55.00


                          REACTOR  DATA

     THE TUBE DIAMETER IS 4.00 INCHES

     THE EMISSIVITY IS  .90

     THE THERMAL CONDUCTIVITY OF THE TUBES IS  12.50 BTU/HR-FT-F.

     THE LENGTH OF TUBES INC. RETURN BEND IS  15.0 FT

     THE FURNACE HAS ONE TUBE ROW PER BANK
```

GAS TEMP DEG F	GAS PRES ATM	TUBE LENGTH FT	RESIDENCE TIME SEC	CONVERSION WT PCT	ETHANE WT PCT	ETHYLENE WT PCT	METHANE WT PCT	HYDROGEN WT PCT
356.	5.46	10.	.12	.00	100.00	.00	.00	.00
450.	5.46	20.	.23	.00	100.00	.00	.00	.00
537.	5.44	30.	.33	.00	100.00	.00	.00	.00
617.	5.42	40.	.42	.00	100.00	.00	.00	.00
692.	5.39	50.	.50	.00	100.00	.00	.00	.00
761.	5.37	60.	.57	.00	100.00	.00	.00	.00
826.	5.34	70.	.64	.00	100.00	.00	.00	.00
887.	5.31	80.	.71	.00	100.00	.00	.00	.00
944.	5.28	90.	.77	.00	100.00	.00	.00	.00
997.	5.25	100.	.83	.00	100.00	.00	.00	.00
1048.	5.22	110.	.89	.00	100.00	.00	.00	.00
1096.	5.18	120.	.95	.00	100.00	.00	.00	.00
1141.	5.15	130.	1.00	.00	100.00	.00	.00	.00
1183.	5.11	140.	1.05	.01	99.99	.01	.00	.00
1224.	5.07	150.	1.10	.02	99.98	.02	.00	.00
1261.	5.03	160.	1.15	.05	99.95	.05	.00	.00
1297.	4.99	170.	1.20	.12	99.88	.11	.00	.01
1330.	4.95	180.	1.24	.27	99.73	.25	.01	.02
1357.	4.91	190.	1.29	.55	99.45	.50	.01	.04
1380.	4.87	200.	1.33	1.02	98.98	.93	.03	.06
1398.	4.82	210.	1.37	1.73	98.27	1.57	.05	.11
1411.	4.78	220.	1.42	2.70	97.30	2.44	.09	.17
1419.	4.73	230.	1.46	3.88	96.12	3.50	.14	.24
1425.	4.68	240.	1.49	5.21	94.79	4.69	.19	.32
1429.	4.63	250.	1.53	6.62	93.38	5.96	.25	.41
1432.	4.58	260.	1.57	8.08	91.92	7.27	.31	.50
1434.	4.53	270.	1.61	9.57	90.43	8.61	.38	.59
1437.	4.48	280.	1.64	11.07	88.93	9.95	.44	.68
1439.	4.43	290.	1.68	12.58	87.42	11.30	.51	.78
1441.	4.37	300.	1.71	14.09	85.91	12.65	.58	.87
1443.	4.32	310.	1.75	15.60	84.40	13.99	.64	.96
1446.	4.26	320.	1.78	17.10	82.90	15.34	.71	1.05
1448.	4.20	330.	1.81	18.61	81.39	16.68	.78	1.14
1450.	4.14	340.	1.84	20.11	79.89	18.02	.85	1.23
1453.	4.08	350.	1.87	21.60	78.40	19.36	.91	1.33
1455.	4.02	360.	1.90	23.09	76.91	20.69	.98	1.42
1457.	3.95	370.	1.93	24.58	75.42	22.02	1.05	1.51
1460.	3.89	380.	1.96	26.06	73.94	23.34	1.12	1.60
1462.	3.82	390.	1.99	27.54	72.46	24.66	1.19	1.69
1465.	3.75	400.	2.01	29.00	71.00	25.97	1.26	1.78
1467.	3.67	410.	2.04	30.47	69.53	27.27	1.33	1.86
1470.	3.60	420.	2.07	31.92	68.08	28.56	1.41	1.95
1473.	3.52	430.	2.09	33.36	66.64	29.85	1.48	2.04
1475.	3.44	440.	2.11	34.80	65.20	31.12	1.55	2.13
1478.	3.36	450.	2.14	36.22	63.78	32.39	1.62	2.21
1481.	3.27	460.	2.16	37.64	62.36	33.65	1.69	2.30
1484.	3.18	470.	2.18	39.04	60.96	34.89	1.76	2.38
1487.	3.09	480.	2.20	40.43	59.57	36.13	1.83	2.47
1490.	2.99	490.	2.22	41.80	58.20	37.35	1.91	2.55
1493.	2.89	500.	2.24	43.16	56.84	38.55	1.98	2.63
1497.	2.78	510.	2.26	44.50	55.50	39.74	2.05	2.71
1500.	2.67	520.	2.27	45.82	54.18	40.91	2.12	2.79

```
     1507.        2.42        540.          2.31        48.39       51.61       43.19       2.26        2.94
     1511.        2.29        550.          2.32        49.64       50.36       44.29       2.33        3.02
     1514.        2.14        560.          2.34        50.84       49.16       45.35       2.40        3.09
     1518.        1.98        570.          2.35        52.01       47.99       46.38       2.47        3.16
     1522.        1.80        580.          2.36        53.11       46.89       47.36       2.53        3.22
     1525.        1.59        590.          2.37        54.15       45.85       48.27       2.59        3.29
     1526.        1.33        600.          2.38        55.08       44.92       49.09       2.65        3.34


        ADDITIONAL OUTPUT INFORMATION

 THE OUTLET TUBE VELOCITY IS   1079.3 FT/SEC

 THE MACH NUMBER  -WHICH MUST BE BELOW 1.0 -IS  .45

 THE HYDROCARBON PRODUCTION RATE IS    6018.3 LB/HR

 THE TOTAL HEAT DUTY IN THE RADIANT SECTION IS          13155969.0 BTU/HR
 *STOP*
```

B. Example No. 2 - Ethane conversion for specified reactor length

The purpose of this example is to determine the ethane conversion and ethylene yield obtained for a specified reactor length. The reactor length specified is 580 ft., all the remaining input data being the same as that in example no. 1.

As can be seen from the attached printout, the profile is the same as example no. 1 to the 580 ft. length where this example ends. The same criterion for design of the reactor as discussed in example no. 1 apply here.

EXAMPLE NO. 2 RESULTS

```
INPUT DATA CHECK
                    PROCESS  DATA

THE MASS FLOW RATE IS   82800.0 LB/HR-FT2

INLET TEMPERATURE TO RADIATION SECTION IS   250.00 F.

INLET PRESSURE TO RADIATION SECTION IS  5.5 ATM

TEMPERATURE IN THE RADIATION SECTION IS  1900.00 F.

THE STEAM TO HYDROCARBON RATIO IS  .20

THE SPECIFIED REACTOR LENGTH IS  580.000 FT


                    REACTOR  DATA

THE TUBE DIAMETER IS 4.00 INCHES

THE EMISSIVITY IS  .90

THE THERMAL CONDUCTIVITY OF THE TUBES IS  12.50 BTU/HR-FT.F.

THE LENGTH OF TUBES INC. RETURN BEND IS  15.0 FT

THE FURNACE HAS ONE TUBE ROW PER BANK
```

GAS TEMP DEG F	GAS PRES ATM	TUBE LENGTH FT	RESIDENCE TIME SEC	CONVERSION WT PCT	ETHANE WT PCT	ETHYLENE WT PCT	METHANE WT PCT	HYDROGEN WT PCT
356.	5.48	10.	.12	.00	100.00	.00	.00	.00
450.	5.46	20.	.23	.00	100.00	.00	.00	.00
537.	5.44	30.	.33	.00	100.00	.00	.00	.00
617.	5.42	40.	.42	.00	100.00	.00	.00	.00
692.	5.39	50.	.50	.00	100.00	.00	.00	.00
761.	5.37	60.	.57	.00	100.00	.00	.00	.00
826.	5.34	70.	.64	.00	100.00	.00	.00	.00
887.	5.31	80.	.71	.00	100.00	.00	.00	.00
944.	5.28	90.	.77	.00	100.00	.00	.00	.00
997.	5.25	100.	.83	.00	100.00	.00	.00	.00
1048.	5.22	110.	.89	.00	100.00	.00	.00	.00
1096.	5.18	120.	.95	.00	100.00	.00	.00	.00
1141.	5.15	130.	1.00	.00	100.00	.00	.00	.00
1183.	5.11	140.	1.05	.01	99.99	.01	.00	.00
1224.	5.07	150.	1.10	.02	99.98	.02	.00	.00
1261.	5.03	160.	1.15	.05	99.95	.05	.00	.00
1297.	4.99	170.	1.20	.12	99.88	.11	.00	.01
1330.	4.95	180.	1.24	.27	99.73	.25	.01	.02
1357.	4.91	190.	1.29	.55	99.45	.50	.01	.04
1380.	4.87	200.	1.33	1.02	98.98	.93	.03	.06
1398.	4.82	210.	1.37	1.73	98.27	1.57	.05	.11
1411.	4.78	220.	1.42	2.70	97.30	2.44	.09	.17
1419.	4.73	230.	1.46	3.88	96.12	3.50	.14	.24
1425.	4.68	240.	1.49	5.21	94.79	4.69	.19	.32
1429.	4.63	250.	1.53	6.62	93.38	5.96	.25	.41
1432.	4.58	260.	1.57	8.08	91.92	7.27	.31	.50
1434.	4.53	270.	1.61	9.57	90.43	8.61	.38	.59
1437.	4.48	280.	1.64	11.07	88.93	9.95	.44	.68
1439.	4.43	290.	1.68	12.58	87.42	11.30	.51	.78
1441.	4.37	300.	1.71	14.09	85.91	12.65	.58	.87
1443.	4.32	310.	1.75	15.60	84.40	13.99	.64	.96
1446.	4.26	320.	1.78	17.10	82.90	15.34	.71	1.05
1448.	4.20	330.	1.81	18.61	81.39	16.68	.78	1.14
1450.	4.14	340.	1.84	20.11	79.89	18.02	.85	1.23
1453.	4.08	350.	1.87	21.60	78.40	19.36	.91	1.33
1455.	4.02	360.	1.90	23.09	76.91	20.69	.98	1.42
1457.	3.95	370.	1.93	24.58	75.42	22.02	1.05	1.51
1460.	3.89	380.	1.96	26.06	73.94	23.34	1.12	1.60
1462.	3.82	390.	1.99	27.54	72.46	24.66	1.19	1.69
1465.	3.75	400.	2.01	29.00	71.00	25.97	1.26	1.78
1467.	3.67	410.	2.04	30.47	69.53	27.27	1.33	1.86
1470.	3.60	420.	2.07	31.92	68.08	28.56	1.41	1.95
1473.	3.52	430.	2.09	33.36	66.64	29.85	1.48	2.04
1475.	3.44	440.	2.11	34.80	65.20	31.12	1.55	2.13
1478.	3.36	450.	2.14	36.22	63.78	32.39	1.62	2.21
1481.	3.27	460.	2.16	37.64	62.36	33.65	1.69	2.30
1484.	3.18	470.	2.18	39.04	60.96	34.89	1.76	2.38
1487.	3.09	480.	2.20	40.43	59.57	36.13	1.83	2.47
1490.	2.99	490.	2.22	41.80	58.20	37.35	1.91	2.55
1493.	2.89	500.	2.24	43.16	56.84	38.55	1.98	2.63
1497.	2.78	510.	2.26	44.50	55.50	39.74	2.05	2.71
1500.	2.67	520.	2.27	45.82	54.18	40.91	2.12	2.79
1503.	2.55	530.	2.29	47.12	52.88	42.06	2.19	2.87

```
     1507.        2.42        540.                 2.31        48.39      51.61      43.19      2.26       2.94
     1511.        2.29        550.                 2.32        49.64      50.36      44.29      2.33       3.02
     1514.        2.14        560.                 2.34        50.84      49.16      45.35      2.40       3.09
     1518.        1.98        570.                 2.35        52.01      47.99      46.38      2.47       3.16
     1522.        1.80        580.                 2.36        53.11      46.89      47.36      2.53       3.22


       ADDITIONAL OUTPUT INFORMATION

  THE OUTLET TUBE VELOCITY IS      854.1 FT/SEC

  THE MACH NUMBER  -WHICH MUST BE BELOW 1.0 -IS  .36

  THE HYDROCARBON PRODUCTION RATE IS     6018.3 LB/HR

  THE TOTAL HEAT DUTY IN THE RADIANT SECTION IS          12827761.0 BTU/HR
  *STOP*
```

C. Example No. 3 - Comparison of stability vs. incremental length size

This example is identical to example no. 2, however the incremental reactor length used in the calculations has been increased from 10 to 50 ft., the purpose being to determine the effect, if any, on the model's stability.

The results of this example (see attached printout) show an oscillation of the gas temperature along the reactor. The process temperature decreased because of the large length increment employed. The large increment produced a high temperature at the end of the preceeding increment, causing the calculated reaction in the next increment to be large, and the negative heat of reaction to exceed the heat transferred which in turn caused the temperature to fall. This phenomena continued to occur along the reactor causing oscillation in the process temperature.

The use of a 10 ft. incremental length in examples nos. 1 & 2 did not produce any oscillations or cause instability in the model, therefore it is concluded that 10 ft. increments are satisfactory for ~~design~~ of the reactor.

It may be necessary on certain problems to reduce the incremental length below 10 ft. to obtain a satisfactory design. This may be especially necessary in problems where conversion is specified, since for the last 10 ft. increment the conversion may go beyond the specified value.

EXAMPLE NO. 3

```
INPUT DATA CHECK
                    PROCESS  DATA

THE MASS FLOW RATE IS   82800.0 LB/HR-FT2

INLET TEMPERATURE TO RADIATION SECTION IS   250.00 F.

INLET PRESSURE TO RADIATION SECTION IS  5.5 ATM

TEMPERATURE IN THE RADIATION SECTION IS  1900.00 F.

THE STEAM TO HYDROCARBON RATIO IS  .20

THE SPECIFIED REACTOR LENGTH IS  580.000 FT


                    REACTOR  DATA

THE TUBE DIAMETER IS 4.00 INCHES

THE EMISSIVITY IS  .90

THE THERMAL CONDUCTIVITY OF THE TUBES IS  12.50 BTU/HR-FT-F.

THE LENGTH OF TUBES INC. RETURN BEND IS  15.0 FT

THE FURNACE HAS ONE TUBE ROW PER BANK
```

```
                                        CONVERSION  PROFILE

   GAS TEMP    GAS PRES    TUBE LENGTH   RESIDENCE TIME    CONVERSION   ETHANE     ETHYLENE    METHANE     HYDROGEN
    DEG F        ATM           FT             SEC            WT PCT     WT PCT      WT PCT      WT PCT      WT PCT

     778.        5.41          50.            .62              .00      100.00        .00         .00         .00
    1097.        5.27         100.            .97              .00      100.00        .00         .00         .00
    1322.        5.10         150.           1.25              .01       99.99        .01         .00         .00
    1478.        4.89         200.           1.48             1.26       98.74       1.14         .03         .08
    1293.        4.66         250.           1.68            21.02       78.98      18.72        1.04        1.27
    1465.        4.41         300.           1.86            21.46       78.54      19.12        1.05        1.30
    1433.        4.12         350.           2.02            31.49       68.51      28.05        1.53        1.91
    1502.        3.79         400.           2.17            35.87       64.13      31.97        1.72        2.16
    1435.        3.41         450.           2.29            47.73       52.27      42.48        2.37        2.69
    1534.        2.96         500.           2.40            50.36       49.64      44.83        2.49        3.05
    1472.        2.41         550.           2.49            61.51       38.49      54.64        3.17        3.71
    1560.        1.68         600.           2.55            63.92       36.08      56.78        3.29        3.85

      ADDITIONAL OUTPUT INFORMATION

 HE OUTLET TUBE VELOCITY IS      716.8 FT/SEC

 HE MACH NUMBER  -WHICH MUST BE BELOW 1.0 -IS  .30

 HE HYDROCARBON PRODUCTION RATE IS     6018.3 LB/HR

 HE TOTAL HEAT DUTY IN THE RADIANT SECTION IS          13453588.0 BTU/HR
*STOP*
```

CHAPTER V

REACTOR CONSTRAINTS THAT CAN BE REMOVED BY FUTURE WORK

To render the model a complete picture of ethane cracking, three items must be added to the cracking simulation. These three items are discussed below:

1. The reversible reaction kinetics of reactions (1) and (2) are necessary additions to the simulation to allow ethane conversions above the present limit of 75 percent.

   An attempt has been made to calculate the reversible rate constants from the equilibrium constants of the cracking reactions. To do this the equilibrium constants are calculated from component partial pressures which are then used to calculate the reverse rate constants as the ratio of the forward rate constant to the equilibrium constant. This method makes the assumption that the reaction is at equilibrium at the end of each length increment, which in actual practice may not be the case. The use of this calculation procedure in the reactor model produced instability and was not successful in predicting the reverse reaction rate constants.

The pyrolysis of ethylene was also investigated as a possible mechanism for the reversible reactions. This approach is not accurate, since the pyrolysis of ethylene forms several high molecular weight compounds in addition to those predicted by the reverse reactions.

It is recommended that a thorough literature search be conducted in an attempt to locate kinetic data applicable to the reverse reactions of the ethane/ethylene system, and that the reactor model be revised to include the reversible kinetics.

2. The model as written provides only for the design of the radiation section of a cracking furnace and excludes the convection or preheating section. At present the exit gas temperature from the convection section (inlet to radiation section) is required as input data to the model. To provide a more complete model the inlet temperature to the radiation section should be calculated based on the design of a furnace convection section.

3. The model lacks a fuel calculation for determination of the amount of natural gas and excess air required to provide the necessary heat to produce cracking temperatures. At present a temperature is assumed for the furnace interior with no regard to fuel or burner requirements. Inclusion of this will aid in determining burner sizing and also assist in predicting natural gas costs.

APPENDIX I

INPUT DATA SHEET

Card No.	Input	Column No.
1.	Length or conversion option 0 - Ethane conversion specified 1 - Reactor tube length specified	3
2.	Length or conversion desired - Conversion specified as percent - Length specified in feet	1 - 10
3.	A. Steam ratio as lb. steam/lb. hydrocarbon	1 - 10
	B. Incremental reactor length (preferred is 10 ft.)	11 - 20
4.	A. Inlet pressure (atm.)	1 - 10
	B. Inlet temperature (^{o}F)	11 - 20
	C. Furnace temperature (^{o}F)	21 - 30
	D. Mass flow rate (lb./hr.-ft.^{2}) (including steam)	31 - 40
5.	A. Inside tube diameter (inches)	1 - 10
	B. Length at center line of one tube plus return bend (ft.)	11 - 20
	C. Tube bank option (integer) 0 - one row per tube bank 1 - two tube rows per bank	30

Card No.	Input	Column No.
	D. Thermal conductivity of tubing (BTU/hr.-ft.-^{o}F)	31 - 40
	E. Tube surface emissivity	41 - 50

APPENDIX II

A. Program Listing

```
0 MAR 29,'71 ID=0031-E01
11335816,LØUGH.
GN M:SI,(FBCD)
GN F:2,(DEVICE,SI)
GN F:3,(DEVICE,LØ)

FLAG VERSIØN 36
AVAILABLE MEMØRY SIZE:
PRØGRAM AND INITIALIZED VARIABLES = 5487 (WØRDS)
NØN-INITIALIZED VARIABLES = 12798 (WØRDS)
TØTAL = 18285 (WØRDS)

C
C
C       PYRØLYSIS  ØF  ETHANE  TØ FØRM  ETHYLENE
C       DEREK J LØUGH
C
C       ETHANE         CØMPØNENT NØ. 1
C       ETHYLENE       CØMPØNENT NØ. 2
C       METHANE        CØMPØNENT NØ. 3
C       HYDRØGEN       CØMPØNENT NØ. 4
C       STEAM          CØMPØNENT NØ. 5
C
        DIMENSIØN HFØRM(5),WTC(5),VB(5),TB(5),XC(5),CC(5)
        DIMENSIØN XB(5),Y(5),CP(5),ENTHC(5),ENTHP(5),U(5),F(5)
        DIMENSIØN THRM(5),THM(5),GFRC(5),SUM(5),HSS(5),DEL(5)
C
C       INPUT   DATA
C
        READ(2,280)LØPT
  280   FØRMAT(I3)
        IF(LØPT-1)250,251,251
  251   READ(2,252)FLN
        GØ TØ 253
  250   READ(2,252)CØ
  253   CØNTINUE
  252   FØRMAT(F10.3)
        READ(2,63)RATIØ,DELTA
        READ(2,51)PRESF,TEMPP,TG,GFLØW
        READ(2,52)DII,EQS,NØPT,THRMD,EMIS
C
C       INPUT  DATA  READBACK
C
        WRITE(3,101)
        WRITE(3,100)
        WRITE(3,53)
   53   FØRMAT(20X,'PRØCESS  DATA'//)
        WRITE(3,532)GFLØW
  532   FØRMAT(1X,'THE MASS FLØW RATE IS',F10.1,' LB/HR-FT2'//)
        WRITE(3,54)TEMPP
   54   FØRMAT(1X,'INLET TEMPERATURE TØ RADIATIØN SECTIØN IS',F9.2,' F.'
     1  )
        WRITE(3,56)PRESF
   56   FØRMAT(1X,'INLET PRESSURE TØ RADIATIØN SECTIØN IS',F5.1,' ATM'//
        WRITE(3,57)TG
   57   FØRMAT(1X,'TEMPERATURE IN THE RADIATIØN SECTIØN IS',F9.2,' F.'//
        WRITE(3,58)RATIØ
   58   FØRMAT(1X,'THE STEAM TØ HYDRØCARBØN RATIØ IS',F5.2//)
        IF(LØPT-1)290,291,291
  290   WRITE(3,59)CØ
        GØ TØ 292
```

```
  291      WRITE(3,293)ELN
  293      FORMAT(1X,'THE SPECIFIED REACTOR LENGTH IS ',F8.3,' FT'///)
  292      CONTINUE
   59      FORMAT(1X,'THE SPECIFIED ETHANE CONVERSION IS  ',F5.2///)
           WRITE(3,530)
  530      FORMAT(20X,'REACTOR  DATA'//)
           WRITE(3,531)DII
  531      FORMAT(1X,'THE TUBE DIAMETER IS',F5.2,' INCHES'//)
           WRITE(3,533)EMIS
  533      FORMAT(1X,'THE EMISSIVITY IS',F5.2//)
           WRITE(3,534)THRMD
  534      FORMAT(1X,'THE THERMAL CONDUCTIVITY OF THE TUBES IS  ',F5.2,' BTU/
         1 HR-FT-F.'//)
           WRITE(3,535)EQS
  535      FORMAT(1X,'THE LENGTH OF TUBES INC. RETURN BEND IS ',F5.1, ' FT'//
         1 )
           IF(NOPT-1)540,541,541
  540      WRITE(3,550)
           GO TO 552
  541      WRITE(3,551)
  552      CONTINUE
  550      FORMAT(1X,'THE FURNACE HAS ONE TUBE ROW PER BANK')
  551      FORMAT(1X,'THE FURNACE HAS TWO TUBE ROWS PER BANK')
C
           COUNT=0.
           GQQ=0.
C     FAC WEIGHTING FACTOR ON HEAT FLUX TO DAMPEN OSCILLATORY BEHAVIOR
           FAC=0.
           HEATG=5000.
           I=0
           RESD=0.
C
C     CALCULATION  OF  CONSTANTS
C
           IF(LOPT-1)260,261,261
  260      CD=100.-CA
  261      CONTINUE
           TEMPF=TEMPF+460.
           DI=DII/12.
           DO=DI+DI/8.
           THICK=(DO-DI)/2.
           IF(NOPT-1)560,561,561
  560      S=2.*DI
           GO TO 562
  561      S=3.*DI
  562      CONTINUE
           IF(S/DI-2.)570,570,571
  570      RK=.75
           GO TO 572
  571      RK=.5
  572      CONTINUE
           AI=3.14*((DI/2.)**2.)
           FLOW=GFLOW*AI
C
C     CONSTANT VALUES
C
           WTC(1)=30.
           WTC(2)=28.
           WTC(3)=16.
           WTC(4)=2.
           WTC(5)=18.
           HFORM(1)=-36400.
```

```
      HFORM(2)=22500.
      HFORM(3)=-32200.
      HFORM(4)=0.
      HFORM(5)=-104000.
      VB(1)=51.2
      VB(2)=44.4
      VB(3)=29.6
      VB(4)=14.3
      VB(5)=18.9
      TB(1)=184.2
      TB(2)=169.5
      TB(3)=111.7
      TB(4)=20.4
      TB(5)=373.2
      XC(2)=0.
      XC(3)=0.
      XC(4)=0.
      XX=RATIO+1.
      XC(1)=1./XX
      XC(5)=1.-XC(1)
      MOLF=XC(1)*FLOW
C
C     BEGINNING  OF  OVERALL  LOOP
C
C
C     MOLECULAR  WEIGHT-----MOLE  FRACTIONS-----DENSITY FLUID
C
   10 XF=0.
      DO 1 J=1,5
      XB(J)=XC(J)/WTC(J)
    1 XF=XF+XB(J)
      WTF=1./XF
      DO 2 J=1,5
    2 Y(J)=XB(J)/XF
      DENSF=PRESF*WTF/(.73*TEMPF)
C
C     ENTHALPY  CALCULATIONS
C
      TEMPO=TEMPF/1.8
      CP(1)=Y(1)*(2.247+.0382*TEMPO-.000011*(TEMPO**2.))
      CP(2)=Y(2)*(2.83+.0286*TEMPO-.0000087*(TEMPO**2.))
      CP(3)=Y(3)*(3.381+.019*TEMPO-.0000043*(TEMPO**2.))
      CP(4)=Y(4)*(6.947-.0002*TEMPO+.0000005*(TEMPO**2.))
      CP(5)=Y(5)*(7.219+.0024*TEMPO+.0000003*(TEMPO**2.))
      HCAPF=0.
      DO 3 J=1,5
    3 HCAPF=HCAPF+CP(J)
      GAMAF=HCAPF/(HCAPF-1.987)
      ENTHF=0.
      DO 83 J=1,5
      IF(Y(J)-.001)80,80,81
   80 ENTHC(J)=HFORM(J)
      GO TO 83
   81 ENTHC(J)=HFORM(J)+CP(J)*(TEMPF-537.)/Y(J)
      ENTHP(J)=Y(J)*ENTHC(J)
   83 ENTHF=ENTHF+ENTHP(J)
C
      VELF=FLOW/(DENSF*AI)
      VEL=VELF/3600.
      SONV=223.*SQRT(GAMAF*TEMPF/WTF)
      AMACH=VEL/SONV
C
```

```
C     VISCOSITY  AND  THERMAL  CONDUCTIVITY
C
          VISCF=0.
          THERM=0.
          DO 82 J=1,5
          IF(Y(J)-.001)112,111,111
  112     CC(J)=0.
          GO TO 113
  111     CC(J)=CP(J)/(Y(J)*WTC(J))
  113     CONTINUE
          U(J)=((.0027)*(WTC(J)**.5)*(TEMPO**1.5))/((VB(J)**.67)*(1.47*TB(J
     1    +TEMPO))
          F(J)=U(J)*Y(J)*2.42
          VISCF=VISCF+F(J)
          THRM(J)=.605*U(J)*(4.*CC(J)*WTC(J)+10.)/WTC(J)
          THM(J)=Y(J)*THRM(J)*.57
   82     THERM=THERM+THM(J)
C
C     REYNOLDS   PRANTL
C
          REYN=DI*VELF*DENSF/VISCF
          PRNTL=(HCAPF/WTF)*VISCF/THERM
C
C     REACTION  RATE  CONSTANTS
C
          R1=(1.535E14)*EXP(-63500./TEMPF)
          R2=(2.58E16)*EXP(-77800./TEMPF)
C
C     GEOMETRIC   CONSIDERATIONS
C     GEOM=1/PHI
C
          OMEGA=S/DO+ATAN((((S/DO)**2.)-1.)**.5)-((S/DO)**2.-1.)**.5
          IF(NOPT-1)6,7,7
    6     GEOM=1./EMIS-1.+3.14/(2.*OMEGA)
          GO TO 8
    7     GEOM=1./EMIS-1.+3.14/(2.*OMEGA-((OMEGA**2.)*DO/S))
    8     CONTINUE
C
C     ITERATIVE  PROCEDURE  FOR CALCULATING  THE HEAT  FLUX
C
          HI=.023*(THERM/DI)*(REYN**.8)*(PRNTL**.4)
          IF(I-1)201,200,200
  201     HEAT=HEATO
          GO TO 202
  200     HEAT=HEAT2
  202     CONTINUE
          DO 10 J=1,20
          TIN=((HEAT*DO)/(HI*DI))+(TEMPF-460.)
          TO=(HEAT*THICK/THRMD)+TIN
          HEAT2=(1.713E-9/GEOM)*((TG+460.)**4.-(TO+460.)**4.)
          IF(ABS(((HEAT2-HEAT)/(HEAT2+HEAT))*2.)-.005)11,11,77
   77     HEAT=(HEAT*FAC+HEAT2)/(FAC+1.)
   10     CONTINUE
          WRITE(3,2000)
   11     FRIC=.0035+.264/(REYN**.42)
          EQL=RK*DI/(4.*FRIC)
          GAMBA=(EQL+EQS)/EQS
          V=1./VEL
C
C     INCREMENTING
C
          GFRC(1)=-V*(R1+R2)*XC(1)
```

```
      GFRC(2)=V*(WTC(2)/WTC(1))*(R1+R2/2.)*XC(1)
      GFRC(3)=V*(WTC(3)/WTC(1))*R2*XC(1)
      GFRC(4)=V*(WTC(4)/WTC(1))*R1*XC(1)
      GFRC(5)=0.
      SM=0.
      DØ 13 J=1,5
      SUM(J)=(1./WTC(J))*GFRC(J)
   13 SM=SM+SUM(J)
      GMWT=-SM*(WTF**2)
      GHEAT=3.14*D0*HEAT2
      VSQ=VEL**2
C
C     CØNSTANTS FØR TEMPERATURE AND PRESSURE
C
      A1=HCAPF/WTF+VSQ/(778.*32.2*TEMPF)
      A2=DENSF*VSQ/(32.2*TEMPF)
      PRESS=PRESF*2116.8
      B1=-VSQ/(778.*32.2*PRESS)
      B2=1.-DENSF*VSQ/(32.2*PRESS)
      HS=0.
      DØ 14 J=1,5
      HSS(J)=(ENTHC(J)/WTC(J))*GFRC(J)
   14 HS=HS+HSS(J)
      C1=HS-(VSQ/(778.*32.2*WTF))*GMWT-GHEAT/FLØW
      C2=(4.*GAMBA*DENSF*VSQ*FRIC)/(2.*32.2*DI)-(DENSF*VSQ*GMWT)/(32.2*W
     1TF)
      GTEMP=((B1/B2)*C2-C1)/(A1-(B1/B2)*A2)
      GPRES=(((A1/A2)*C2-C1)/(B1-(A1/A2)*B2))/2116.8
C
C     NEW ITERATIVE VALUES
C
      DØ 15 J=1,5
   15 DEL(J)=GFRC(J)*DELTA
      DELQ=GHEAT*DELTA
      DELT=GTEMP*DELTA
      DELP=GPRES*DELTA
      TEMPF=TEMPF+DELT
      TEMPP=TEMPF-460.
      PRESF=PRESF+DELP
      QQQ=QQQ+DELQ
C
C     ØUTPUT
C
      DØ 16 J=1,5
   16 XC(J)=DEL(J)+XC(J)
      XCC=XC(1)+XC(2)+XC(3)+XC(4)
      X1=(XC(1)/XCC)*100.
      X2=(XC(2)/XCC)*100.
      X3=(XC(3)/XCC)*100.
      X4=(XC(4)/XCC)*100.
      CØUNT=1.+CØUNT
      ELNTH=CØUNT*DELTA
      RES=DELTA/VEL
      RESD=RESD+RES
      CØNV=100.-X1
      IF(I-1)850,851,851
  850 CØNTINUE
      WRITE(3,101)
      WRITE(3,700)
  700 FØRMAT(50X,'CØNVERSIØN  PRØFILE'//)
      WRITE(3,701)
  701 FØRMAT(6X,'GAS TEMP',3X,'GAS PRES',3X,'TUBE LENGTH',3X,'RESIDENCE
```

```
     1 TIME',3X,'CØNVERSIØN',3X,'ETHANE',4X,'ETHYLENE',4X,'METHANE',5X,'H
     1 YDRØGEN')
       WRITE(3,702)
  702  FØRMAT(8X,'DEG F',7X,'ATM',9X,'FT',13X,'SEC',11X,'WT PCT',5X,'WT P
     1 CT',5X,'WT PCT',6X,'WT PCT',6X,'WT PCT'//)
  851  CØNTINUE
       WRITE(3,703)TEMPP,PRESF,ELNTH,RESD,CØNV,X1,X2,X3,X4
  703  FØRMAT(8X,F5.0,7X,F4.2,7X,F4.0,12X,F5.2, 9X,F5.2,5X,F6.2,7X,F5.2,7
     1 X,F5.2,7X,F5.2)
  100  FØRMAT(1X,'INPUT DATA CHECK')
  101  FØRMAT(1H1)
   51  FØRMAT(4F10.3)
   52  FØRMAT(2F10.3,I10,2F10.3)
   68  FØRMAT(2F10.3)
 2000  FØRMAT(11X,'THE SPECIFIED NUMBER ØF HEAT FLUX ITERATIØNS HAS BEEN
     1  EXCEEDED')
       I=I+1
       IF(LØPT-1)270,271,271
  270  IF(X1-CD)17,17,18
   17  GØ TØ 272
  271  IF(ELNTH-ELN)18,272,272
  272  CØNTINUE
       WRITE(3,1001)
 1001  FØRMAT(//,'              ADDITIØNAL ØUTPUT INFØRMATIØN'//)
       WRITE(3,810)VEL
  810  FØRMAT(1X,'THE ØUTLET TUBE VELØCITY IS',F10.1,' FT/SEC'//)
       WRITE(3,812)AMACH
  812  FØRMAT(1X,'THE MACH NUMBER  -WHICH MUST BE BELØW 1.0 -IS',F5.2//)
       WRITE(3,811)WALF
  811  FØRMAT(1X,'THE HYDRØCARBØN PRØDUCTIØN RATE IS',F10.1,' LB/HR'//)
       WRITE(3,1000)QQQ
 1000  FØRMAT(1X,'THE TØTAL HEAT DUTY IN THE RADIANT SECTIØN IS',F20.1,'
     1 BTU/HR')
       CALL EXIT
       END
```

```
CTUAL PRØGRAM SIZE:
RØGRAM AND INITIALIZED VARIABLES = 1951 (WØRDS)
ØN-INITIALIZED VARIABLES = 191 (WØRDS)
ØTAL = 2142 (WØRDS)
```

B. Definition of Fortran Nomenclature

A1 - Constant for calculation of temperature and pressure gradients

A2 - Constant for calculation of temperature and pressure gradients

AI - Cross sectional area of tube (ft.^{2})

AMACH - Mach number

B1 - Constant for calculation of temperature and pressure gradients

B2 - Constant for calculation of temperature and pressure gradients

C1 - Constant for calculation of temperature and pressure gradients

C2 - Constant for calculation of temperature and pressure gradients

CC - Individual component heat capacity (BTU/lb.)

CO - Desired ethane conversion (lb. ethane reacted/ lb. ethane fed)* 100

CONV - Ethane conversion along reactor tube (lb. ethane reacted/ lb. ethane fed)* 100

CP - Individual component contribution to total gas heat capacity (BTU/lb. mole)

DII - Inside tube diameter (inches)

DI - Inside tube diameter (ft.)

DEL - Change in weight concentration over incremental length

DELQ - Change in heat input over incremental length (BTU)

DELP - Change in pressure over incremental length (atm.)

DELT - Change in temperature over incremental length ($^{\circ}$F.)

DELTA - Incremental length (ft.)

DO - Outside tube diameter (ft.)

ELN - Specified reactor tube length (ft.)
ELNTH - Total length of tube (ft.)
EMIS - Emissivity of tube surface
ENTHC - Enthalpy of individual component (BTU/lb. mole)
ENTHF - Enthalpy of total gas (BTU/lb. mole)

FAC - Weighting factor on heat flux to dampen oscillatory behavior
FLOW - Production rate (lb./hr.)
FRIC - Fanning friction factor

GAMAF - Specific heat ratio (const. pressure/constant volume) of gas
GAMBA - Ratio of equivalent length (friction) to straight length
GEOM - Tube bank geometry - emissivity factor
GFLOW - Mass velocity (lb./hr.-ft^2)
GFRC - Change in component concentration with length (1/ft.)
GHEAT - Change in heat input with length (BTU/ft.)
GMWT - Change in molecular weight of gas with length (lb./lb. mole-ft.)
GPRES - Change in pressure of gas with length (ATM/ft.)
GTEMP - Change in temperature of gas with length (°F./ft.)

HCAPF - Heat capacity of the total gas (BTU/lb. mole)
HEAT2 - Actual heat flux across tube (BTU/ft^2)
HEATG - Initial guess at HEAT2
HFORM - Heat of formation of individual components (BTU/lb. mole)
HI - Heat transfer film coefficient, inside tube, (BTU/hr.-ft^2-°F.)

LOPT - Option for selection of conversion or length problem
NOPT - Tube bank geometry option

PRESF - Pressure of the gas (ATM)
PRNTL - Prantl number of the gas

QQQ - Total amount of heat input to gas in tube (BTU)

R_1 - Reaction rate constant of reaction No. 1 (sec^{-1})
R_2 - Reaction rate constant of reaction No. 2 (sec^{-1})
RES - Gas residence time in incremental length (sec)
RATIO - Steam to ethane ratio (lb. steam/lb. ethane)
RESD - Accumulated residence time of gas in tube (sec)
REYN - Reynolds number of gas
RK - Factor for added resistance of return bends

S - Tube spacing (pitch), center to center (ft.)
SONV - Sonic velocity (ft./sec.)

TB - Constant for calculation of viscosity and thermal cond. (°K)
TEMPF - Temperature of gas (°F.)
TEMPO - Temperature of gas (°K)
TEMPP - Temperature of gas (°R)
TG - Temperature inside furnace (°F.)
THICK - Tube wall thickness (ft.)

THERM - Thermal conductivity of gas (BTU/hr.-ft.-°F.)

THRMD - Thermal conductivity of tubing (BTU/hr.-ft.-°F.)

TIN - Temperature of inside tube surface (°F.)

TO - Temperature of outside tube surface (°F.)

VB - Constant for calculation of viscosity and thermal cond. (CC/g. mole)

VEL - Velocity of gas (ft./sec.)

VISCF - Viscosity of gas (lb./ft.-hr.)

WOLF - Hydrocarbon production rate (lb./hr.)

WTC - Molecular weight of component (lb./lb. mole)

WTF - Molecular weight of gas (lb./lb. mole)

XC - Weight fraction of individual component (including steam)

X1 - Weight fraction individual component (no steam)

X2 - Weight fraction individual component (no steam)

X3 - Weight fraction individual component (no steam)

X4 - Weight fraction individual component (no steam)

Y - Mole fraction of individual components (including steam)

BIBLIOGRAPHY

1. Davenport, C.H.; "Ethylene...What you Should Know", Petroleum Refiner, Vol. 39, No. 3, March, 1960.

2. Kunugi et. al.; "Kinetics and Mechanism of the Thermal Reaction of Ethylene", Industrial and Engineering Fundamentals, Vol. 8, No. 3, Aug., 1969.

3. McCabe, W.L. and Smith, J.C., Unit Operations of Chemical Engineering; 2nd Ed., 1967.

4. Perry, J.H., Chemical Engineers Handbook, McGraw-Hill; 4th Ed., 1963.

5. Schutt, H.C., Chem. Eng. Prog., Vol 55, p. 68, Jan., 1959.

6. Zdonik, S.B., Green, E.J., Hallee, L.P.; "Finding Desireable Feedstocks is Problem for Ethylene Producers", The Oil and Gas Journal, Dec. 19, 1966.

7. ibid., "How Cracking Proceeds in the Ethylene-Pyrolysis Reaction", The Oil and Gas Journal, June 26, 1967.

8. ibid., "Here's More on How Cracking Occurs in Ethylene Pyrolysis", The Oil and Gas Journal, July 10, 1967.

9. ibid., "How Products Form From Hydrocarbon Pyrolysis", The Oil and Gas Journal, July 24, 1967.

10. ibid., "Free-Radical Chain Mechanisms Applied to Specific Paraffins", The Oil and Gas Journal, Sept. 11, 1967.

11. ibid., "Product Distribution as a Function of Conversion or Severity", The Oil and Gas Journal, Feb. 19, 1968.

12. ibid., "Product Distribution vs. Temperature Residence Time", The Oil and Gas Journal, March 11, 1968.

13. ibid., "Function of Dilution Steam in Cracking", The Oil and Gas Journal, May 27, 1968.