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Ethane Pyrolysis in a Tubular Reactor Using a Modified Computer Solution of Differential Equations System

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In this paper the pyrolysis of ethane in a tubular reactor is represented essentially by irreversible first order chemical reaction. The required thermodynamic properties, kinetic information and physical constants are given. The steady state material and energy balances are established. We derived a system of two differential equations describing the axial temperature and conversion profiles for pyrolysis of ethane in a tubular reactor. It is required to calculate the length of tube for producing a desired maximum conversion of decomposition of ethane to ethylene and hydrogen. A modified method, which is numerically stable and convergent, is applied for solving the differential equations system. A computer flow-chart is constructed and represented in a computer FORTRAN IV program for solving the problem. The program has been run using the parameters given with several different values for the length increment and the internal diameter of reactor tube. The total reactor length and the temperature at the reactor outlet corresponding to the desired maximum conversion of ethane are explicitly calculated.

PROBLEM STATEMENT

The pyrolysis of ethane in the temperature range 1200 to 1700°F is represented essentially by the irreversible first-order chemical reaction

$$C_2H_6 \rightarrow C_2H_4 + H_2 \qquad (1)$$

$$\text{ethane} \rightarrow \text{ethylene} + \text{hydrogen.}$$

Pure ethane is fed at a rate of 1800 lb/hr at 1200°F to a 4.026 in I.D. steel tube contained in an ethane pyrolysis furnace. Heat is supplied by the furnace to the tube at a rate of 5000 BTU/hr sq ft (of inside tube area). The tube contains no internal obstructions (*e.g.* catalyst) and any pressure drop along the length of the tube can be ignored; the mean pressure for the gases in the tube may be assumed equal to 30 psia. Assuming gas flow in the tube, it is required to calculate the length of tube for producing 75 per cent decomposition of the ethane to ethylene and hydrogen. We should include provision for reading important parameters (ethane feed rate, inlet temperature, tube diameter, mean pressure, etc.) and conversion profiles along the length of the tube (ft) at desired intervals.

Required thermodynamic properties (standard heats of formation, ΔH_f, temperature-dependent specific heat capacities, C_p), kinetic information (the temperature-dependent rate constant for reaction (1), and physical constants are given in Table (1)[1].

TABLE 1

DATA FOR ETHANE PYROLYSIS REACTION

	ΔH_f at 298°K (cal/g mole)	C_p (cal/g mole°K)
C_2H_6 (gas)	−20236	$3.75 + 35.7\times10^{-3}\,\bar{T} - 10.12\times10^{-6}\bar{T}^2$
C_2H_4 (gas)	12496	$5.25 + 24.2\times10^{-3}\,\bar{T} - 6.88\times10^{-6}\bar{T}^2$
H_2 (gas)	0	$7.00 - 0.385\times10^{-3}\,\bar{T} + 0.6\times10^{-6}\bar{T}^2$

Reaction rate constant : $K = 5.764\times10^{16} - {}_{e}41310/\bar{T}$ (sec)$^{-1}$

Atomic weights : C = 12. H = 1.

Gas Constant : R = 10.73 psia cu ft/lb mol °R.

$\bar{T}$ is temperature in °K (Kelvin).

NOTATION AND FUNDAMENTAL RELATIONS

The problem is stated in mixed units, but will be solved using the BTU, lb mole, °R (Rankine), ft, and hr system. Adopt the following notations:

A = Cross-sectional area of tube, sq ft.

C = Concentration of ethane, lb moles/cu ft.

C_p = Specific heat capacity, BTU/lb mole °R.

K = Reaction rate constant, sec^{-1}.

L = Length measured from reactor inlet, ft.

n_O = Inlet molal feed rate of ethane, lb moles/hr.

$n_{C_2H_4}$ = Molal flow rate of ethylene at any point, lb moles/hr.

$n_{C_2H_6}$ = Molal flow rate of ethane at any point, lb moles/hr.

n_{H_2} = Molal flow rate of hydrogen at any point, lb moles/hr.

p = Total pressure, psia.

q = Heat input from furnace, BTU/hr ft (of tube length).

r = Specific reaction rate, lb moles ethane/cu ft hr.

T = Absolute temperature, °R.

$\bar{T}$ = Absolute temperature, °K.

V = Reactor volume, cu ft.

X = Mole fraction of ethane.

Z = Fraction of ethane converted to ethylene and hydrogen.

ΔH_f = Heat of formation, cal/g mole.

ΔH_R = Heat of reaction, BTU/lb mole.

The following conversion constants will be useful in generating a consistent set of units for the solution of the problem :

The Kelvin, Rankine, and Fahrenheit temperature scales are related by:

$$°R = °F + 460,$$
$$°K = °R/1.8.$$

The value of the specific heat capacity in cal/g mole °K is numerically equal to the specific heat capacity in BTU/lb mole °R.

The heat of reaction ΔH_R in BTU/1b mole is equal to 1.8 times its numerical value in cal/g mole.

The molal flow rates of the three constituents are:

	C_2H_6	=	C_2H_4 +	H_2
Inlet molal flow rate:	n_0		0	0
Molal flow rate when the conversion is:	$n_0(1 - Z)$		n_0Z	n_0Z

Thus the total number of moles flowing at any point in the tubular reactor is $n_0(1 + Z)$ and the corresponding mole fraction of ethane[2] is

$$x = (1 - Z)/(1 + Z)$$

STEADY STATE MATERIAL AND ENERGY BALANCES

Material Balance

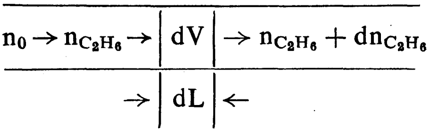


Fig. 1. Differential element of tubular reactor

The material balance for ethane over the differential volume element dV = AdL is:

Flowing In + From Reaction = Flowing Out

$$n_{C_2H_6} \quad + \quad rdV \quad = n_{C_2H_6} + dn_{C_2H_7}, \text{ (Figure 1)} \qquad (2)$$

Rearranging (2) we have:

$$r = \frac{dn_{C_2H_6}}{dV} = \frac{d[n_0(1 - Z)]}{AdL} = -\frac{n_0}{A} \cdot \frac{dZ}{dL}. \qquad (3)$$

For the given first-order irreversible reaction, the rate, r, is

$$r = -3600\ KC$$

where the conversion constant 3600 sec/hr is introduced for dimensional consistency. At the low pressure of the reacting gas mixture, the ideal gas law holds, so that (4) becomes

$$r = -3600\ K\frac{xP}{RT} = -3600\ K\frac{(1-Z)}{(1+Z)}\frac{P}{RT}. \tag{5}$$

From (3), (5) and Table (1), the conversion Z as a function of reactor length, L, is described by the solution of the first-order differential equation:

$$\begin{aligned}\frac{dZ}{dL} &= \frac{3600\ AP}{n_0 R}\cdot\frac{K}{T}\cdot\frac{1-Z}{1+Z}\\ &= \frac{2.07504\times10^{20}\ AP}{n_0}\cdot\frac{e^{-41310/T}}{T}\cdot\frac{1-Z}{1+Z}.\end{aligned} \tag{6}$$

For a given tube I.D., reactor pressure, and inlet ethane flow rate, the first factor on the right-hand side of (6) is constant; the second factor is a function of temperature only[3,4].

Energy Balance

The energy balance over the differential volume element dV must account for heat liberated due to reaction, heat introduced from the furnace through the tube wall, and sensible heat effects (because of temperature change) in the flowing gas stream. For a change dZ in conversion in the differential element, the heat liberated by the reaction is $n_0dZ\,(-\Delta H_R)$. The energy introduced into the differential element through the tube wall is qdL. The corresponding gain in enthalpy of the flowing gases is given by

$$\begin{aligned}\Delta H_s &= [n_{C_2H_6}\,C_{P_{C_2H_6}} + n_{C_2H_4}\,C_{P_{C_2H_4}} + n_{H_2}\,C_{P_{H_2}}]\,dT\\ &= [n_0(1-Z)C_{P_{C_2H_6}} + n_0Z(C_{P_{C_2H_4}} + C_{P_{H_2}})]\,dT,\end{aligned} \tag{7}$$

where dT is the temperature change across the differential element.

The energy balance is

$$n_0dZ(-\Delta H_R) + qdL = n_0[(1-Z)C_{P_{C_2H_6}} + Z(C_{P_{C_2H_4}} + C_{P_{H_2}})]\,dT. \tag{8}$$

Then the change in temperature as a function of length is described by the first-order differential equation:

$$\frac{dT}{dL} = \frac{\dfrac{q}{n_0} + (-\Delta H_R)\dfrac{dZ}{dL}}{(1-Z)C_{P_{C_2H_6}} + Z(C_{P_{C_2H_6}} + C_{P_{H_2}})}. \tag{9}$$

Provided that the temperature $\bar{T}$ is computed from temperature T, the heat capacity relationships from Table 1 can be introduced directly into the denominator of (9).

The heat of reaction, ΔH_R, varies with temperature according to[5,6]

$$\frac{d(\Delta H_R)}{dT} = C_{P_{C_2H_4}} + C_{P_{H_2}} - C_{P_{C_2H_6}}. \tag{10}$$

The heat of reaction at 298°K can be calculated from the heats of formation of Table 1 as $12496 + 20236 = 32732$ cal/g mole °K. Introducing the heat capacity relationships on Table 1 into (10), and integrating, yields the heat of reaction at any temperature T(°R),

$$\Delta H_R = 1.8[32732 + 8.5(\bar{T} - 298) - 0.005942(\bar{T}^2 - 298^2) + 1.28\times 10^{-6}(\bar{T}^3 - 298^3)] \text{ BTU/lb mole.} \tag{11}$$

MODIFIED METHOD FOR SOLVING THE DIFFERENTIAL EQUATIONS SYSTEM

Equations (6) and (9) are two nonlinear first order differential equations which should be solved simultaneously. The length L is the independent variable, and Z and T are the dependent variables.

The initial conditions are:

$$Z(L_0) = Z(0) = Z_0 = 0 \text{ (no conversion at inlet),}$$

$$T(L_0) = T(0) = T_0 = T_f \text{ (inlet feed temperature).}$$

The two differential equations (6) and (9) can be solved using a modified method as follows:

Let the vectors Y, F and Y_0 be:

$$Y(L) = \begin{bmatrix} Z \\ T \end{bmatrix}, F(L, Y) = \begin{bmatrix} f_1(L, Z, T) \\ f_2(L, Z, T) \end{bmatrix}, Y_0 = \begin{bmatrix} Z_0 \\ T_0 \end{bmatrix} = \begin{bmatrix} 0 \\ T_f \end{bmatrix}.$$

Let the step-length be $\Delta L = h$.

Thus (6) and (9) are reduced to a vectorial differential equation:

$$\frac{dY}{dL} = F(L, Y), Y(L_0) = Y_0, L \in [L_0, L_{max}].$$

Using the modified method[7], we get:

First Approximation:

$$Y^*_{n+1} = Y_n + hF(L_n, Y_n). \tag{12}$$

This formula has a truncation error of order two i.e. $O(h^2)$.

Modified Approximation:

$$Y_{n+1} = Y_n + \frac{h}{2}[F(L_n, Y_n) + F(L_{n+1}, Y^*_{n+1})]. \tag{13}$$

This formula has a third order truncation error *i.e.* $O(h^3)$.
Thus, the modified method may be written in the form:

$$\begin{bmatrix} Z^*_{n+1} \\ T^*_{n+1} \end{bmatrix} = \begin{bmatrix} Z_n \\ T_n \end{bmatrix} + h \begin{bmatrix} f_1(L_n, Z_n, T_n) \\ f_2(L_n, Z_n, T_n) \end{bmatrix}, \qquad (12')$$

$$\begin{bmatrix} Z_{n+1} \\ T_{n+1} \end{bmatrix} = \begin{bmatrix} Z_n \\ T_n \end{bmatrix} + \frac{h}{2} \left\{ \begin{bmatrix} f_1(L_n, Z_n, T_n) \\ f_2(L_n, Z_n, T_n) \end{bmatrix} + \begin{bmatrix} f_1(L_{n+1}, Z^*_{n+1}, T^*_{n+1}) \\ f_2(L_{n+1}, Z^*_{n+1}, T^*_{n+1}) \end{bmatrix} \right\}, \qquad (13')$$

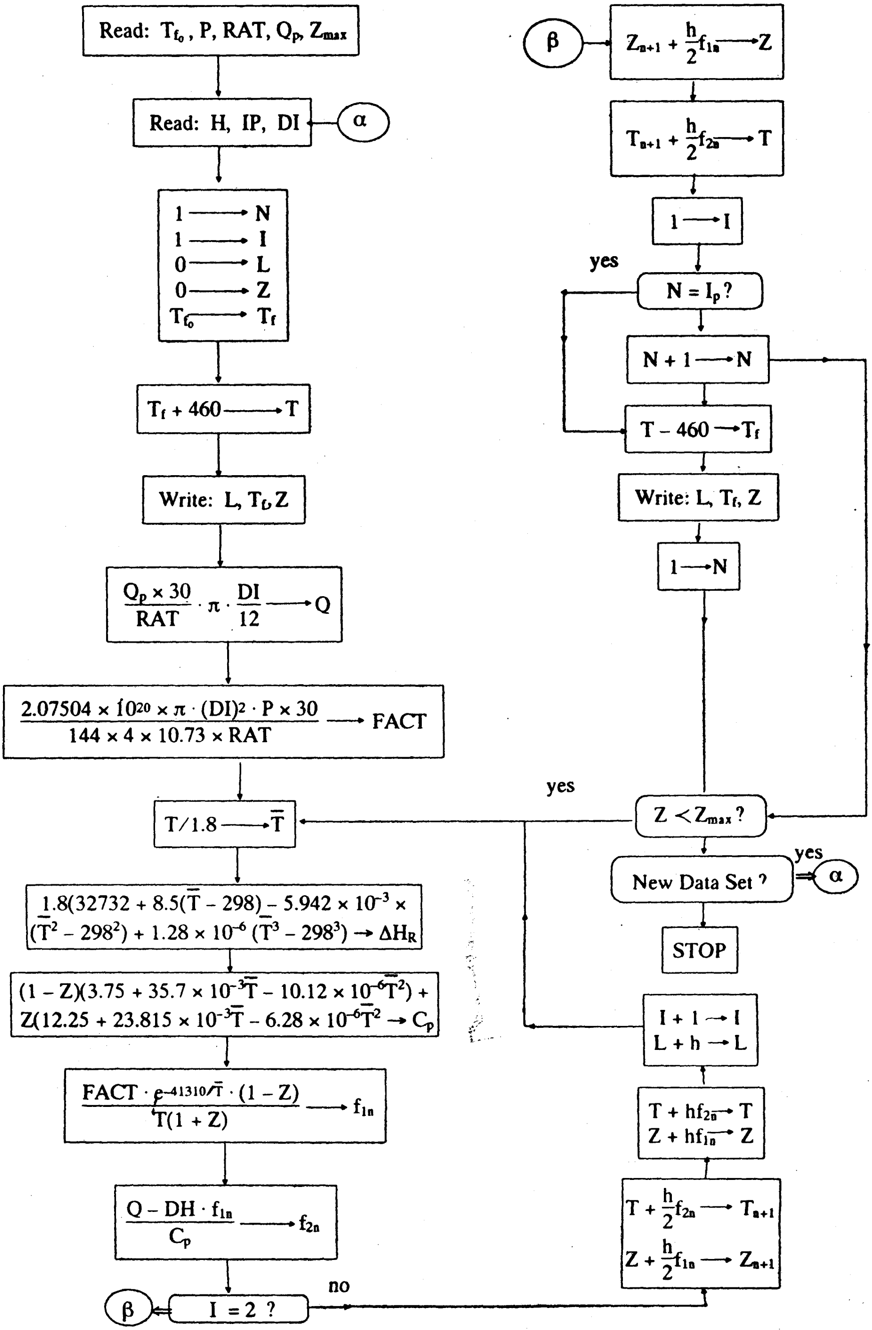
Here Z_{n+1} and T_{n+1} are, respectively, the conversion and temperature at $L_{n+1} = (n + 1)h$. At the beginning of the (n + 1)th step, the values of Z_n and T_n have already been calculated. The values of $F(L_n, Z_n, T_n)$ and $F(L_{n+1}, Z^*_{n+1}, T^*_{n+1})$ in the right hand side of (12) and (13) can be computed from (6) and (9). Then after this, Z_{n+1} and T_{n+1} can be computed. The process is repeated for subsequent steps until Z_{n+1} exceeds some desired upper limit Z_{max}, where $0 < Z_{max} \leqslant 1$.

The modified method is numerically stable in the sense that the error introduced at any stage tends to decay than build up. Also, the convergence of the method is guaranteed[8].

FORTRAN IMPLEMENTATION

Program Symbol	*Definition*
T, TF, TK	Temperature, °R, °F and °K respectively.
P	Pressure in the reactor, P, psia.
RAT	Inlet mass feed rate of ethane, lb/hr.
Q	q/n_0, BTU/lb mole ft.
QP	Heat input from furnace, BTU/hr sq ft. (of inside tube surface area).
Z	Fraction of ethylene converted, Z_n.
ZMAX	Desired conversion fraction for ethane, Z_{max}.
H	Length increment, ΔL, ft.
I, N	Step counters.
IP	Intermediate print control. Results are printed every IP steps.
DI	Internal diameter of reactor tube, D, in.
DH	ΔH_R, BTU/lb mole, equation (11).
AL	Length, L, ft.
FACT	The factor $2.075 \times 10^{20} \cdot AP/(n_0R)$.
CP	Denominator of equation (9), BTU/lb mole °R.
FIN	$(dZ/dL)_n$, ft^{-1}, equation (9).
F2N	$(dT/dL)_n$, R°/ft, equation (6).

A COMPUTER FLOW CHART FOR SOLVING THE DIFFERENTIAL EQUATIONS SYSTEM USING THE MODIFIED METHOD



CONCLUSION

The program (details can be obtained from the author) has been run using the parameters given in the problem statement with several different values for the length increment and the internal diameter of reactor tube. The total reactor length and the temperature at the reactor outlet corresponding to 75 per cent conversion of ethane, determined by linear extrapolation on the computed results, are shown in Table 2.

TABLE 2

TOTAL REACTOR LENGTH AND OUTLET TEMPERATURE FOR 75 PER CENT CONVERSION OF ETHANE

Internal diameter of reactor tube (inches)	Length increment (ft.)	Total reactor length (ft.)	Outlet temperature (°F)
3.548	0.02	708.601	1480.788
	0.05	708.825	1480.783
	0.10	708.932	1480.782
	0.50	708.973	1480.768
3.068	0.02	823.097	1488.379
	0.05	823.148	1488.390
	0.10	823.278	1488.379
	0.50	823.373	1488.378

The results are almost identical for length increments, suggesting that the truncation errors are small and the results accurate. Since the derivatives of (6) and (9) are small and virtually constant over a substantial portion of the reactor length, then the modified method produces rather accurate results for substantial length increments.

There is very little conversion of ethane in the first 70 ft of tube length; the gas temperature is rising because of heat input from the furnace through the tube wall, but the reaction velocity constant is quite small, and only a small amount of decomposition takes place. Once the temperature is high enough, the rate of reaction becomes significant. The temperature rises only very slowly thereafter, the heat introduced from the furnace is roughly balanced by the heat of reaction for the endothermic (energy-consuming) pyrolysis reaction.

In this work we assumed simply that the pressure is constant throughout the length of the reactor. This assumption would be unjustified for certain combinations of feed rate and tube diameter. The pressure drop along the reactor is almost entirely due to wall friction and not to the acceleration of the gases, so that a momentum balance yields a differential equation describing the rate of change of the pressure in the reactor with respect to the length of the reactor tube. The equation will augment the differential equations (6) and (9). This is what we intend to do in the future.

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