

TUBE BY TUBE DESIGN OF LIGHT HYDROCARBON
CRACKING FURNACES USING A
DIGITAL COMPUTER

By

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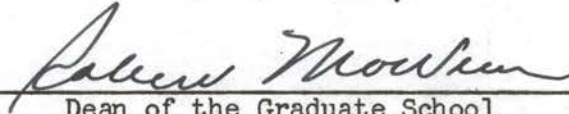
Thesis Approved:



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PREFACE

Thermal cracking of light hydrocarbons is of growing industrial importance for the production of olefins which are used in the manufacture of petrochemicals. The design of a furnace for pyrolysis of hydrocarbons involves a multiplicity of kinetic, heat transfer, and pressure drop calculations. A procedure and program have been developed by which these lengthy calculations may be conveniently performed on a medium-sized digital computer.

By machine computation, a thermal cracking furnace design may be obtained with speed and precision of calculation for ethane, propane, or butane feedstock. For a given furnace design, the effect of such variables as type of feedstock, heat flux, pressure, temperature, steam rate, and feed rate on furnace operation and olefin yield may be predicted.

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CHAPTER I

INTRODUCTION

The increasing use of olefins as raw materials for the manufacture of various polymers and chemical products has resulted in greater interest in the processes used in the petroleum industry to produce olefins. One method of producing olefins such as ethylene and propylene is by thermal cracking of the light hydrocarbons ethane, propane, or butane in a tube furnace of the type shown in Figure 1.

The light hydrocarbon feed is introduced into the convection section of the furnace where it is heated to a point at which cracking is incipient. For ethane, propane, or butane feed, this temperature is approximately 1000 °F. Steam is introduced with the light hydrocarbon feed to reduce coke formation during the cracking operation. The preheated feed enters the radiant section where it is thermally cracked to form olefins. The cracked gas effluent passes to quench, recovery, and separation equipment.

Well established methods are available for hand calculating the design of the preheating tubes in the convection section of the furnace since the convection section is essentially a preheater in which no cracking occurs. However, it was felt that use of a digital computer would be very advantageous in designing the radiant section in which the feed is cracked to form olefins. The design of tubes for the radiant section involves a multiplicity of kinetic, heat transfer, and pressure

drop calculations. To handle these lengthy calculations, a procedure and program were developed for use with a medium sized digital computer. The computer calculates composition, temperature, pressure, and enthalpy of the gas and skin temperature of the tube for each tube of the radiant section in a relatively short time. The machine routine is such that a choice of ethane, propane, or butane feedstock is easily made. Impurities in the feedstock are taken into consideration, and steam to hydrocarbon feed ratio may be varied as desired.

CHAPTER II

EQUATIONS

In this chapter the numerous equations required in automatic digital computation for the design of radiant tubes are developed. These include the stoichiometric and kinetic relationships, pressure drop and heat transfer equations, and the enthalpy calculations necessary for an energy balance across each tube.

Stoichiometric and Kinetic Equations

In the furnace design method, semi-empirical stoichiometric equations are used to express the overall reactions which take place in the thermal cracking. A reaction rate equation is formulated for each stoichiometric equation so that the rate of formation or disappearance of each component is expressed as a function of temperature, pressure, and cracked gas composition. This is the approach originally used by Myers and Watson (10) in 1946.

Development of the stoichiometric and kinetic equations for the thermal cracking of butane is described in detail in the following paragraphs. Stoichiometric and rate equations have been proposed for the thermal cracking of propane by Myers and Watson (10) and for the thermal cracking of ethane by Snow and Schutt (11). These proposed equations for propane and ethane were incorporated in the routine for the digital computer. Primary reactions in the thermal cracking of

propane are presented in Figure 5. Secondary reactions in the thermal cracking of propane are shown in Figure 6. Primary and secondary reactions in the thermal cracking of ethane are given in Figure 7 and Figure 8, respectively.

The type of fundamental cracking data from which the stoichiometric and kinetic equations for butane cracking were derived is illustrated in Figure 2. The curves in Figure 2 represent the products from the thermal cracking of butane at 1200 °F and one atmosphere and were plotted from the data of Egloff, Thomas, and Linn (3). Similar data are available at 1065 °F from the work of Steacie and Puddington (12) and Frey and Hepp (7), at 1112 °F from the work of Egloff, Thomas, and Linn (3), and at 1560 °F from the work of Frey and Hepp (8).

From Figure 2 it is apparent that the products of the primary reactions are methane and propylene, ethane and ethylene, and hydrogen and butylene. Therefore, the three primary stoichiometric equations for the thermal cracking of butane are expressed with these pairs of compounds as products as shown in Figure 3. For the reaction velocity constants of the accompanying reaction rate equations, recourse was made to the over-all reaction velocity constant for butane cracking as expressed by Steacie and Puddington (12). By proportioning the over-all velocity constant among the three primary reactions according to their reaction rate at zero conversion, the velocity constant of each primary reaction was determined.

The Arrhenius equation was used to evaluate the effect of temperature on the reaction velocity constants. By determining reaction velocity constants at two temperatures, two equations were obtained with two unknowns corresponding to the frequency factor and energy of

activation of the Arrhenius equation. The equations were solved, thereby determining the relationships shown between reaction velocity constants and temperature.

In addition to the variation of the over-all velocity constant with temperature, Steacie and Puddington (12) report that the velocity constant is also a function of butane conversion at conversions below 25 per cent. This variation of the reaction velocity constant with conversion was taken into consideration in the note shown in Figure 3.

Reversibility of the reactions was investigated by calculating equilibrium constants from the free energy function data of API Research Project 44 (2). Apparent order of reaction was checked by comparing the equations formulated at one atmosphere pressure with the data of Egloff, Thomas, and Linn (3) for the thermal cracking of butane at 100 psia and equivalent temperature levels. The results calculated from the equations were in agreement with the data at 100 psia, thereby confirming that the cracking followed a first order reaction.

The relationships of Figure 3 were used to calculate product distributions at various conversion levels for the primary reactions. The differences between these calculated product distributions and the distribution as shown by the data were attributed to secondary reactions. This served to identify the secondary reactions and provided a means of developing rate equations which were consistent with the primary reactions. The secondary reactions determined in this manner are shown in Figure 4.

A more detailed development of the reaction equations for butane cracking is shown in APPENDIX B. It should be emphasized that these equations were selected merely to represent the data obtained in thermal

cracking and are not meant to imply any particular reaction route or mechanism.

A total of fifteen elements and compounds were used to represent the products from the thermal cracking of ethane, propane, and butane. These products were hydrogen, carbon, methane, acetylene, ethylene, ethane, propylene, propane, butadiene, butylene, butane, C₅H₈, C₆H₁₀, C₆H₆, and C₁₀H₈.

Where C₅H₈, C₆H₁₀, C₆H₆, and C₁₀H₈ appear in the stoichiometric equations, they are not meant to imply any particular compound but instead represent the C₅ fraction, C₆ fraction, aromatic fraction, and tar fraction, respectively. Many compounds which are higher boiling than butane are formed in the cracking reactions. However, in cracking for olefin production, such compounds do not represent a major portion of the total products, and no attempt was made to express such compounds except as one of the fractions described above.

To calculate the change in composition across a furnace tube, the reaction rate (r) for each stoichiometric equation is determined. The product of the reaction rate and the tube volume to feed rate ratio (V/F) represents the change in composition (Δn) as follows:

$$r \text{ mols reacted/sec-ft}^3 \frac{V \text{ ft}^3}{F \text{ mols/sec}} = \Delta n \frac{\text{mols reacted}}{\text{mol feed}}$$

Composition of the cracked gas is expressed as mols/mol feed throughout the routine so that Δn may be applied directly to each stoichiometric equation to compute the composition of the tube effluent.

Pressure Drop and Heat Transfer Equations

Pressure drop and heat transfer through the tubes were calculated

by the equations shown in Figure 9. The equation for pressure drop is that given by Hougen and Watson (9) for gases flowing at high velocities and was derived from the general Fanning equation. The heat transfer equation which was used to determine the outside skin temperature of the tube takes into consideration the temperature drop across the gas film inside the tube and across the tube wall. The gas film heat transfer coefficient was calculated by the Dittus-Boelter equation (1).

In calculating pressure drop and tube skin temperature, the properties of the gas which were involved in the calculations (viscosity, density, heat capacity, and conductivity) were determined for each tube from the equations of Figure 9.

The calculations were made assuming the gas to behave ideally throughout the radiant section of the furnace. The relationship between reduced viscosity and reduced temperature of Figure 9 represents the straight line portion of the curve (plotting reduced viscosity as a function of reduced temperature and reduced pressure) between reduced temperatures of 2.5 and 5.0 for a reduced pressure of zero as shown by Hougen and Watson (9).

Enthalpy Calculations

In carrying out the design of the radiant section of the furnace, an energy balance is necessary across each tube in order to calculate outlet temperature. The energy balance is made by determining the difference in enthalpy between the material leaving and entering the tube and making this difference equal to the heat absorbed as given by the heat flux for the tube. This does not take into consideration the increase in kinetic energy of the gas, but the change in kinetic energy

is not significant in this problem.

A heat flux value is assigned for each radiant tube. The heat absorbed by the tube is the product of the heat flux value and the heat transfer area of the tube. Enthalpy of the gas is determined by summing the enthalpies of each component of the gas for the temperature in question. Enthalpy of each component is expressed as a polynomial in temperature. Coefficients of the polynomials were determined from curve fits and are stored in the computer as part of the program.

CHAPTER III

AUTOMATIC COMPUTING EQUIPMENT

The automatic electronic computer used in the furnace calculations is a DATATRON Digital Computer Model 204 (called the DATATRON). The DATATRON is a digital, medium-speed, internally programmed computer manufactured by the ElectroData Division of Burroughs Corporation. The DATATRON has a magnetic drum storage capacity of 4,080 words, a word consisting of ten digits plus sign. Operating characteristics, computer commands, general programming procedures, and operation and controls of the DATATRON are fully explained in DATATRON Bulletin 3021 (4).

Auxiliary equipment used with the DATATRON in the furnace calculations consists of a card reader for punched card input and a line printer for output. A Model 500 Card Converter is used as the connecting link between the card reader and the computer and between the computer and the line printer. The card reader is a Type 528 Accumulating Reproducer with a capacity of 200 cards per minute. The line printer is a Type 419 Numerical Accounting Machine with a capacity of 150 lines per minute. The card reader and line printer are manufactured by International Business Machines Corporation. The card reader, line printer, and card converter are described in DATATRON Bulletin 3023 (5).

Floating Point Control Unit Model 360 is used with the computer to automatically scale results and keep them within the range of the computer. The floating point operations are covered in DATATRON Bulletin

3028 (6).

In operating the computer, the program providing detailed calculation instructions is read in from paper tape, specific design data are read in from punched cards, and the answers are printed out by the line printer.

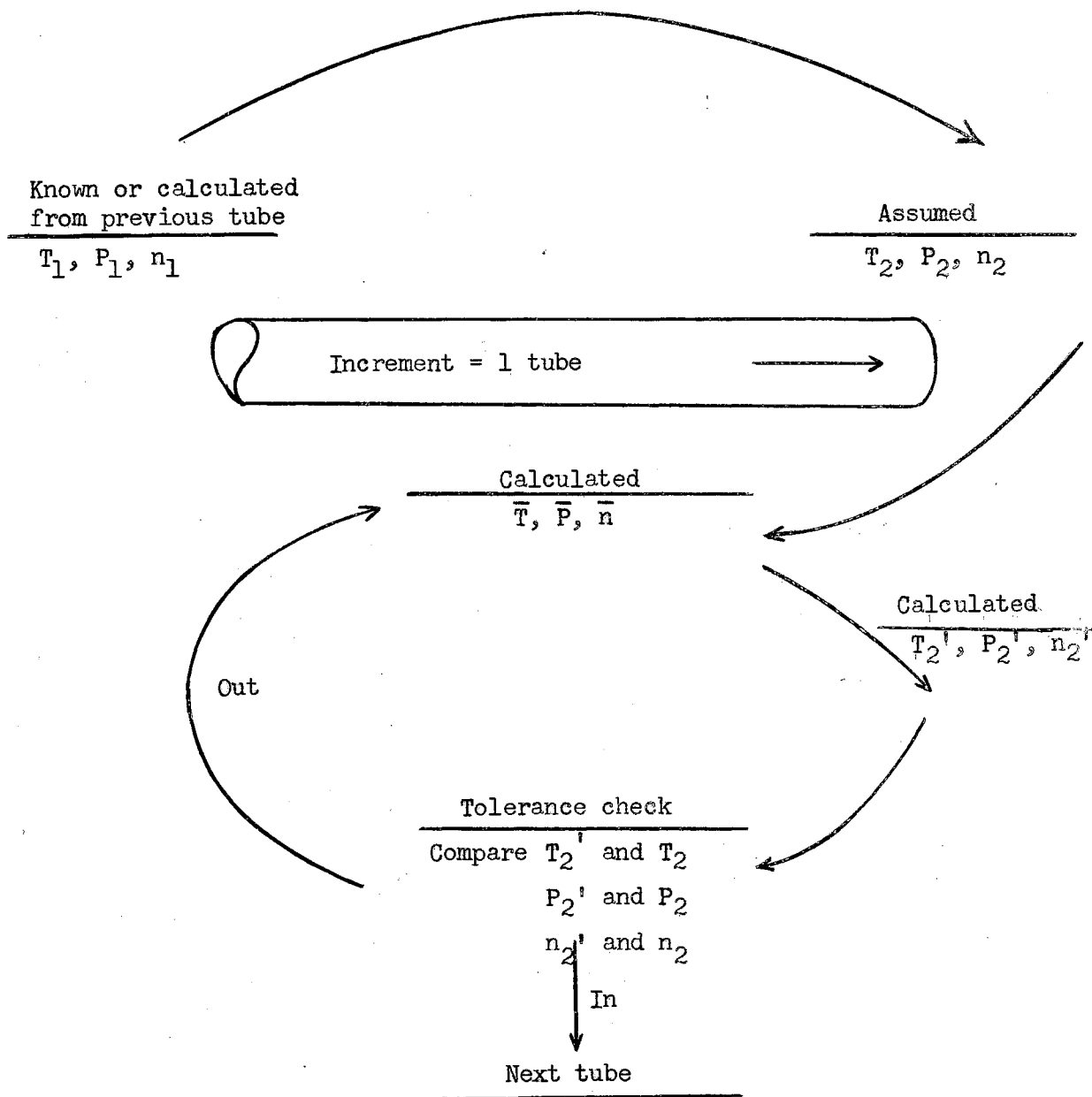
CHAPTER IV

DESIGN METHODS

The furnace may be calculated in any increment of tube length desired. For convenience, an increment of one tube is usually chosen. For the customary commercial furnace, an increment of one tube length is sufficiently small so that the approximations involved in the calculations do not affect the accuracy of the results. At the same time, the use of one tube length affords an easy physical interpretation of the change in temperature, pressure, and composition as the gas flows through the furnace.

The flow of calculations around the one tube increment is shown by Figure 10. At the inlet of the tube, the temperature, pressure, and composition (T_1, P_1, n_1) are known for the first tube of the radiant section or have been calculated from the previous tube for each tube following the first. The outlet temperature, pressure, and composition (T_2, P_2, n_2) are assumed. The arithmetic average temperature, pressure, and composition ($\bar{T}, \bar{P}, \bar{n}$) are computed. Based on the average temperature, pressure, and composition, the change in temperature, pressure, and composition are calculated across the tube, and the outlet temperature, pressure, and composition (T_2', P_2', n_2') are determined.

The calculated values of outlet temperature, pressure, and composition (T_2', P_2', n_2') are compared with the assumed values (T_2, P_2, n_2). If the differences between calculated and assumed values are within a speci-



CALCULATION FLOW

Figure 10

fied tolerance, the calculated outlet values are printed out for the tube, and the next tube is considered. If the differences are not within tolerance, average temperature, pressure, and composition (\bar{T} , \bar{P} , \bar{n}) are computed again based on the inlet values and previously calculated outlet values. This procedure is repeated until the outlet values are within tolerance.

The step by step calculation procedure is given below:

1. Read program into computer from paper tape.
2. Read load data for the particular furnace design into computer from punched cards. Load data consists of inlet pressure to the first tube of the radiant section of the furnace (P_1), outlet pressure from the last tube of the furnace (P_0), inlet temperature to the first tube (T_1), tube length for calculation of pressure, volume, and heat transfer ($L_{\Delta P}$, $L_{\Delta V}$, $L_{\Delta H}$), conductivity of the metal tube (C_m), inside diameter of the tube (D_i), total feed rate (W), tube wall thickness $\left(\frac{D_o - D_i}{2}\right)$, feed composition (n_1), and assumed outlet composition for the first tube (n_2).
3. Assume T_2 and P_2 .
4. Calculate average molecular weight of the feed.
5. Calculate all expressions of which the terms are constant, which include the quantities involving D_o , D_i , $L_{\Delta P}$, $L_{\Delta V}$, $L_{\Delta H}$, W , and C_m .
6. Calculate enthalpy of the feed.
7. Calculate \bar{T} , \bar{P} , and \bar{n} .
8. Calculate μ and ρ .
9. Calculate ΔP .

10. Calculate reaction velocity constants and equilibrium constants.
11. Calculate rate of reaction for each stoichiometric equation.
12. Calculate extent of each reaction ($\Delta n = r V/F$).
13. Calculate outlet composition (n_2').
14. Calculate enthalpy of gas at tube outlet (H_2).
15. Read in heat flux value for the tube from a punched card.
16. Calculate difference between change in enthalpy of gas leaving and entering the tube ($H_2 - H_1$) and heat absorbed.
17. Calculate the temperature difference (ΔT) corresponding to the above energy difference ($\Delta T = T_2 - T_2'$).
18. If $|T_2 - T_2'| > 1.0$ °F, assume a new outlet temperature.
19. Return to step (7).
20. Repeat until $|T_2 - T_2'| < 1.0$ °F.
21. If $|T_2 - T_2'| < 1.0$ °F, check pressure for tolerance.
22. If $|P_2 - P_2'| > 0.10$ psia, assume a new outlet pressure.
23. Return to step (7).
24. Repeat until $|P_2 - P_2'| < 0.10$ psia.
25. If $|P_2 - P_2'| < 0.10$ psia, check composition for tolerance.
26. If $|n_{2t} - n_{2t}'| > 0.0001$, assume a new outlet composition.
27. Return to step (7).
28. Repeat until $|n_{2t} - n_{2t}'| < 0.0001$.
29. If $|n_{2t} - n_{2t}'| < 0.0001$, calculate C_p .
30. Calculate $(Re)^{0.8}$.
31. Calculate C_g .
32. Calculate $(Pr)^{0.4}$.
33. Calculate overall heat transfer coefficient (U).
34. Calculate average skin temperature (T_s) of the tube.

35. Store T_2' , P_2' , n_2' as T_1 , P_1 , n_1 for next tube.
36. Assume T_2 , P_2 , and n_2 for next tube.
37. Store H_2 as H_1 for next tube.
38. Print out the tube number, skin temperature, effluent gas temperature, effluent pressure, effluent enthalpy, heat flux value, over-all heat transfer coefficient, and effluent composition.
39. If $P_2' - P_0$ is positive, return to step (7) to calculate the next tube.
40. If $P_2' - P_0$ is negative, stop the computer.
41. Continue until the desired number of tubes have been calculated or step (40) occurs.

Steps (1) through (3), (5), (7) through (9), and (14) through (41) represent the common portion of the program in that they are independent of the type of feedstock used. Steps (4), (6), and (10) through (13) are coded separately for each feedstock, and the program is designed to branch to the proper location depending on the feedstock. Therefore, it is possible to add new feedstocks by providing the data and equations to calculate step (4) (the molecular weight of the feed), step (6) (the enthalpy of the feed), and steps (10) through (13) (the stoichiometric and kinetic equations).

CHAPTER V

RESULTS

To illustrate the results of the tube by tube calculation method using the DATATRON, a furnace design representative of the commonly used cracking furnace in the petroleum industry was chosen as a basis. The radiant section of the furnace was assumed to consist of 27-4 7/8" inside diameter by 28' long tubes with 24.5' of each tube inside the firebox. Such tubes are connected by 180° close return bends which were assumed to be 11" from center line to center line. The tubes were assumed to be fabricated of type 304 stainless steel which is commonly used in this service and to have walls of 0.3125" thickness. For this arrangement, $L_{\Delta P} = 40.2'$, $L_{\Delta V} = 29.44'$, $L_{\Delta H} = 24.5'$,

$$C_m = 15 \text{ BTU/hr ft}^2 \text{ } ^\circ\text{F/ft}, \quad D_i = 4.875", \quad \text{and} \quad \frac{D_o - D_i}{2} = 0.3125".$$

With this furnace design, heat flux values were assumed for each tube of the radiant section as listed below. These values were selected as typical for the type of burner arrangement normally employed for such a furnace.

Tube Number*	Heat Flux Value (BTU/hr ft ²)
1-5	17,000
6	15,000
7	12,000
8	9,000
9-13	7,500
14-18	6,500
19-23	5,500
24-27	4,000

*Tube number from inlet of radiant section.

The program was run on the DATATRON to investigate furnace performance and product distribution for ethane, propane, and butane feedstocks. Results for each feedstock are described below. A summary of calculated furnace conditions and olefin yields for all three feedstocks is presented in Table I.

Ethane Feedstock

An ethane flow rate to the furnace of 7,425 lb/hr was assumed. Steam rate was set at 1,610 lb/hr, outlet pressure from the furnace was set at 38.5 psia, and inlet temperature to the radiant section was set at 995 °F.

Calculated results for these conditions are shown in Figures 17, 18, and 19. Figure 17 shows tube skin temperature, cracked gas temperature, and pressure profiles for ethane cracking. Major and minor product distributions are presented in Figures 18 and 19, respectively.

Propane Feedstock

Propane flow rate to the furnace was assumed as 7,870 lb/hr, and steam rate was set at 1,165 lb/hr. This results in the same mass flow rate and mol per cent steam as was used for ethane feedstock. Outlet pressure and inlet temperature were kept the same as for ethane feedstock.

Results for propane cracking are plotted in Figures 14, 15, and 16. Figure 14 shows temperature and pressure gradients through the furnace. Figures 15 and 16 show major and minor product distributions, respectively.

Butane Feedstock

Butane flow rate to the furnace was assumed as 8,120 lb/hr, and steam rate was set at 915 lb/hr. This is the same mass flow rate and mol per cent steam as was used for ethane and propane cracking. Outlet pressure and inlet temperature were the same as for ethane and propane feedstock.

Results for butane cracking are presented in Figures 11, 12, and 13. Figure 11 shows temperature and pressure gradients through the furnace. Figures 12 and 13 show major and minor product distributions, respectively.

CHAPTER VI

CONCLUSIONS

A procedure and program have been developed for use with a medium sized digital computer to perform rapidly cracking furnace calculations. By the described method of machine computation, a thermal cracking furnace design may be obtained with speed and precision of calculation for ethane, propane, or butane feedstock. Composition, temperature, pressure, and enthalpy of the gas and skin temperature of the tube are determined for each tube in the radiant section of the furnace. With the DATATRON, average machine time required to calculate one tube is less than two minutes. With this speed of calculation, it will be possible to investigate a variety of designs and to select the tube diameter, tube length, and number of tubes to meet desired specifications.

For a given furnace design, the effect of such variables as type of feedstock, heat flux, pressure, temperature, steam content, and feed rate on furnace operation and olefin yield may be predicted.

The semi-empirical stoichiometric and kinetic equations used in the furnace routine were derived from experimental laboratory data. In general, reaction rate data of this nature are somewhat unreliable due to the difficulty of accurately determining true effective temperature and reactor volume. Variations in over-all velocity constants by as much as a factor of three were found in the laboratory data. However,

the effect of a threefold change in over-all velocity constant was found to alter furnace design by less than three tubes out of twenty-seven or by less than ten per cent. Therefore, the routine is believed to be sufficiently accurate to obtain furnace designs with a maximum error of plus or minus ten per cent. in number of tubes required.

The treatment of stoichiometric and kinetic equations in the routine is semi-empirical and cannot serve as a reliable basis for extended extrapolation. The routine is applicable only in the temperature range of 1000 °F to 1600 °F and pressure range from atmospheric to 100 psia.

For the minor components which appear in the furnace effluent at mol fractions of less than 0.05, the kinetic data are sketchy and inconsistent. For these components it will be desirable to check the calculated results with actual results from a commercial furnace. In this manner the stoichiometric and kinetic equations may be verified or modified as necessary to simulate actual furnace operation.

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NOMENCLATURE

C_g	gas conductivity, BTU/hr ft ² °F/ft.
C_m	tube conductivity, BTU/hr ft ² °F/ft.
D_{avg}	average tube diameter, in.
D_i	inside diameter of tube, in.
D_o	outside diameter of tube, in.
H_1	enthalpy of gas at tube inlet, BTU/mol feed.
H_2	enthalpy of gas at tube outlet, BTU/mol feed.
K	equilibrium constant, atm.
$L_{\Delta H}$	effective length of tube for heat transfer, ft.
$L_{\Delta P}$	effective length of tube for pressure drop, ft.
$L_{\Delta V}$	effective length of tube for volume, ft.
M	molecular weight of feed, lb/lb mol.
P	total pressure, atm.
P_1	gas pressure at tube inlet, atm.
P_2	gas pressure at tube outlet, atm.
P_2'	calculated gas pressure at tube outlet, atm.
\bar{P}	average gas pressure in the tube, atm.
ΔP	pressure drop, psia.
P_r	Prandtl Number.
Q	heat flux, BTU/hr ft ² of outside area.
Re	Reynolds Number

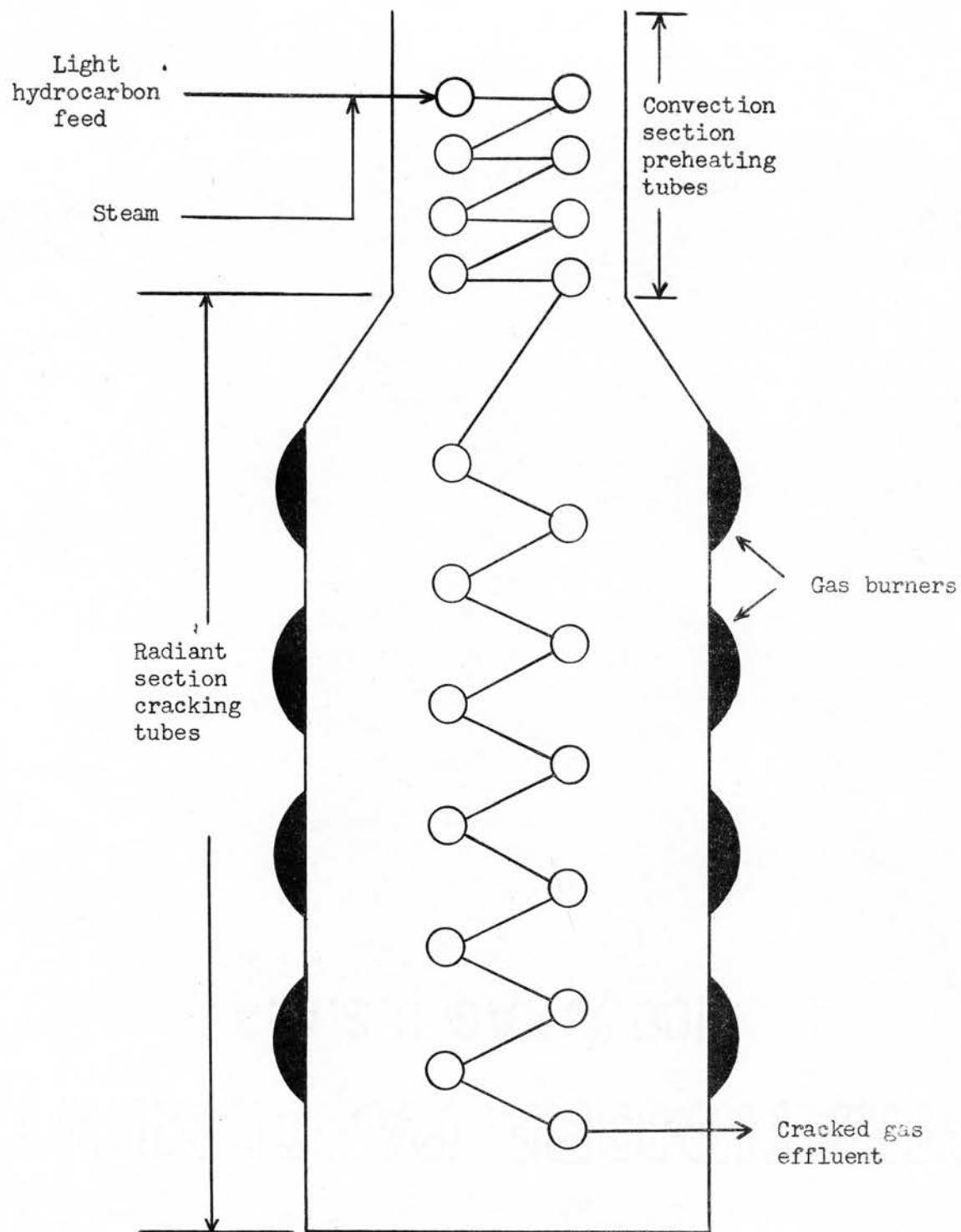
T	gas temperature, $^{\circ}\text{K}$.
T_1	gas temperature at tube inlet, $^{\circ}\text{F}$.
T_2	gas temperature at tube outlet, $^{\circ}\text{F}$.
T_2'	calculated gas temperature at tube outlet, $^{\circ}\text{F}$.
\bar{T}	average gas temperature in the tube, $^{\circ}\text{F}$.
T_r	reduced temperature.
T_s	average skin temperature of the tube, $^{\circ}\text{F}$.
U	overall heat transfer coefficient, $\text{BTU/hr ft}^2 \text{ }^{\circ}\text{F}$.
W	total feed rate, lb/hr .
k	reaction velocity constant, $\text{mols/sec ft}^2 \text{ atm}$.
n_1	amount of component at tube inlet, mols/mol feed .
n_2	amount of component at tube outlet, mols/mol feed .
n_2'	calculated amount of component at tube outlet, mols/mol feed .
\bar{n}	average amount of component in the tube, mols/mol feed .
n_t	total mols/mol feed .
r	reaction rate, mols/sec ft^3 .
μ	gas viscosity, micropoises.
μ_c	reduced viscosity of gas.
μ_r	critical viscosity of gas, micropoises.
ρ	gas density, lb/ft^3 .

APPENDIX A

TABLE I
SUMMARY OF FURNACE CONDITIONS AND OLEFIN YIELDS

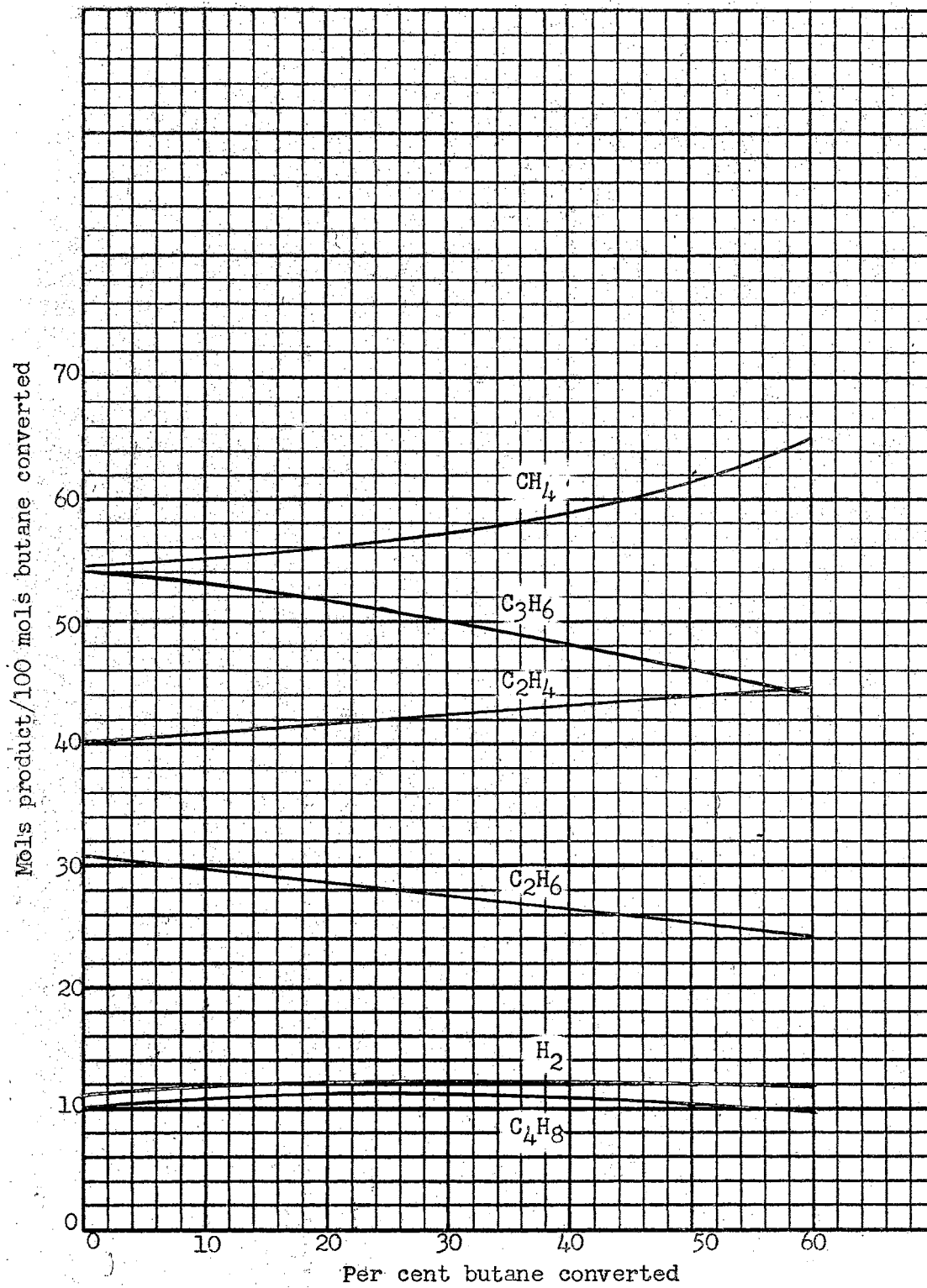
FEEDSTOCK	BUTANE	PROPANE	ETHANE
Inlet temperature to radiant section	995 °F	995 °F	995 °F
Outlet temperature from furnace	1431 °F	1406 °F	1422 °F
Skin temperature of outlet tube	1467 °F	1443 °F	1461 °F
Inlet pressure to radiant section	62.0 psia	65.0 psia	70.0 psia
Outlet pressure from furnace	38.4 psia	38.3 psia	39.0 psia
Ethylene yield*			
mols/mol feed	0.520	0.490	0.308
lb/lb feed	0.251	0.312	0.287
Propylene yield*			
mols/mol feed	0.180	0.166	0.007
lb/lb feed	0.130	0.158	0.010
Mol fraction in furnace effluent*			
Ethylene	0.245	0.268	0.229
Propylene	0.085	0.091	0.005
Feedstock conversion	88.8 %	86.6 %	36.8 %

*Water free basis



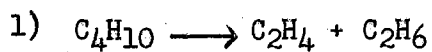
SCHEMATIC CROSS-SECTION OF CRACKING FURNACE

Figure 1



PRIMARY PRODUCTS FROM THERMAL CRACKING OF BUTANE AT 1200F, 1ATM

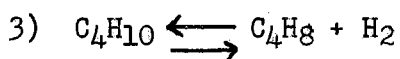
Figure 2



$$r = kP \frac{n_{\text{C}_4\text{H}_{10}}}{n_t}, \quad k = 7.58 \times 10^8 e^{\frac{-29,350}{T}}$$



$$r = kP \frac{n_{\text{C}_4\text{H}_{10}}}{n_t}, \quad k = 9.90 \times 10^6 e^{\frac{-24,900}{T}}$$



$$r = kP \left(\frac{n_{\text{C}_4\text{H}_{10}}}{n_t} - \frac{n_{\text{C}_4\text{H}_8} n_{\text{H}_2} P}{K n_t^2} \right), \quad k = 2.88 \times 10^{10} e^{\frac{-33,860}{T}}$$

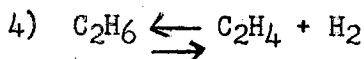
$$K = e^{\left(\frac{-16,250}{T} + 17.27 \right)}$$

Note: All rate equations multiplied by $\left[1.48 - 1.92 \left(1 - \frac{n_{\text{C}_4\text{H}_{10}}}{n_{\text{C}_4\text{H}_{10} \text{ feed}}} \right) \right]$

$$\text{when } \left(1 - \frac{n_{\text{C}_4\text{H}_{10}}}{n_{\text{C}_4\text{H}_{10} \text{ feed}}} \right) \leq 0.25.$$

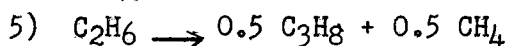
PRIMARY REACTIONS IN THERMAL CRACKING OF BUTANE

Figure 3

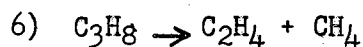


$$r = kP \left(\frac{n_{\text{C}_2\text{H}_6}}{n_t} - \frac{n_{\text{C}_2\text{H}_4} n_{\text{H}_2} P}{K n_t^2} \right), \quad k = 1.175 \times 10^{10} e^{\frac{-33,200}{T}}$$

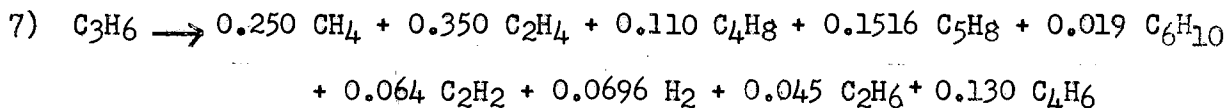
$$K = e^{\left(\frac{-17,450}{T} + 16.4 \right)}$$



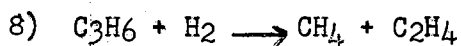
$$r = kP \frac{n_{\text{C}_2\text{H}_6}}{n_t}, \quad k = 2.34 \times 10^{11} e^{\frac{-34,200}{T}}$$



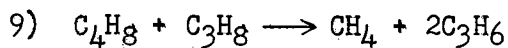
$$r = kP \frac{n_{\text{C}_3\text{H}_8}}{n_t}, \quad k = 4.30 \times 10^8 e^{\frac{-28,700}{T}}$$



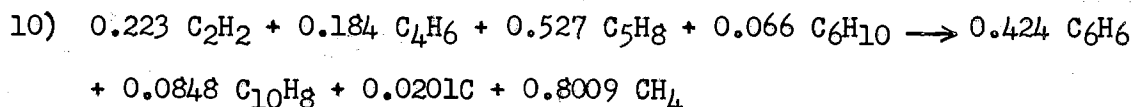
$$r = kP \frac{n_{\text{C}_3\text{H}_6}}{n_t}, \quad k = 1.936 \times 10^{10} e^{\frac{-31,600}{T}}$$



$$r = kP \frac{n_{\text{C}_3\text{H}_6}}{n_t}, \quad k = 5.62 \times 10^4 e^{\frac{-22,850}{T}}$$



$$r = kP \frac{n_{\text{C}_3\text{H}_8}}{n_t}, \quad k = 1.585 \times 10^{11} e^{\frac{-32,300}{T}}$$

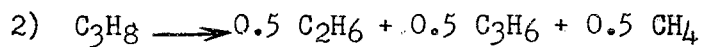


$$r = kP \frac{n_{\text{C}_2\text{H}_2} + n_{\text{C}_4\text{H}_6} + n_{\text{C}_5\text{H}_8} + n_{\text{C}_6\text{H}_{10}}}{n_t}, \quad k = 1.10 \times 10^7 e^{\frac{-24,000}{T}}$$

Note: All equations multiplied by $\left[1.48 - 1.92 \left(1 - \frac{n_{\text{C}_4\text{H}_{10}}}{n_{\text{C}_4\text{H}_{10} \text{ feed}}} \right) \right]$
 when $\left(1 - \frac{n_{\text{C}_4\text{H}_{10}}}{n_{\text{C}_4\text{H}_{10} \text{ feed}}} \right) \leq 0.25$.



$$r = kP \frac{n_{\text{C}_3\text{H}_8}}{n_t}, \quad k = 8.37 \times 10^{10} e^{\frac{-33,500}{T}}$$

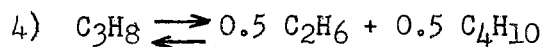


$$r = kP \frac{n_{\text{C}_3\text{H}_8}}{n_t}, \quad k = 1.02 \times 10^{10} e^{\frac{-32,700}{T}}$$



$$r = kP \left(\frac{n_{\text{C}_3\text{H}_8}}{n_t} - \frac{n_{\text{C}_3\text{H}_6} n_{\text{H}_2}}{n_t^2 K} \right), \quad k = 2.77 \times 10^9 e^{\frac{-30,200}{T}}$$

$$K = e^{\left(\frac{-15,400}{T} + 16.5 \right)}$$



$$r = kP \left(\frac{n_{\text{C}_3\text{H}_8}}{n_t} - \sqrt{\frac{n_{\text{C}_2\text{H}_6} n_{\text{C}_4\text{H}_{10}}}{n_t^2 K}} \right), \quad k = 6.92 \times 10^6 e^{\frac{-27,200}{T}}$$

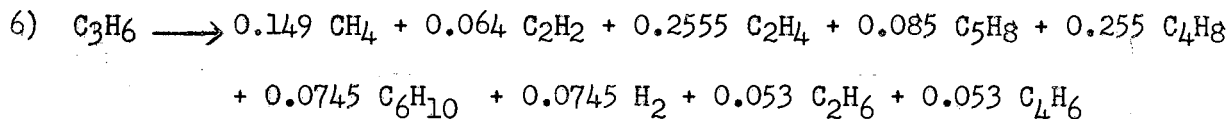
$$K = 1.30$$

PRIMARY REACTIONS IN THERMAL CRACKING OF PROPANE

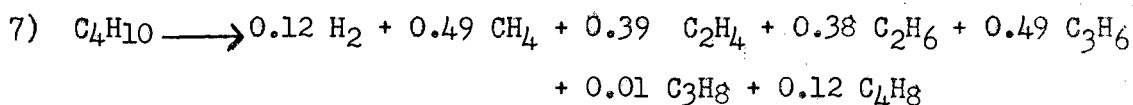
Figure 5



$$r = kP \frac{n_{\text{C}_3\text{H}_6}}{n_t}, \quad k = 1.46 \times 10^4 e^{\frac{-19,100}{T}}$$



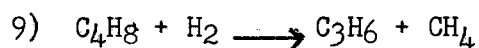
$$r = kP \frac{n_{\text{C}_3\text{H}_6}}{n_t}, \quad k = 7.62 \times 10^8 e^{\frac{-28,200}{T}}$$



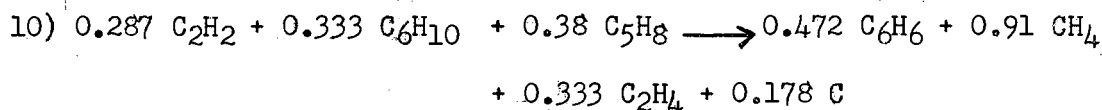
$$r = kP \frac{n_{\text{C}_4\text{H}_{10}}}{n_t}, \quad k = 1.33 \times 10^{11} e^{\frac{-31,700}{T}}$$



$$r = kP \left(\frac{n_{\text{C}_2\text{H}_6}}{n_t} - \frac{n_{\text{C}_2\text{H}_4} n_{\text{H}_2}}{n_t^2 K} \right), \quad k = 2.73 \times 10^9 e^{\frac{-31,700}{T}} \\ K = e^{\left(\frac{-17,300}{T} + 16.2 \right)}$$



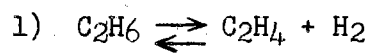
$$r = kP \frac{n_{\text{C}_4\text{H}_8}}{n_t}, \quad k = 1.32 \times 10^{12} e^{\frac{-33,700}{T}}$$



$$r = kP^2 \left(\frac{n_{\text{C}_2\text{H}_2} + n_{\text{C}_6\text{H}_{10}} + n_{\text{C}_5\text{H}_8}}{n_t} \right)^2, \quad k = 2.59 \times 10^6 e^{\frac{-17,600}{T}}$$

SECONDARY REACTIONS IN THERMAL CRACKING OF PROPANE

Figure 6

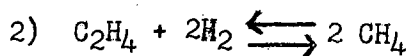


$$r = kP \left(\frac{n_{\text{C}_2\text{H}_6}}{n_t} - \frac{n_{\text{C}_2\text{H}_4} n_{\text{H}_2}}{n_t^2 K} \right), \quad k = \frac{3.46 \times 10^{14}}{T} e^{\frac{-36,300}{T}}$$

$$K = 3.31 \times 10^{-7} e^{0.014T}$$

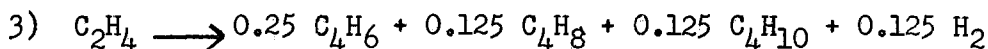
PRIMARY REACTION IN THERMAL CRACKING OF ETHANE

Figure 7



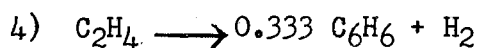
$$r = kP \left(\frac{P^n \text{C}_2\text{H}_4}{n_t^2} \sqrt{n \text{C}_2\text{H}_6 n \text{H}_2} - \frac{n \text{CH}_4}{n_t K} \right), \quad k = 7.50 \times 10^7 e^{\frac{-29,300}{T}}$$

$$K = 1.0$$

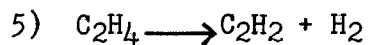


$$r = 0.012 kP^2 \left(\frac{n \text{C}_2\text{H}_6}{n_t} - \frac{n \text{C}_2\text{H}_4 n \text{H}_2 P}{n_t^2 K} \right), \quad k = \frac{3.46 \times 10^{14}}{T} e^{\frac{-36,300}{T}}$$

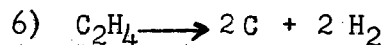
$$K = 3.31 \times 10^{-7} e^{-0.014/T}$$



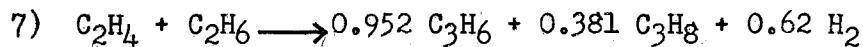
$$r = \frac{kP^2}{n_t^2} n^2 \text{C}_2\text{H}_4, \quad k = 4.09 \times 10^9 e^{\frac{-33,400}{T}}$$



$$r = \frac{kP}{n_t^2} n^2 \text{C}_2\text{H}_4, \quad k = 9.13 \times 10^7 e^{\frac{-30,800}{T}}$$



$$r = \frac{kP^2}{n_t^2} n^2 \text{C}_2\text{H}_4, \quad k = 4.51 \times 10^4 e^{\frac{-24,500}{T}}$$



$$r = kP \left(\frac{n \text{C}_2\text{H}_6}{n_t} - \frac{n \text{C}_2\text{H}_4 n \text{H}_2 P}{n_t^2 K} \right), \quad k = 1.04 \times 10^{14} e^{\frac{-46,200}{T}}$$

$$K = 3.31 \times 10^{-7} e^{-0.014/T}$$

SECONDARY REACTIONS IN THERMAL CRACKING OF ETHANE

Figure 8

$$\Delta P = 0.0235 \left(\frac{W}{1000} \right)^{1.8} \frac{L}{D_i} \frac{\Delta P}{4.8} \frac{\mu^{0.2}}{\rho}$$

$$U = \frac{1}{\frac{D_o}{(Re)^{0.8} (12)(0.0225)(C_g)(Pr)^{0.4}} + \frac{D_o \left(\frac{D_o - D_i}{2} \right)}{C_m D_{avg} (12)}}$$

$$T_s = \frac{T_1 + T_2}{2} + Q/U$$

$$\ln \mu_r^{0.2} = 0.1354 \ln T_r - 0.1208$$

$$\mu = \mu_r \mu_c$$

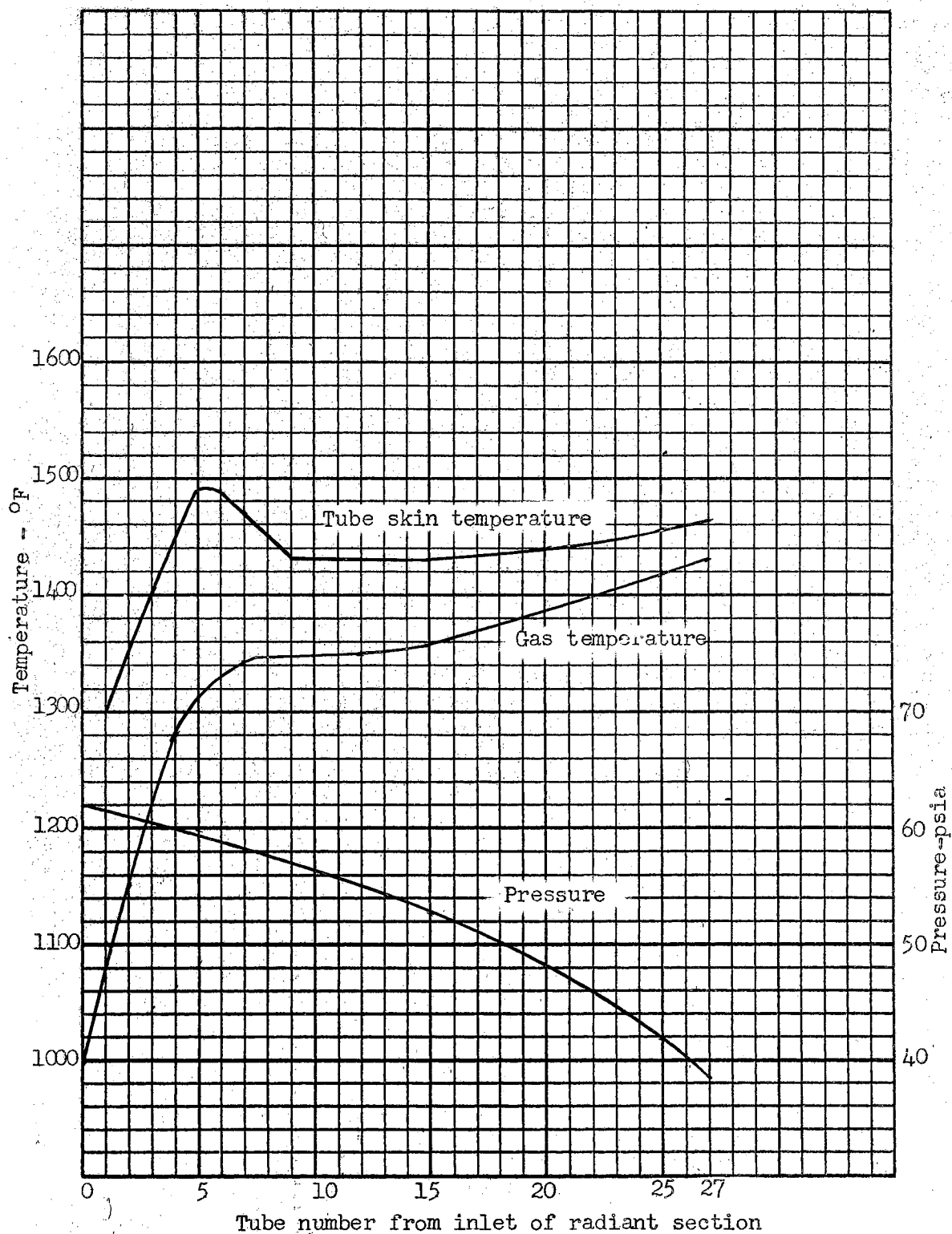
$$\rho = \frac{PM}{n_t (\bar{T})(0.729)}$$

$$C_p = \frac{H_2 - H_1}{T_2 - T_1}$$

$$C_g = 0.00017 T_2 - 0.1490$$

PRESSURE DROP AND HEAT TRANSFER EQUATIONS

Figure 9



TEMPERATURE AND PRESSURE GRADIENTS FOR BUTANE CRACKING

Figure 11

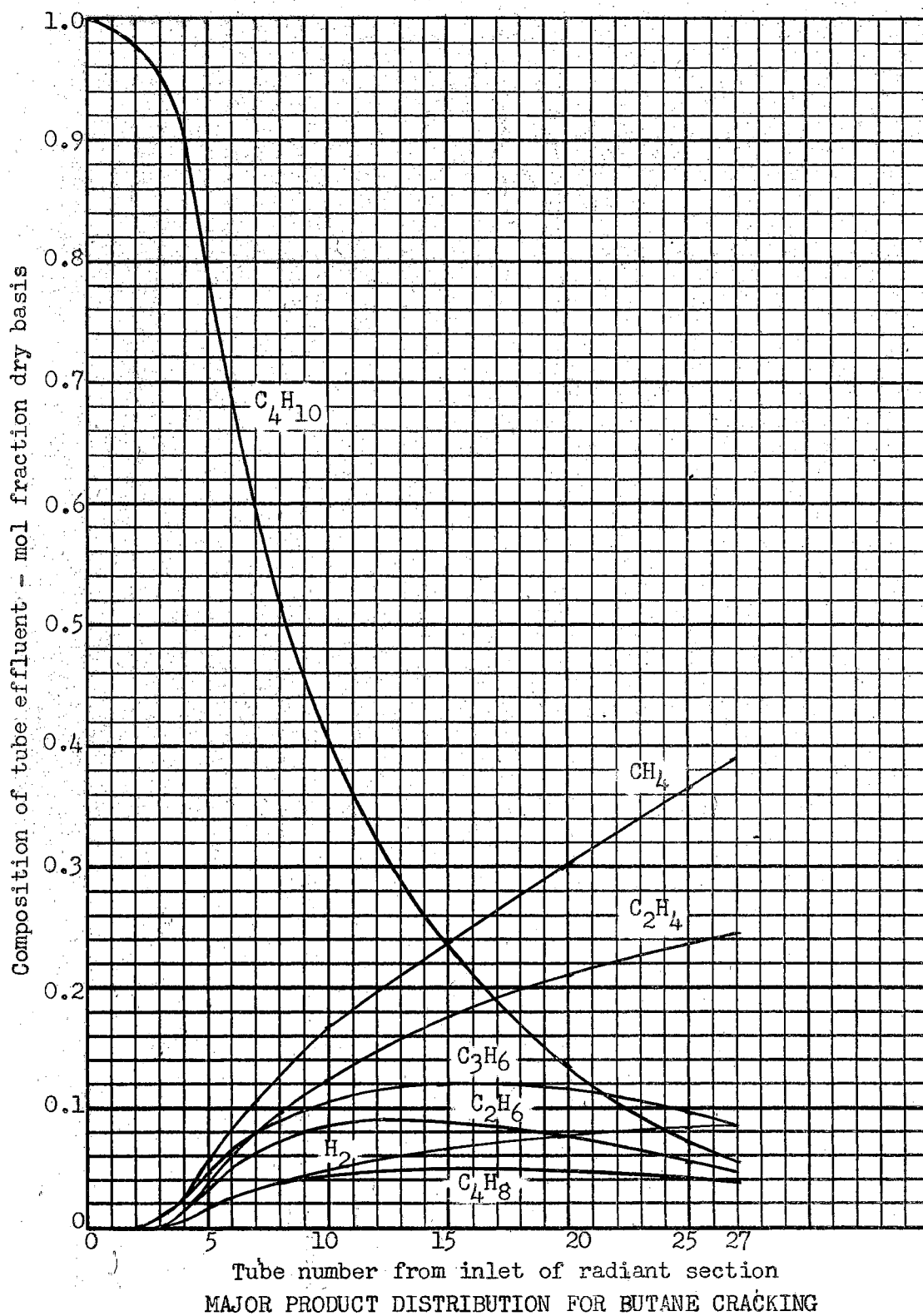


Figure 12

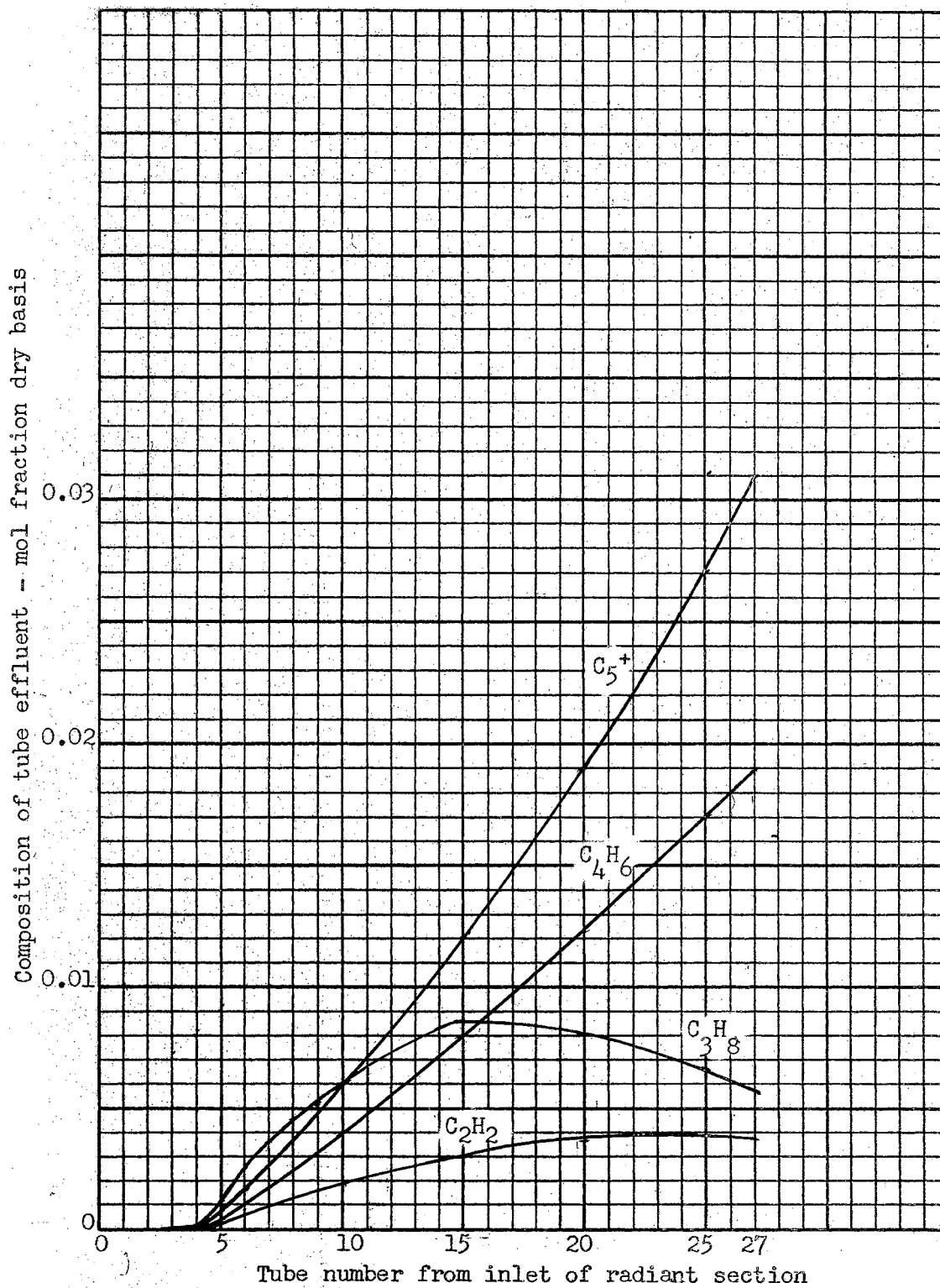
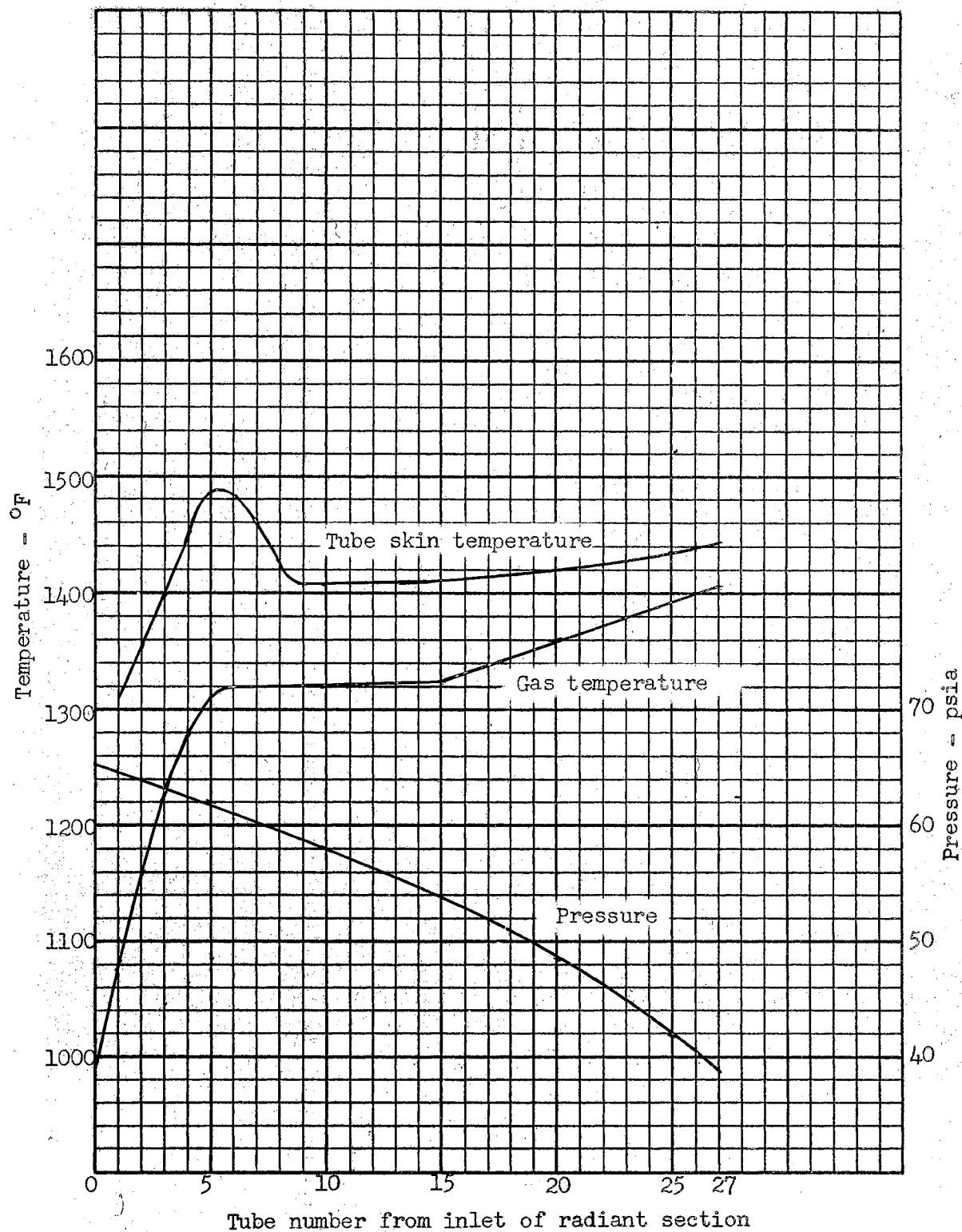
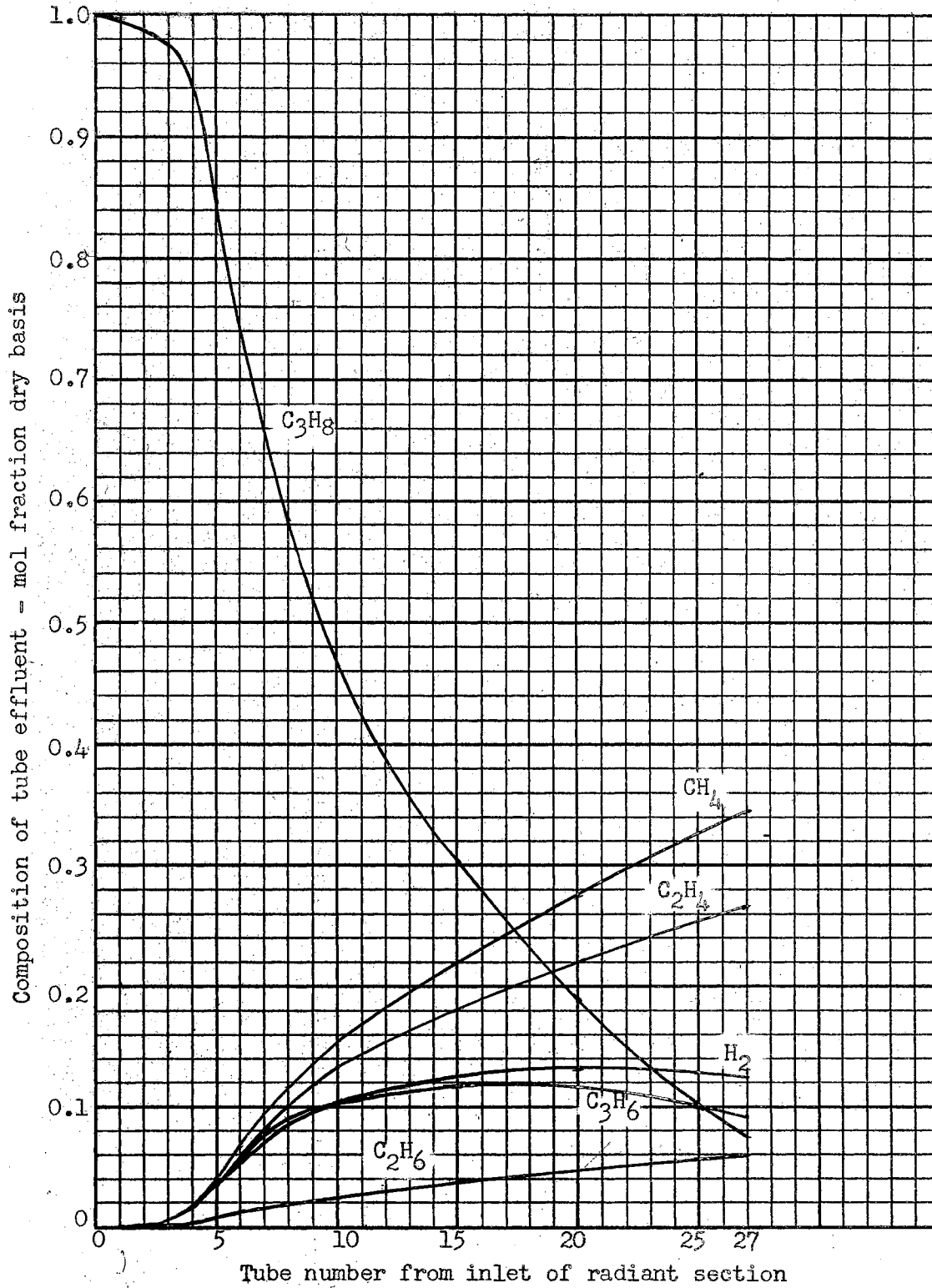


Figure 13



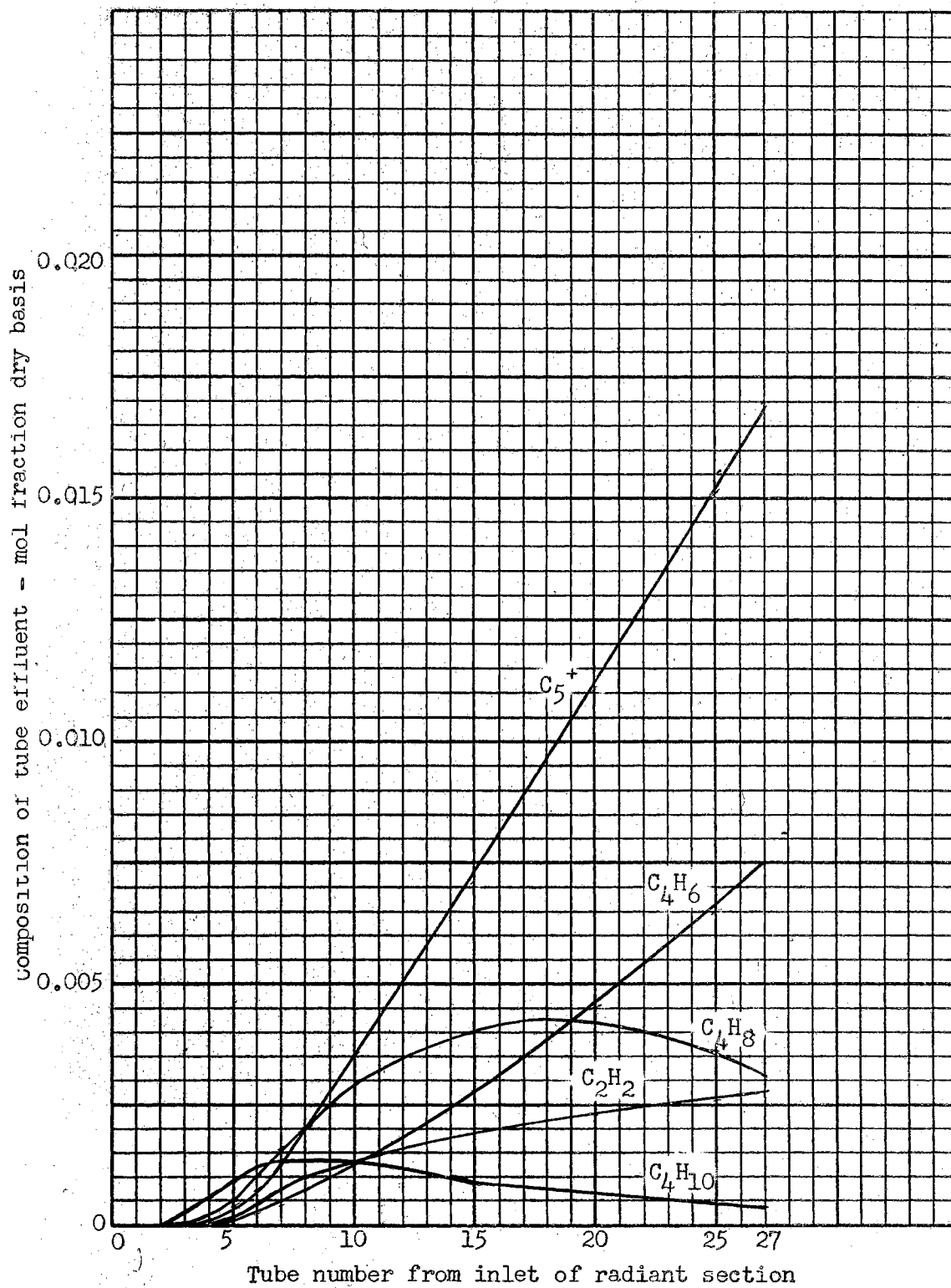
TEMPERATURE AND PRESSURE GRADIENTS FOR PROPANE CRACKING

Figure 14



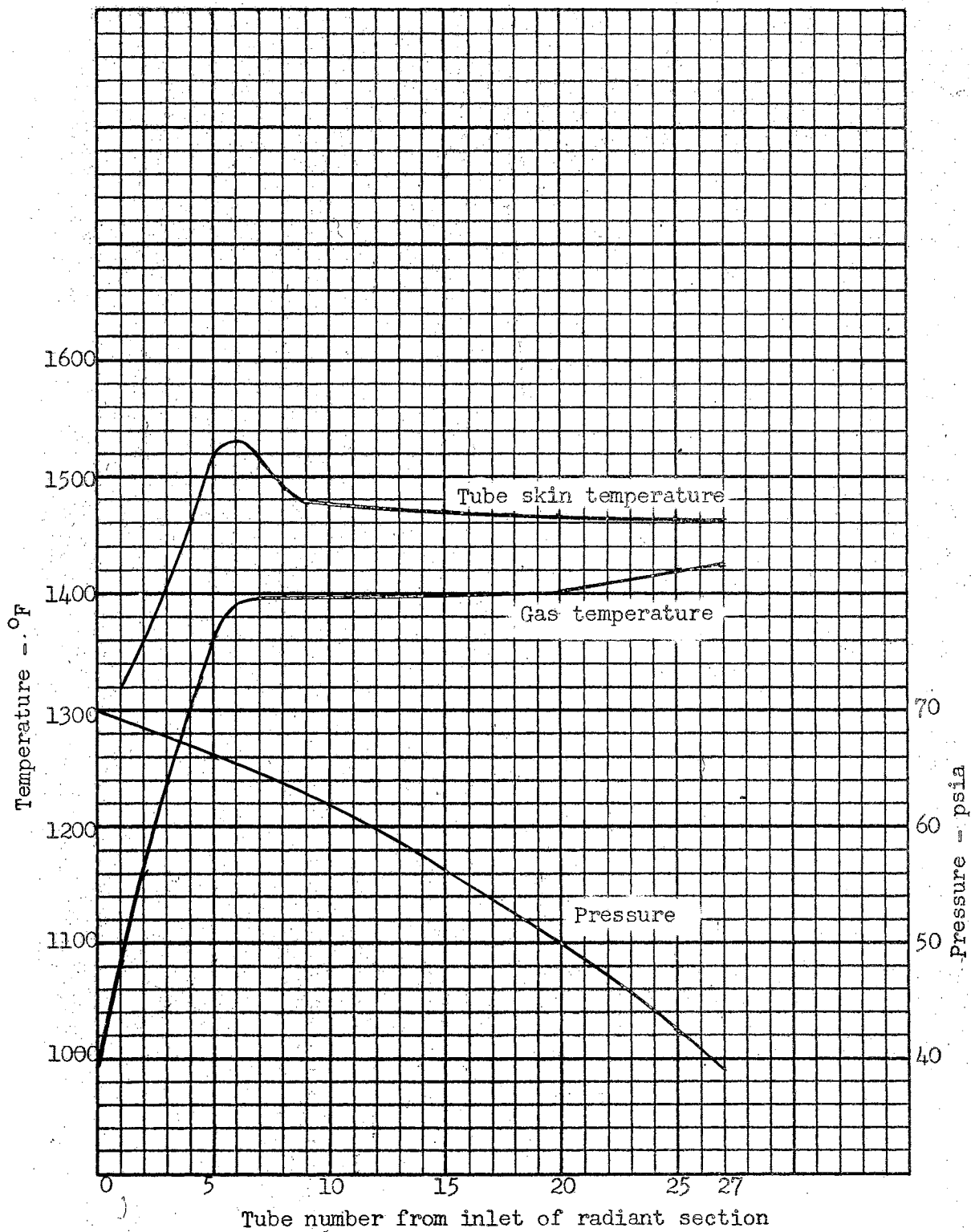
MAJOR PRODUCT DISTRIBUTION FOR PROPANE CRACKING

Figure 15



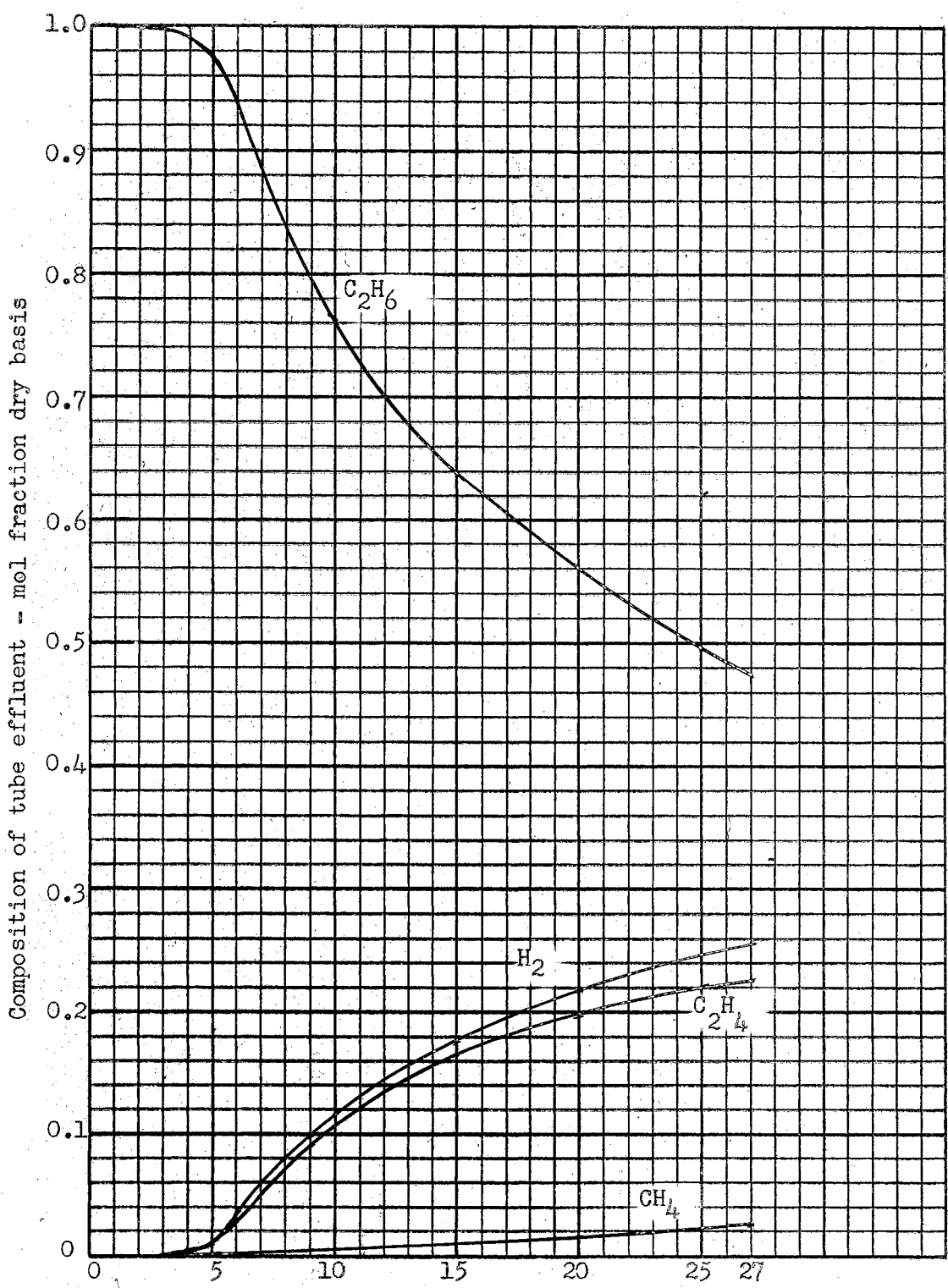
MINOR PRODUCT DISTRIBUTION FOR PROPANE CRACKING

Figure 16

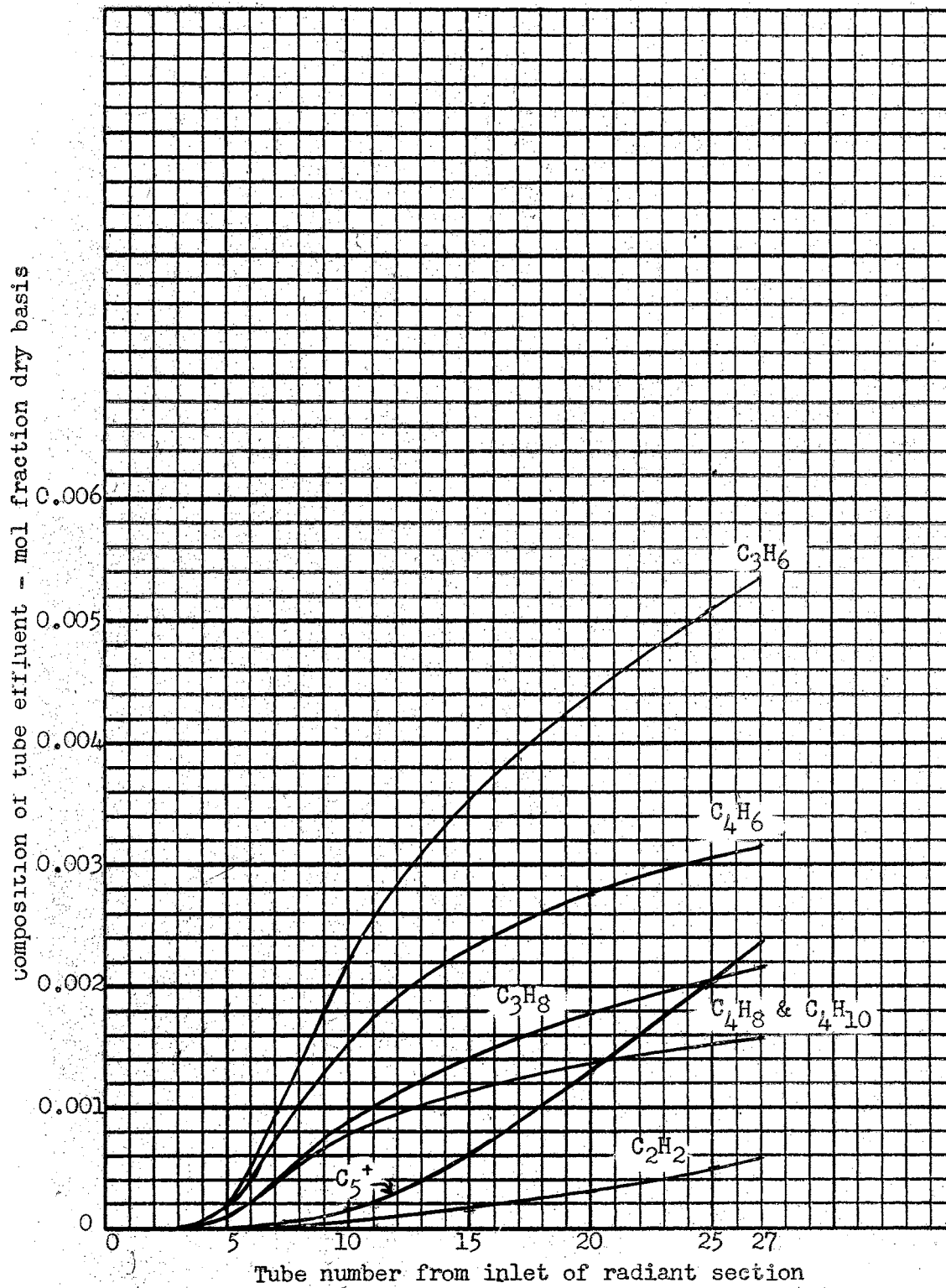


TEMPERATURE AND PRESSURE GRADIENTS FOR ETHANE CRACKING

Figure 17



Tube number from inlet of radiant section
MAJOR PRODUCT DISTRIBUTION FOR ETHANE CRACKING
Figure 18



MINOR PRODUCT DISTRIBUTION FOR ETHANE CRACKING

Figure 19

APPENDIX B

DEVELOPMENT OF REACTION EQUATIONS FOR BUTANE CRACKING

From Figure 2 it is apparent that the products of the primary reactions for butane cracking are methane and propylene, ethane and ethylene, and hydrogen and butylene. Therefore, the three primary stoichiometric equations for the thermal cracking of butane were expressed with these pairs of compounds as products as shown in Figure 3. For the reaction velocity constants of the accompanying reaction rate equations, recourse was made to the over-all reaction velocity constant for butane cracking as expressed by Steacie and Puddington (12). From Figure 2 it is seen that at zero conversion reaction 1 of Figure 3 comprises 35.5 per cent of the total over-all reaction. Reaction 2 represents 54.5 per cent of the initial total reaction, and reaction 3 represents the remaining 10 per cent. By proportioning the over-all velocity constant among the three primary reactions according to the above percentages, the velocity constant of each primary reaction was determined.

Reaction velocity constants for the primary reactions were determined at another temperature in the same manner as described above. Knowing the value of the velocity constant at two temperatures, the constants of the Arrhenius equation were determined.

In addition to the variation of the over-all velocity constant with temperature, Steacie and Puddington (12) report that the velocity constant is also a function of butane conversion at conversions below

25 per cent. Steacie and Puddington show that the velocity constant at zero conversion has a value 1.48 times greater than that at conversions above 25 per cent at the same temperature. The note in Figure 3 considers that the velocity constant at zero conversion is 1.48 times that at 25 per cent conversion. The correction factor decreases linearly until it reaches a value of 1.00 at 25 per cent conversion. The factor is not applied at conversions above 25 per cent.

Considering a tube section of volume dV with a feed rate F , the following differential material balance may be written:

$$F dx = r dV \text{ or } V/F = \int \frac{dx}{r}$$

where F is feed rate in mols/sec, x represents conversion in mols/mol feed, r is equal to the combined rate of the three primary reactions, and V is tube volume in ft^3 .

This equation was integrated for fixed conditions of temperature and pressure. At any selected value of x , the value of V/F required for this conversion was determined. Using the relationship established between conversion and V/F , the amount of each product formed by the three primary reactions was calculated for various conversion levels. The amount of each product formed was calculated directly by the equation:

$$\Delta n = r V/F$$

The calculated amount of each primary product was compared with the amount shown by experimental data (as in Figure 2) at various conversion levels. Differences in the calculated quantities and the quantities shown in the data were attributed to secondary reactions. When the calculated quantity was greater than that shown by the data, it was

considered that the difference was the amount of this component which was reacted in a secondary equation. When the calculated quantity was less than that shown by the data, it was considered that the difference was the amount of this component which was formed in a secondary equation. In this manner the stoichiometric equations for the secondary reactions were established.

The net formation or destruction of each primary product was calculated at various conversion levels. A first order reaction rate equation was formulated for each secondary stoichiometric equation. For such a reaction rate equation:

$$r = kP \frac{n}{n_t} \text{ where } n \text{ refers to mols of reactant}$$

$$\text{then } k = \frac{r n_t}{P n} = \frac{F \Delta n n_t}{V P n}$$

For each increment of conversion, Δn was calculated. Then for the increment of $F/\Delta V$ corresponding to the increment of conversion, k was calculated. In this manner a series of k values was obtained at various conversion levels. The constancy of these values served as an indication of the accuracy of the equation. By performing these calculations at two different temperatures, it was possible to express k as a function of temperature in the Arrhenius equation in the same manner as was used for the primary reactions.

The establishment of the rate of one reaction permitted others to be evaluated in a progressive procedure. In this manner the rate of formation or disappearance of all components was expressed as a function of temperature, pressure, and cracked gas composition.

VITA

Alvin J. Andrews

Candidate for the Degree of

Master of Science

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USING A DIGITAL COMPUTER

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