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The Optimization Of A Catalytic Methanol Reactor Using Quench Feed

By

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A Thesis

Presented In Partial Fulfillment Of

The Requirements For The Degree

Of

Master Of Science In Chemical Engineering

At

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Abstract

The production of methanol in a catalytic quench feed reactor is studied by means of a computerized model and optimized in terms of total reactor length necessary to achieve a given production rate. The methanol reaction rate can be maximized in a quench reactor through the use of cold stream feeds along the length of reactor.

Since the methanol reaction temperature is restricted to an upper limit of 405°C, the addition of cold stream feed along the adiabatic reactor enables the desired conversion to be reached. For two given levels of conversion, 12% and 15%, an optimum inlet temperature, quench temperature, and quench feed fraction is found.

Approval Of Thesis

THE OPTIMIZATION OF A CATALYTIC
METHANOL REACTOR USING QUENCH FEED

By

John Paul McBurney

For

Department Of Chemical Engineering
Newark College Of Engineering

By

Faculty Committee

Approved: _____

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Introduction

The methanol reaction is catalytic and reversible. The rate of reaction can be expressed as:

$$(-r_{CO}) = \eta \cdot \frac{f_{CO}\, f^2_{H_2} - f_{CH_3OH}/K_{eq}}{(A + Bf_{CO} + Cf_{H_2} + Df_{CH_3OH})^3} \qquad (1)$$

where η is defined as the catalyst effectiveness, and A, B, C, and D are temperature dependent constants defined by Natta.[9]

The reaction is carried out in a catalytic plug flow reactor. Natta[9] defines the differential design as:

$$(-r_{CO})\, dW = F\, dy \qquad (2)$$

where dW is the differential weight of catalyst, F is the molar feed rate of gas, and dy is the fraction of the number of moles of inlet gas converted to methanol.

A quench converter can be effectively used when an exothermic, reversible reaction, such as the formation of methanol from carbon monoxide and hydrogen, causes the equilibrium conversion to be lowered as the temperature of the reactants along the plug flow reactor increases. As the temperature in the reactor increases, the conversion is limited to the equilibrium value of conversion at that temperature. Since this value can

be lower than the required conversion in the reactor, a reduction in reactant temperature is done through the use of a cold stream quench feed, made up of the same composition as the inlet feed to the reactor, being introduced at various points along the reactor length. The temperature reduction will raise the value of equilibrium conversion and enable the reactor to achieve the required conversion. The quench feed is a given percentage of the total feed and is fixed for a particular reactor system. The quench stream is divided into fractions for introduction at each reactor stage inlet. The section of reactor between the introduction of two feed streams is known as a stage. For an n stage converter there are n-1 quench feed fractions. There are n-2 variables for the quench feed stream since the last quench fraction F_Q (N-1) must be equal to

$$1 - \sum_{I=1}^{N-2} F_Q(I).$$

The reactor can be optimized in terms of reactor length once certain other operating conditions are specified. In the design equation the differential weight of catalyst, dW, is equal to the catalyst bulk density times the differential volume element which is the product of the cross sectional reactor area and the differential reactor length, dL.

Since the length of reactor is related to the investment cost for the converter, the minimum cost can be approximated by summing the cost of each catalyst section in terms of dollars per unit length and using this as a basis for comparision with other methods of producing methanol. The optimization problem can be then defined as follows: For a given inlet flow rate, feed composition, and production rate of methanol, find the reaction system which minimizes the reactor length. The reaction system includes the individual bed lengths, fraction of the total feed used for quenching, temperature of the quench stream, and inlet temperature to the first reactor stage.

The reactor length can best be minimized by keeping the reaction temperature in each stage as close as possible to the temperature limit for the methanol reaction, which for the purpose of this investigation was set at 405^{o}C, since above this temperature undesirable side reactions occur. The computer model of the methanol reactor was developed so that each reaction stage would convert carbon monoxide and hydrogen to methanol until the temperature limit was reached. In the last reaction stage the reaction would proceed until the desired conversion was achieved.

Procedure

A tubular, catalytic, quench feed reactor for the production of methanol can be optimized in terms of many variables as they effect reactor length. These include temperature of inlet gases, ratio of carbon monoxide to hydrogen in the feed, number of reactor stages, reaction pressure, catalyst effectiveness, and fraction of the total feed used for quenching. For purposes of this computer study many of these variables are held constant and reactor length is optimized on inlet temperature, quench feed fraction, and quench temperature. Reaction pressure is assumed constant for all cases at 280 atmospheres. Inlet molar ratio of hydrogen to carbon monoxide is fixed at three to one. The catalyst used in the model to develop the expression for catalyst effectiveness consists of 75% ZnO and 25% Cr_2O_3. This effectiveness factor is held constant at a value of 0.67.

Review of the Literature

The basic texts in the area of reactor design include books by Aris[1][2] and Kramer and Westerkelp[6]. Aris[1] discusses the use of cold shot as well as interchange cooling in the development of optimal design. Other work done in the area of optimal design of tubular reactors for an exothermic, reversible process was done by Siebenthal and Aris[9]. They developed a method whereby the length of reactor was minimized by optimally distributing the feed along the reactor length. This work was expanded by Shipman and Hickman[8] to apply particularly to the ammonia reaction.

In their work, Shipman and Hickman developed a computer model to simulate an optimum quench converter. This model permits the user to obtain optimum conditions of bed length, heat exchanger area, catalyst volume, and quench stream feeds. All that is required as input data is production rate, inlet flow rate and composition, and allowable pressure drop. The objective function, total length of reactor and heat exchanger, was minimized by an optimization algorithm which performs a modified gradient optimization which reaches a desired minima by derivative finding.

FIVE STAGE QUENCH REACTOR SYSTEM

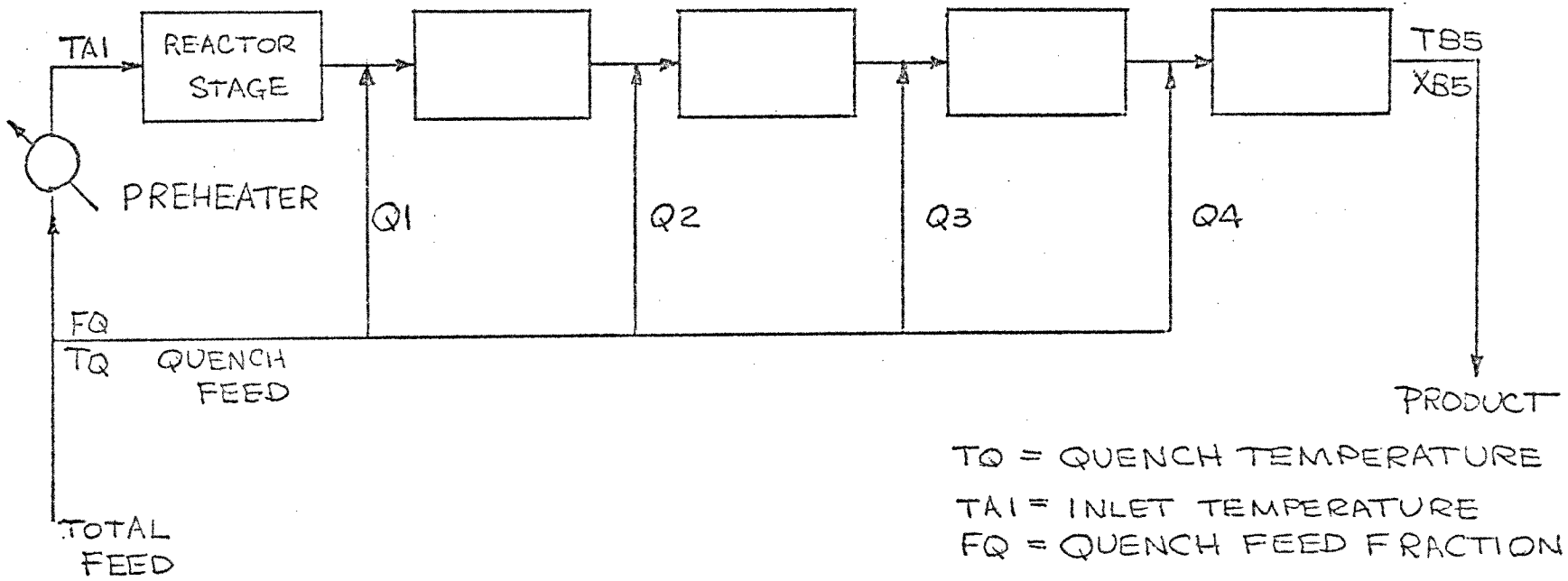


Figure 1

TQ = QUENCH TEMPERATURE

TA1 = INLET TEMPERATURE
FQ = QUENCH FEED FRACTION

Q1 = FRACTION OF QUENCH TO FIRST STAGE EXIT

TB5= EXIT TEMPERATURE
XB5= EXIT CONVERSION

Theory

The production of methanol is affected through the use of a catalytic, plug flow reactor. The exothermic reaction requires both a heat and material balance in order to design the reactor. The design of reactors in which exothermic reversible reactions take place is complicated by the fact that the equilibrium conversion decreases with increasing temperature. Therefore, instead of approaching high conversions in longer plug flow reactors, only the equilibrium conversion can be reached. The methanol reaction is further complicated by the fact that at temperatures in excess of $405^{o}C$, undesirable side reactions occur. The use of a quench feed reactor is beneficial for an exothermic reaction and lends itself readily for optimization. Quench feeds are selectively introduced so that the reaction rate can be kept as high as possible.

Methanol is formed by the reaction $CO + 2H_2 \rightleftharpoons CH_3OH$. The material balance needed to design the reactor is performed on a differential volume element dV. The input to the volume element equals the output plus the disappearance or appearance of the component by reaction. In terms of carbon monoxide the equation can be

expressed as:

$$F_{CO_o} dX_{CO} = (-r_{CO})\, dV \qquad (3)$$

where F_{CO_o} is the initial molar flow rate of the carbon monoxide to the reactor dX_{CO} is the conversion of carbon monoxide to methanol in the differential volume element dV and $-r_{CO}$ is the rate of reaction. The differential volume element can be replaced by the differential weight of catalyst dW. For consistency the expression for the rate of reaction must have units of weight per time per weight of catalyst.

The differential weight of catalyst can be replaced by the product of the bulk density of the catalyst, the cross sectional area of the reactor, and the differential reactor length. The equation can now be expressed as

$$F_{CO_o} dX_{CO} = (-r_{CO})\, \rho_b\, A_{cr}\, dL \qquad (4)$$

on rearrangement

$$dL = \frac{F_{CO_o} dX_{CO}}{(-r_{CO})\, \rho_b\, A_{cr}} \qquad (5)$$

The heat balance is then performed on the same volume element. The heat formed by the reaction minus the heat transferred is equal to the heat accumulated in the gases and the catalyst. Symbolically

$$(-\Delta H_r)\, F_{CO_o}\, dX_{CO} - UA\,(T_g - T_s) = F_i c_{pi} dT \qquad (6)$$

In order to simplify the probelm slightly it will be assumed that the reactor is operating adiabatically. Therefore the term $UA(T_g - T_s)$ will become equal to zero.

The rate of reaction for methanol in a catalytic system has been derived by Wrampe[14] and is expressed as a function of equilibrium constant, component fugacities, and catalyst effectiveness factor.

$$(-r_{CO}) = \eta \cdot \frac{(\phi_{CO} N_{CO} P)\ (\phi_{H_2} N_{H_2} P)^2 - (\phi_{CH_3OH} H_{CH_3OH} P) \ / \ K_{eq}}{(A+B(\phi_{CO} N_{CO} P)+C(\phi_{H_2} N_{H_2} P)+D(\phi_{CH_3OH} N_{CH_3OH} P))^3} \quad (7)$$

The rate expression is a function of both temperature and conversion. In order to solve these equations for a temperature profile along the length of reactor, it is necessary to resort to iterative techniques.

At some point along the reactor length it becomes necessary to introduce a certain percentage of the quench feed in order to reduce the temperature and maximize the reaction rate. At this point of introduction it is necessary to perform an enthalpy balance to obtain the inlet feed temperature to the next reactor stage. The temperature profile is again calculated using the iterative technique and after a given length of reactor, quench feed is again added. For an n stage reactor there are n-1 quench feeds. Gases

leaving the nth stage are at temperature T_N. For the optimum reactor length this exit temperature should be the maximum allowable temperature, which has been arbitrarily fixed at 405°C for this reactor simulation.

The optimization was achieved after examining numerous computer runs which generated data of reactor length versus temperature of inlet feed, quench feed fraction, and quench feed temperature. For different levels of conversion there exist optimum values of inlet temperature, quench temperature, and quench fraction which minimize reactor length. The computer simulation of the reaction system allows each reactor section to reach an exit conversion which corresponds to an exit temperature of about 400°C. At that point quench feed is added and the computer performs an enthalpy balance to arrive at the inlet temperature for the succeeding stage. Only temperatures and quench fractions which allow the desired conversion to be achieved without violating the temperature constraint can be considered in selecting the minimum reactor length.

Discussion

One method for the commercial production of methanol is by the reaction

$$CO + 2H_2 \rightleftharpoons CH_3OH \qquad (8)$$

Since this reaction is exothermic and reversible it is conceivable that it can be carried out in a quench feed reactor. This type of reaction is well suited for optimization since once the reaction temperature gets too high, conversion is limited by the equilibrium value. A quench feed reactor acts as a series of plug flow reactors. In the case of the methanol reaction these reactor sections are packed with catalyst. The feed to the first stage is comprised of carbon monoxide, hydrogen, and inerts. The inlet temperature feed composition and feed rate are specified for a given system. The feed reacts catalytically and for a given conversion of carbon monoxide to methanol, the resulting temperature of the gas stream and the length of reactor section needed to achieve this conversion can be calculated.

When the gases leave the first stage, they are combined with a certain percentage of the quench feed. The quench feed for this problem consists of the same concentration of carbon monoxide, hydrogen, and inerts as the feed to the first stage. The temperature of

the quench stream is lower and is used to lower the temperature of the combined streams. The feed entering the second stage of the reactor will have a different composition than that entering the first stage. There is now more methanol present in the inlet stream to the second stage. Also the ratio of hydrogen to carbon monoxide has changed. If the moles are initially present in a three to one ratio and ten percent of the carbon monoxide is converted, the resulting ratio would be 2.8:0.9 or 3.11:1. The change is reactant ratio must be accounted for in the calculations. The calculation is repeated for each stage in the reactor system. The gases leaving the n^{th} reactor stage contain the product at the desired level of conversion and at an elevated temperature.

The rate expression for the methanol reaction has been derived by Wrampe[14] as

$$-r_{CO} = \frac{(\phi_{CO}N_{CO}P)\,(\phi_{H_2}N_{H_2}P)^2 - (\phi_{CH_3OH}N_{CH_3OH}P)/K_{eq}}{(A + B(\phi_{CO}N_{CO}P) + C(\phi_{H_2}N_{H_2}P) + D(\phi_{CH_3OH}N_{CH_3OH}P))^3} \quad (9)$$

The fugacity coefficient of each component, ϕ_i, can be calculated once the specific volume of the gas V_i, is known. The equation for the specific volume is given by Ewell[4] as

$$V_i = \frac{RT}{P + \frac{b_i}{V_i^{7/4}T}} \quad (10)$$

The values of b_i and c_i, which are critical temperature and pressure dependent constants, have been calculated by Wrampe[14] and are found in Table I. The specific volume can be calculated by an iterative procedure which varies the left hand side of the equation until it matches the right. The specific volume of the gas at the given temperature and pressure is then used to calculate the fugacity coefficient through the equation derived by Ewell.[4]

$$\phi_i = \exp\left(\ln\left(\frac{RT}{P(V_i - C_i)}\right) + \frac{C_i}{V_i - C_i} - \frac{7b_i}{3RT^2 V_i^{3/4}}\right) \qquad (11)$$

In determining the mole fraction of each component it is necessary to perform a material balance at a point along the reactor length.

COMPONENT	INITIAL	REACTING	REMAINING
CO	F_{CO_o}	$x\ F_{CO}$	$F_{CO_1}\ (1-x)$
H_2	$F_{H_{2o}}$	$2 \times F_{CO}$	$F_{H_{2o}} - 2 \times F_{CO_o}$
CH_3OH	$F_{CH_3OH_o}$	0	$F_{CH_3OH_o} + x\ F_{CO_o}$
I(inerts)	F_I	0	F_I

The total molar flow rate in the reactor element at any time can be found by taking the sum of all the components.

$$F_{TOT} = F_{CO_o} + F_{H_{2o}} + F_{CH_3OH_o} + F_I - 2 \times F_{CO_o} \qquad (12)$$

If the feed ratio of hydrogen to carbon monoxide is

TABLE I

Critical Constants For Specific Volume

Component	b	$Cx10^2$
Carbon Monoxide	265.96	2.5127
Hydrogen	12.44	1.6957
Methanol	5878.4	4.2593

replaced by M, the equation can be reduced to

$$F_{TOT} = F_{COo}\left(1 + M - 2x + \frac{F_{CH_3OHo} + F_I}{F_{CO}}\right) \qquad (13)$$

and by letting $Z = 1 + M - 2x + \frac{F_{CH_3OH_o} + F_I}{F_{COo}}$, the equation can be further simplified.

The mole fractions of the components at any time t and conversion x can be expressed as follows

$$N_{CO} = \frac{1-x}{Z} \qquad (14)$$

$$N_{H_2} = \frac{M-2x}{Z} \qquad (15)$$

$$N_{CH_3OH} = \frac{\frac{N_{CH_3OHo} + x}{N_{COo}}}{Z} \qquad (16)$$

These values can then be substituted into the rate expression. The equilibrium constant, K_{eq}, has been calculated by Wrampe[14] from the free energy equation given by Othmer.[3]

$$K_{eq} = \exp\left(\frac{8975}{T} - 8.093\ \ln T - .00563T - 0.5124 \times 10^{6}T^{2} - 0.0408 \times 10^{9}T^{3} + 24.31\right) \qquad (17)$$

The constants A, B, C, and D in equation[1] are temperature dependent and were derived by Wrampe.[14] The value of A reported by Wrampe is incorrect and has

been recalculated by regression analysis from the original data given by Natta.[9] The values for B, C, and D are correct and all can be found in Table II. At a given temperature, pressure, and conversion the rate of disappearance of carbon monoxide can be found.

The volume of reactor needed to produce a given amount of methanol for a given flow rate can then be found once the rate is known. The solution is complicated by the fact that the rate varies with conversion and temperature. It is necessary to solve simultaneous heat and mass balances in order to find the length of reactor needed to effect the desired conversion and the temperature of the product gas stream. From the plug flow reactor design equation the length of reactor, dL can be found by

$$dL = \frac{F_{CO_o}\, dx}{-r_{CO}\, \rho_b\, A_{cr}} \tag{18}$$

For a computer solution the equation must be transformed to difference notation.

$$\Delta L = \frac{F_{CO_o} \Delta X}{\rho_b\, A_{cr}} \left(\frac{1}{-r_{CO}}\right)_{avg.} \tag{19}$$

TABLE II

Temperature Dependent Constants
In The Rate Expression

Temp, ^{o}C	A	B	C	D
320	50	4.1	.92	22.5
330	66	3.3	.70	19.0
340	80	3.0	.54	15.5
350	93	2.6	.40	12.2
360	180	2.1	.30	9.9
370	117	1.9	.23	7.6
380	122	1.6	.18	6.0
390	126	1.2	.14	4.8
400	127	1.0	.10	4.0

$A = 2.265 \times 10^{-5}\ T^3 - .0539T^2 + 41.99T - 1.06 \times 10^4$

$B = 6.8829 \times 10^4\ \exp(-1.6368 \times 10^{-2}T)$

$C = 7.2655 \times 10^6\ \exp(-2.679 \times 10^{-2}T)$

$D = 2.0985 \times 10^7\ \exp(-2.3046 \times 10^{-2})$

The heat rise in the catalyst bed section can be found from the heat balance.

$$(-\Delta H_r)_{avg.} F_{CO_o} dx = \sum (F_i C_{pi})_{avg.} \, dT \qquad (20)$$

The heat capacities and heat of reaction vary with temperature. The molar flow rate of each component varies with conversion. The temperature change can be found with the aid of the computer through the use of delta notation.

$$\Delta T = \frac{(-H_r)_{avg} F_{CO_o} \Delta X}{\Sigma F_i \, C_{pi \; avg}} \qquad (21)$$

To solve this equation it is first necessary to develop an expression for the heat of reaction as a function of temperature. The expression for the heat of reaction, ΔH_r, can be derived by considering the following equations. The equation for the synthesis of methanol from carbon monoxide and hydrogen is of the form

$$aA + bB \rightarrow cC \qquad (22)$$

The change in heat of reaction with temperature can be expressed as

$$\Delta H_{r_2} = \Delta H_{r_1} + \int_{T_1}^{T_2} \nabla C_p \, dT \qquad (23)$$

where

$$\nabla Cp = cCp_c - aCp_a - bCp_b \qquad (24)$$

The values of a, b, and c are the coefficients of the general synthesis equation. The heat capacity of each

component, C_{p_i}, is of the form

$$Cp_i = \alpha_i + \beta_i T + \gamma_i T^2 \qquad (25)$$

In order to evaluate ∇C_p it is necessary to break it down into its α, β, and γ portions. Then

$$\nabla\alpha = C\alpha_c - a\alpha_a - b\alpha_b \qquad (26)$$

Values for $\nabla\beta$ and $\nabla\gamma$ are similarly calculated. The heat capacities of carbon monoxide, hydrogen, and methanol are given by Smith and Van Ness and are presented in Table III.

With the heat capacity broken down into its components the equation can be integrated. The integration results in

$$\Delta H_{r_2} = \Delta H_{r_1} + \nabla\alpha(T-T_1) + \frac{\nabla\beta}{2}(T^2-T_1^2) + \frac{\nabla\gamma}{3}(T^3-T_1^3) \qquad (27)$$

Since the value of the heat of reaction can be found in the literature at a temperature of 298°K(25°C) [3] the heat of reaction as a function of temperature can then be written.

$$H_r(+) = -48{,}100 - 15.92T + .0115045T^2 - 2.53967 \times 10^{-6}T^3 \qquad (28)$$

Since the moles of any component vary with the conversion, the average value of the molar flow rate of each component must be used for the computation over the delta interval.

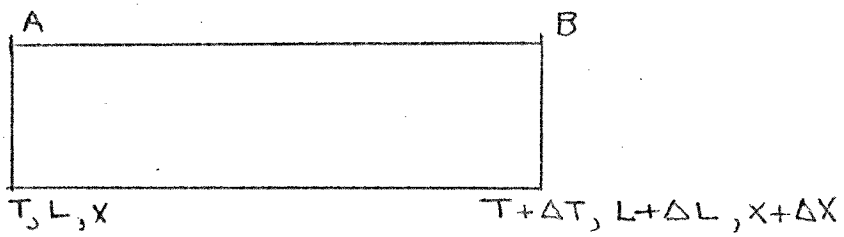
Once all the terms have been defined it becomes possible to perform an iterative calculation to determine the length of reactor needed and the temperature of the gas stream at a given conversion. This calculation is best performed on

TABLE III

Heat Capacity Constants

Component	α	$\beta \times 10^3$	$\gamma \times 10^6$
Carbon Monoxide	6.42	1.665	-0.196
Hydrogen	6.947	-0.2	0.48
Nitrogen	4.394	24.274	-6.855

a computer since it requires a repetitive trial and error procedure to arrive at the correct answer. The first step is to pick a desired conversion, Δx, over a small increment of reactor length, ΔL.



The temperature at T is known and a value of temperature at $T + \Delta T$ is guessed at. Having values of temperature and conversion at two points along the reactor, it is possible to calculate values of heat capacity and heat of reaction, which are temperature dependent, component molar flow rates, which are conversion dependent, and reaction rate which varies with both temperature and conversion.

The values of the rate expression at the two points in the reactor are then averaged. This must be done by averaging the reciprocal of the rate at T with the reciprocal of the rate at $T + \Delta T$. Using this average value the length of the reactor interval can be calculated by equation 19. This value then permits the weight of catalyst to be calculated.

$$W_{cat} = \rho_{bulk} + A_{cr} + \Delta L \qquad (29)$$

Since heat and material balances must be solved simultaneously, the temperature guessed at point B in the reactor can be checked through the use of equation 21.

The average values of ΔH_r and $F_i C_{pi}$ are determined by summing the values calculated at points A and B and taking half of that amount. If the value of ΔT calculated by equation 21 equals the value guessed at point B then both equations are satisfied and the values of temperature, conversion, and length at point B are obtained. If the value of ΔT in equation 21 does not equal the value guessed at point B, then this value of ΔT is used as the new guess. The check of these guesses is then performed using the procedure previously described. Once the guess of ΔT and the value of ΔT from equation 21 agree within a reasonable variation ($.05^{\circ}K$) then the equations can be considered solved.

If all of the variables in equations 19 and 21 varied linearly then the value of conversion in a total reactor stage could be used and a corresponding stage length calculated. This is not the case since the rate expression contains an Arrhenius dependent rate constant. It is necessary therefore to take values of ΔX small enough so that the expressions do not deviate from linearity sufficiently enough to affect the arithematic averages used in the calculations. With the value of conversion sufficiently small, for example $\Delta X = 0.002$, the values of T, L, and x at point B are computed. The values are then made equal to new point A values and the procedure is continued until the desired conversion is reached.

Exiting the first reactor stage at conversion XB1 and temperature TB1 the gas stream is cooled by a fraction of the quench stream. The temperature of the entrance stream to the second stage TA2 is that temperature. In order to find TA2 it is necessary to perform an enthalpy balance at the mixing point. It will be assumed for this model that there is no enthalpy of mixing at this junction. Since the change in enthalpy of any system is based upon the difference of two temperatures it is possible to choose a lower temperature that can be used as a reference. The most convenient temperature to use for this reference point is the quench feed temperature, TQ.

Since the temperature of the quench stream is used as the reference temperature the enthalpy of the stream can be found by the equation.

$$\Delta H = \sum \int_{TQ}^{TB1} F_i \, Cp_i \, dT \qquad (30)$$

The expression for the variance of heat capacity with temperature, equation 15, has to be inserted and the change in enthalpy can then be represented as

$$\Delta H = \sum \int_{TQ}^{TB1} F_i \, (\alpha_i + \beta_i T + \gamma_i T^2) \, dT \qquad (31)$$

Upon integration the equation reduces to

$$\Delta H = \sum F_i \, (\alpha_i (TB1 - TQ) + \frac{\beta_i}{2} (TB1^2 - TQ^2) + \frac{\gamma_i}{3} (TB1^3 - TQ^3)) \qquad (32)$$

Since all the values are known, the enthalpy of the exit stream can be found. When the quench feed is added, the moles of each component are increased without increasing the heat content of the mixed stream. If the heat content is the same while the molar quantities are increased, then the temperature of the combined stream must be lowered.

$$\Delta H = Q = \sum \int_{TQ}^{TA2} F_i' C_{pi}\, dT \qquad (33)$$

The value of N_i is equal to the moles in the first stage exit stream, N_i, plus the moles of the each component present in the quench feed fraction, N_{iQ}. The temperature, TA_2, can then be found as one root of the cubic equation that results. The expansion of equation 23 yields.

$$\Delta H = \sum \int_{TQ}^{TA2} F_i' (\alpha_i + \beta_i T + \gamma_i T^2)\, dT \qquad (34)$$

The integration gives the following result

$$\Delta H = \Sigma F_i' \alpha_i (TA2-TQ) + \frac{\Sigma F_i' \beta_i}{2} (TA2^2-TQ^2) + \frac{\Sigma F_i' \gamma_i}{3} (TA2^3-TQ^3) \qquad (35)$$

Since TQ is constant it can be removed from the expression and the equation can be written as

$$K_3(TA2)^3 + K_2(TA2)^2 + K_1(TA_2) - K_4 = 0 \qquad (36)$$

where

$$K_3 = \frac{\Sigma N_i' \alpha_i}{3} \qquad (37)$$

$$K_2 = \frac{\Sigma N_i' \beta_i}{2} \qquad (38)$$

$$K_1 = \sum N_i \alpha_i \tag{39}$$

and

$$K_4 = \Delta H + K_1(TQ) + K_2(TQ)^2 + K_3(TQ)^3 \tag{40}$$

The solution of equation 36 for TA2 can be obtained through a computerized numerical method of root finding. If y is a function of TA2 then it has a positive or negative value for all temperatures except the desired root. The computer examines a range of temperatures and evaluates y for each of these temperatures. If at any point the computer finds that successive values of y have differing signs then it determines that a root exists in the interval. Since the interval is relatively large the computer must continue to halve the interval until the root can be isolated to within a reasonable degree of precision. Through the use of this half interval technique the computer will continue to search for the root in this manner until the successive values of temperature are within 0.0004 degrees where upon the equation is considered solved.

The calculations for length of reactor versus conversion and for various inlet reactor temperatures are repeated for each of the five arbitrarily chosen stages. If quench temperature, inlet temperature, and quench fraction values are selected properly then the required conversion can be achieved in the reactor without exceeding the temperature constraint.

The variations possible in this quench feed reactor system that are optimized by this computer study are quench feed fraction, quench temperature, and inlet temperature. At a production rate of 300 tons/day with 24 hr/day operation the required feed rate of carbon monoxide to the reactor is 5200 lb moles/hr. for 15% conversion. For the case of 12% conversion the same inlet flow rate was used so the production from this unit would be 240 tons/day. Kirk and Othmer[3] report normal operating conditions for a methanol reactor of 12 to 15% conversion, an M ratio of 2 to 6, and reactor temperatures between 250 and 400°C.

The optimization of the quench feed methanol reactor was achieved by allowing the rate of reaction in each stage to be as high as possible. The reaction rate increases with increasing temperature so that operation of the reaction at temperatures approaching the temperature constraint would be ideal. To take advantage of this, the computer model was arranged in such a way that the temperature at the reactor exit would always be maximumallowable. The results of varying inlet temperature, quench temperature, and quench fraction in the reaction system are compiled in Tables IV through XV. In many of the computer runs values were chosen such that the required conversion could not be achieved without violating the temperature restriction.

CONCLUSIONS

The optimum reactor length for an adiabatic, five stage, quench feed, methanol reactor is 42.79 feet for 12% conversion and 70.60 feet for 15% conversion. For 12% conversion the optimum conditions for inlet temperature, quench temperature, and quench feed fraction are 613°K, 316°K and .19 respectively. The conversion, inlet temperature, and exit temperature for each of the five stages can be found in Table 16. For the reactor operating at 15% conversion the optimum conditions are: inlet temperature, 613.16°K; quench temperature, 313.16°K; quench fraction, .275. The computer simulation of this reactor can be found in Table 17.

The quench feed reactor, operating adiabatically, is not particularly suited for the methanol reaction, because the reaction temperature limit is much more restrictive than the equilibrium conversion restrictions which made quench feed reactors a good choice for other reactions involving a reversible exothermic process.

DISCUSSION OF RECULTS

A reactor length of 70.6 feet is necessary to achieve the required production of methanol at 15% conversion. A reactor operating isothermally at 395°C would meet production requirements at a length of 46 feet. Other methods of operating a methanol reactor along with reactor length needed to meet required production can be found in the Appendix. All of these reactors are all shorter than the quench feed reactor.

This does not necessarily mean that the quench reactor should be excluded from consideration in the design of a methanol reactor. If a methanol quench reactor could be fabricated and operated to allow a controlled rate of heatloss along the reactor length then it is conceivable that shorter reactor stages wouldbe required since more conversion could be achieved in any given stage before the reaction heat raises the temperature above the restraint threshhold. Since some heat would be dissipated through the insulation, the reaction temperature could be kept at a high value for a longer time thereby decreasing the needed reactor volume.

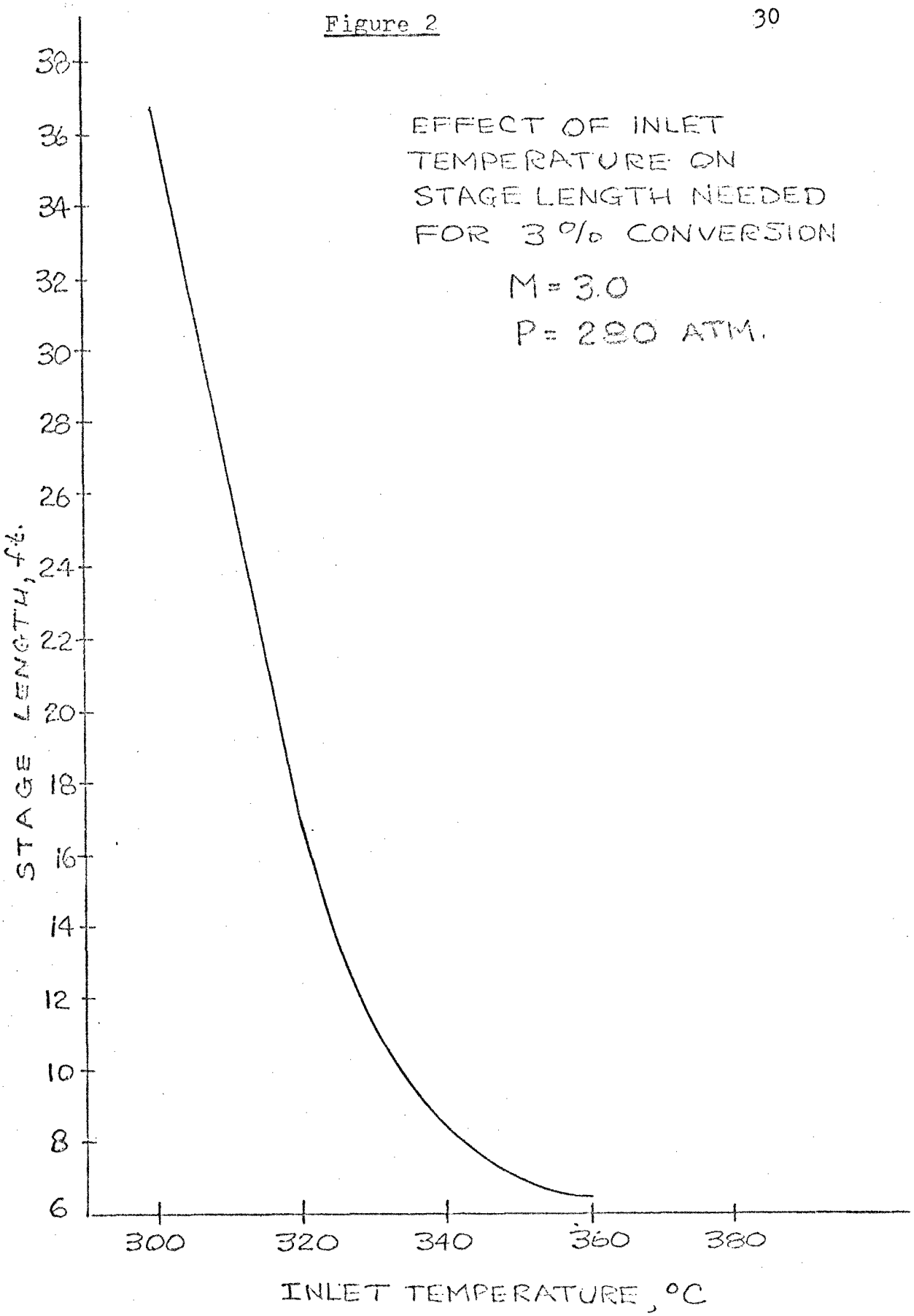
Another consideration in the choice of reactor would be the capital cost of equipment. It is conceivable that the quench feed reactor would be more economical since it would not involve the use of inside tubes for cooling.

When the other methanol reactors were sized for length comparison only the catalytic cross sectional area was taken into account. The incorporation of a tube bundle for cooling inside the packed bed effectively increases the reactor cross section and consequently the weight of metal needed for the fabrication of the shell. Once design information was obtained to calculate the area required for the tube bundle then the total reactor volume could be compared on an equal basis with the quench feed reactor. Of further importance in terms of cost in the design of the optimum temperature reactor or the isothermal reactor would be the control equipment needed to ensure that the reaction follows the required temperature path.

Figure 2 shows the effect that inlet temperature has on the reactor length needed to achieve 3% conversion cannot be achieved without violating the temperature constraint on the system. Figure 3 illustrates the effect that a varying percentage of the total feed used as quench feed has on the reactor length. Below a quench percentage of about 30 percent the conversion in a five stage reactor will not reach 15 percent without exceeding a reaction temperature of 405°C. Figure 4 demonstrates the effect of inlet temperature on overall reactor length for a given quench percentage and a given quench temperature. Figure

5 shows the effect on reactor length produced by varying the quench temperature with a fixed quench fraction and inlet temperature.

Figure 2


EFFECT OF INLET TEMPERATURE ON STAGE LENGTH NEEDED FOR 3 % CONVERSION
M = 3.0
P = 290 ATM.
STAGE LENGTH, ft.
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
300
320
340
360
380
INLET TEMPERATURE, °C

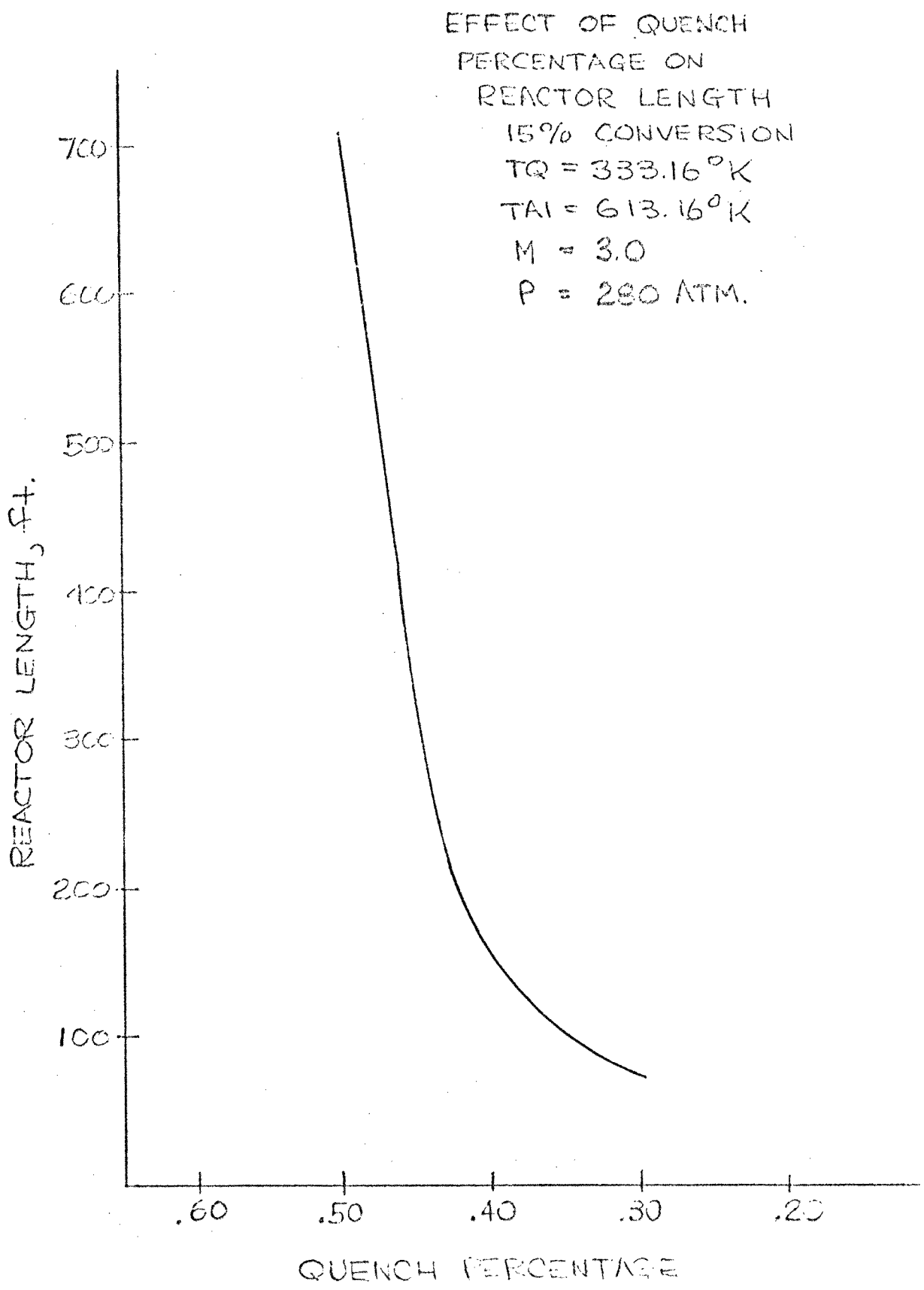

EFFECT OF QUENCH
PERCENTAGE ON
REACTOR LENGTH
15% CONVERSION
TQ = 333.16°K
TAI = 613.16°K
M = 3.0
P = 290 ATM.
700
600
500
400
300
200
100
REACTOR LENGTH, ft.
.60
.50
.40
.30
.20
QUENCH PERCENTAGE

Figure 4

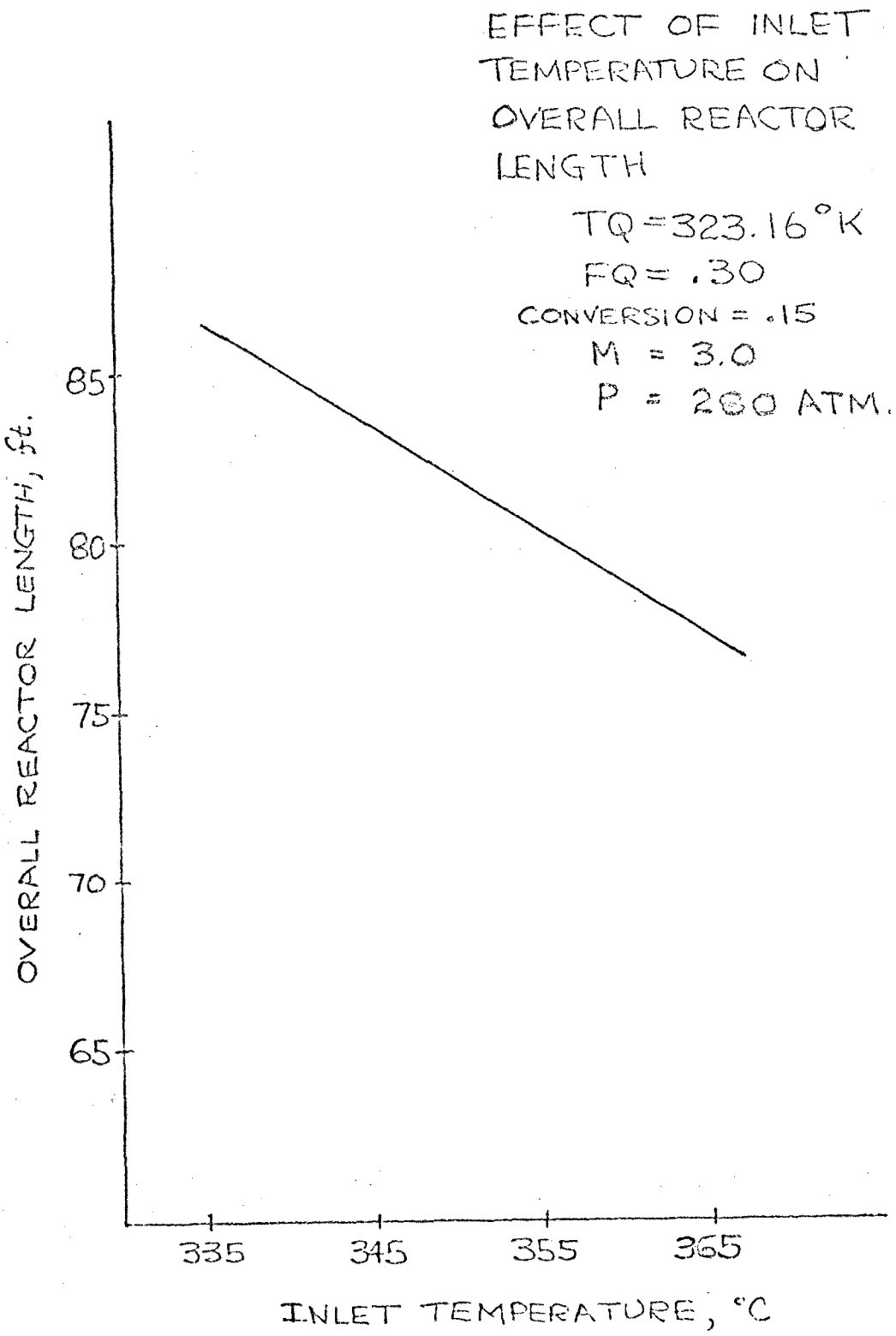
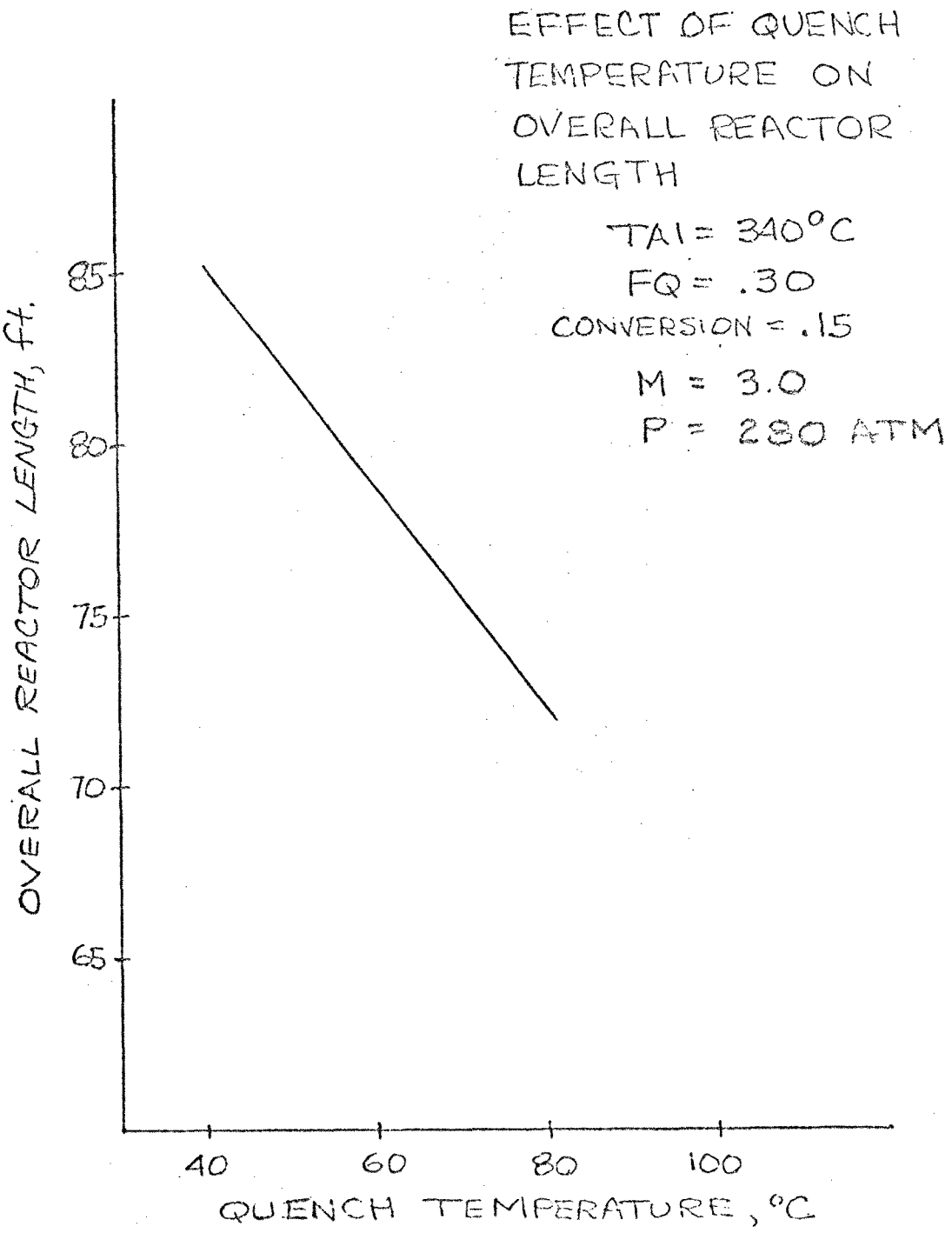

EFFECT OF INLET TEMPERATURE ON OVERALL REACTOR LENGTH
TQ = 323.16 °K
FQ = .30
CONVERSION = .15
M = 3.0
P = 260 ATM.
OVERALL REACTOR LENGTH, ft.
85
80
75
70
65
335
345
355
365
INLET TEMPERATURE, °C

Figure 5


EFFECT OF QUENCH TEMPERATURE ON OVERALL REACTOR LENGTH
TA1 = 340°C
FQ = .30
CONVERSION = .15
M = 3.0
P = 280 ATM
OVERALL REACTOR LENGTH, ft.
85
80
75
70
65
40
60
80
100
QUENCH TEMPERATURE, °C

NOMENCLATURE

A	Temperature dependent rate constant, (moles-gm catalyst/hr)$^{-1/3}$
A_{cr}	Reactor cross sectional area, cm^2
B	Temperature dependent rate constant, (moles-gm catalyst/hr)$^{-1/3}$
b	Critical temperature and pressure constant, atm-liters^2/mole^2
C	Temp. dep. rate constant, (moles-gm catalyst/hr)$^{-1/3}$
c	Critical temp. and pressure constant, atm-liters^2/mole^2
C_p	Heat capacity, Cal/gm-^oC
D	Temp. dep. rate constant, (moles-gm catalyst/hr)$^{-1/3}$
F	Molar flow rate of gas, moles/hr.
FQ	Quench feed fraction, dimensionless
f	Fugacity, dimensionless
$-\Delta H_r$	Heat of reaction. Cal/gm
I	Inert gas flow, moles/hr.
Keq	Equilibrium constant, dimensionless
L	Reactor length, cm
M	Ratio of hydrogen to carbon monoxide, dimensionless
N	Moles
P	Reaction pressure, atmospheres
R	Gas constant, li-atm/g mole ^oK
$-r_{co}$	Reaction rate of carbon monoxide to methanol, moles/gm catalyst/hr
V	Molar specific volume, liters/gm mole
W	Catalyst weight, gm
α	Heat capacity coefficient, Cal/gm ^oC
β	Heat capacity coefficient, Cal/gm
γ	Heat capacity coefficient, Cal-^oC/gm
ϕ	Fugacity coefficient, atm^{-1}
η	Catalyst effectiveness factor, dimensionless
ρ_b	Catalyst bulk density, gm/cm^3

APPENDIX

APPENDIX A

Sample Problem

The computer simulation of the methanol quench feed reactor has been programmed generally enough so that it can be used with various operating conditions. Values used for computations are arbitrary but are matched, where possible, with known industrial conditions. The production rate of 300 tons of methanol per day typifies medium scale methanol reaction systems. It has been reported by Kirk and Othmer that most methanol reactors operate between 12 and 16% conversion. With a 15% conversion of carbon monoxide to methanol, the molar feed rate of carbon monoxide to the reactor is 5200 lb moles/hr. This feed is divided into a preheated fraction and a quench feed fraction. This rate assumes that the reactor operates 24 hours/day. The inlet stream also contains hydrogen in a ratio of from 3 to 4 times as much as carbon monoxide. The remainder of the inlet is comprised of 10% inerts which are assumed to be nitrogen.

Each reactor stage is 70 centimeters in diameter and is packed with catalyst pellets at a bulk density of 0.82508 gm/cm^3. The reactor operates at a pressure of 280 atmospheres which has been assumed constant to simplify the problem slightly.

The initial conditions of inlet temperature, quench temperature, quench fraction, and quench distribution are specified as input data and are listed at the beginning of the computer output. Each reactor stage length is printed individually and the total quench reactor length is outputted at the end of the problem. The exit conversion is the highest possible under the temperature restriction imposed on the methanol reaction.

INITIAL CONDITIONS

INLET TEMPERATURE	613.1599
QUENCH TEMPERATURE	313.1599
REACTOR PRESSURE,ATM.	280.0000
REACTOR CROSS SECTION,SQ. CM.	3848.44751
CATALYST BULK DENSITY,GM/CU CM	0.82508
QUENCH FRACTION OF TOTAL FEED	0.300
FRACTION OF QUENCH TO SECOND STAGE	0.250
FRACTION OF QUENCH TO THIRD STAGE	0.250
FRACTION OF QUENCH TO FOURTH STAGE	0.250
FRACTION OF QUENCH TO FIFTH STAGE	0.250
FIRST REACTOR STAGE	
INLET MOLES CARBON MONOXIDE	0.165147E 07
M RATIO	3.000000
TEMPERATURE AT EXIT	674.630
STAGE LENGTH, CM.	285.407
MOLE FRACTION METHANOL	0.03600
LENGTH OF REACTOR STAGE,FT.	9.364
SECOND REACTOR STAGE	
TEMPERATURE AT INLET	605.68530
MOLE FRACTION METHANOL	0.03252
INLET MOLES CARBON MONOXIDE	0.176896E 07
M RATIO	3.033609
TEMPERATURE AT EXIT	675.178
STAGE LENGTH, CM.	510.197
MOLE FRACTION METHANOL	0.07452
LENGTH OF REACTOR STAGE,FT.	16.739
THIRD REACTOR STAGE	
TEMPERATURE AT INLET	611.21826
MOLE FRACTION METHANOL	0.06794
INLET MOLES CARBON MONOXIDE	0.186911E 07
M RATIO	3.072896
TEMPERATURE AT EXIT	675.110
STAGE LENGTH, CM.	571.173
MOLE FRACTION METHANOL	0.10794
LENGTH OF REACTOR STAGE,FT.	18.739
FOURTH REACTOR STAGE	

TEMPERATURE AT INLET	615.54565
MOLE FRACTION METHANOL	0.09919
INLET MOLES CARBON MONOXIDE	0.196584E 07
M RATIO	3.110113
TEMPERATURE AT EXIT	674.321
STAGE LENGTH, CM.	649.680
MOLE FRACTION METHANOL	0.13719
LENGTH OF REACTOR STAGE,FT.	21.315

FIFTH REACTOR STAGE

TEMPERATURE AT INLET	618.70117
MOLE FRACTION METHANOL	0.12690
INLET MOLES CARBON MONOXIDE	0.205985E 07
M RATIO	3.145345
TEMPERATURE AT EXIT	654.806
STAGE LENGTH, CM.	579.797
MOLE FRACTION METHANOL	0.15090
LENGTH OF REACTOR STAGE,FT.	19.022
TOTAL LENGTH OF QUENCH REACTOR	85.17889

APPENDIX B

The computer simulation of an adiabatic five stage methanol reactor operating with quench feed has been programmed generally enough so that it can be used with varying conditions. Values of limiting conversion in each stage, quench fraction to each stage, quench temperature, and inlet temperature are supplied as data. After defining various constants initial molar flow rates are calculated. These values are used to calculate reactor length and temperature for a given value of conversion beginning at statement 135. An interval of conversion is set and values of equilibrium constant, fugacity coefficients, and others are calculated for both ends of the interval to establish a reaction rate in statements 200 through 435.

Statement 440 calculates an incremental reactor length using an average value of reaction rae. Statement 525 calculates a temperature rise and compares it to an initial guess. If the value is in close agreement the calculation continues in the next increment of length. This procedure will continue until either the conversion restraint or the temperature restraint is violated.

At this point the gases exit the first reactor stage and mixed with quench gases. An enthalpy balance and material balance are calculated in statements 600 through 745. This enthalpy balance is used to determine an inlet temperature to the second stage. The material balance

defined the quantity of each component entering the next stage. This procedure is repeates so that conversions, temperatures, and lengths can be found and outputted for the five reactor stages.

```
      REAL LB,LA,M
      COMMON TA1,TQ,P,ACR,ROB,FQ,Q1,Q2,Q3,Q4
C     ****************************************************************
C     COMPUTER SIMULATION OF A FIVE STAGE METHANOL QUENCH REACTOR
C     ****************************************************************
    5 FORMAT(I2)
   10 READ(5,5)LIMIT
      IF (LIMIT) 25,760,15
   15 READ(5,20)XB1,XB2,XB3,XB4,XB5,Q1,Q2,Q3,Q4
   20 FORMAT(9F8.0)
   25 READ(5,30)TQ,TA1,FQ
   30 FORMAT(3F10.0)
      CTOT = 2.35924E06
      HTOT = 7.07772E06
      ETOT = 0.0
      OTOT = 1.04805E06
      P = 280.0
      ACR = 3848.44775
      ROB = 0.82508
      CALL OUTPU
      WRITE(6,35)
   35 FORMAT(20X,'FIRST REACTOR STAGE'/ )
   40 ALPCO = 6.42
   45 ALPIN = 6.524
   50 ALPHY = 6.947
   55 ALPME = 4.394
   60 BETCO = 1.665E - 03
   65 BETIN = 1.250E - 03
   70 BETHY = - 0.20E - 03
   75 BETME = 24.274E - 03
   80 GAMCO = - 0.196E - 06
   85 GAMIN = - 0.001E - 06
   90 GAMHY = 0.48E - 06
   95 GAMME = - 6.855E - 06
      FCO1 = CTOT * (1. - FQ)
      FHY1 = HTOT * (1. - FQ)
      FME1 = ETOT * (1. - FQ)
      FIN1 = OTOT * (1. - FQ)
      FCOQ = FQ * CTOT
      FHYQ = FQ * HTOT
      FMEQ = FQ * ETOT
      FINQ = FQ * OTOT
      XA1 = 0.0
      KTO = 1
      ITO = 1
      ITEM = 1
      JTEM = 1
  100 CONTINUE
      GOTO(105,110,115,120,130),ITEM
  105 TA = TA1
      XA = XA1
      XB = XB1
      FCO = FCO1
      FHY = FHY1
      FME = FME1
      FIN = FIN1
      GOTO 135
  110 TA = TA2
      XA = XA2
      XB = XB2
      FCO = FCO2
```

```
      FHY = FHY2
      FME = FME2
      FIN = FIN2
      GOTO 135
  115 TA = TA3
      XA = XA3
      XB = XB3
      FCO = FCO3
      FHY = FHY3
      FME = FME3
      FIN = FIN3
      GOTO 135
  120 TA = TA4
      XA = XA4
      XB = XB4
      FCO = FCO4
      FHY = FHY4
      FME = FME4
  125 FORMAT(15X,E15.7)
      FIN = FIN4
      GOTO 135
  130 TA = TA5
      XA = XA5
      XB = XB5
      FHY = FHY5
      FME = FME5
      FIN = FIN5
      GOTO 135
  135 CONTINUE
      WRITE(6,140)FCO
  140 FORMAT(10X,'INLET MOLES CARBON MONOXIDE',13X,E12.6)
      LA = 0.0
  145 CME = 4.2593E - 02
  150 CHY = 1.6957E - 02
  155 CCO = 2.5127E - 02
  160 BME = 5.8784E3
  165 BHY = 1.2414E1
  170 BCO = 2.6596E2
  175 R = 0.08257
  180 ETTA = 0.67
  185 M = FHY / FCO
      WRITE(6,190)M
  190 FORMAT(10X,'M RATIO',33X,F10.6/)
      DELX = 0.002
      I = (XB - XA) / DELX
      DO 550 J=1,I
  195 DELT = 0.1
  200 XB = XA + DELX
  205 TB = TA + DELT
  210 BOLD = DELT
  215 AKQA = EXP( (8975. / TA) - (8.093 * ALOG(TA)) + (0.00563 * TA) - (
     1 (0.5124E - 06) * (TA * * 2)) - ( (0.0408E - 09) * (TA * * 3)) + 2
     24.31)
  220 AKQB = EXP( (8975. / TB) - (8.093 * ALOG(TB)) + (0.00563 * TB) - (
     1 (0.5124E - 06) * (TB * * 2)) - ( (0.0408E - 09) * (TB * * 3)) + 2
     24.31)
      SOMEF = (R * TA) / P
  225 EN = SOMEF
      SOMEF = ( (R * TA) / (P + (BME / (TA * (EN * *1.75))))) + CME
      TUV = ABS(SOMEF - EN)
      IF (TUV - 0.01) 230,230,225
```

```
230 VMEA = SOMEF
    SOMEF = (R * TB) / P
235 EN = SOMEF
    SOMEF = ( (R * TB) / (P + (BME / (TB * (EN * * 1.75))))) + CME
    TUV = ABS(SOMEF - EN)
    IF (TUV - 0.01) 240,240,235
240 VMEB = SOMEF
    SOMEF = (R * TA) / P
245 EN = SOMEF
    SOMEF = ( (R * TA) / (P + (BCO / (TA * (EN * * 1.75))))) + CCO
    TUV = ABS(SOMEF - EN)
    IF (TUV - 0.01) 250,250,245
250 VCOA = SOMEF
    SOMEF = (R * TB) / P
255 EN = SOMEF
    SOMEF = ( (R * TB) / (P + (BCO / (TB * (EN * * 1.75))))) + CCO
    TUV = ABS(SOMEF - EN)
    IF (TUV - 0.01) 260,260,255
260 VCOB = SOMEF
    SOMEF = (R * TA) / P
265 EN = SOMEF
    SOMEF = ( (R * TA) / (P + (BHY / (TA * (EN * * 1.75))))) + CHY
    TUV = ABS(SOMEF - EN)
    IF (TUV - 0.01) 270,270,265
270 VHYA = SOMEF
    SOMEF = (R * TB) / P
275 EN = SOMEF
    SOMEF = ( (R * TB) / (P + (BHY / (TB * (EN * * 1.75))))) + CHY
    TUV = ABS(SOMEF - EN)
    IF (TUV - 0.01) 280,280,275
280 VHYB = SOMEF
    FUCA = EXP(ALOG( (R * TA) / (P * (VCOA - CCO))) + (CCO / (VCOA - C
   1CO)) - ( (7. * BCO) / (3. * R * (TA * * 2) * (VCOA * * 0.75))))
    FUCB = EXP(ALOG( (R * TB) / (P * (VCOB - CCO))) + (CCO / (VCOB - C
   1CO)) - ( (7. * BCO) / (3. * R * (TB * * 2) * (VCOB * * 0.75))))
    FUHA = EXP(ALOG( (R * TA) / (P * (VHYA - CHY))) + (CHY / (VHYA - C
   1HY)) - ( (7. * BHY) / (3. * R * (TA * * 2) * (VHYA * * 0.75))))
    FUHB = EXP(ALOG( (R * TB) / (P * (VHYB - CHY))) + (CHY / (VHYB - C
   1HY)) - ( (7. * BHY) / (3. * R * (TB * * 2) * (VHYB * * 0.75))))
    FUMA = EXP(ALOG( (R * TA) / (P * (VMEA - CME))) + (CME / (VMEA - C
   1ME)) - ( (7. * BME) / (3. * R * (TA * * 2) * (VMEA * * 0.75))))
    FUMB = EXP(ALOG( (R * TB) / (P * (VMEB - CME))) + (CME / (VMEB - C
   1ME)) - ( (7. * BME) / (3. * R * (TB * * 2) * (VMEB * * 0.75))))
285 ZA = 1. + M - (2. * XA) + ( (FME + FIN) / FCO)
290 ZB = 1. + M - (2. * XB) + ( (FME + FIN) / FCO)
295 ACOA = (1. - XA) / ZA
300 AHYA = (M - XA) / ZA
305 AMEA = ( (FME / FCO) + XA) / ZA
    ATA = 2.265E - 05 * (TA * * 3) - 0.0539 * (TA * * 2) + 41.99 * TA
   1 -1.062E04
    ATB = 2.265E - 05 * (TB * * 3) - 0.0539 * (TB * * 2) + 41.99 * TB
   1 -1.062E04
310 BTA = 6.8829E4 * (EXP( - 1.6368E - 02 * TA))
315 BTB = 6.8829E4 * (EXP( - 1.6368E - 02 * TB))
320 CTA = 7.2655E6 * (EXP( - 2.679E - 02 * TA))
325 CTB = 7.2655E6 * (EXP( - 2.679E - 02 * TB))
330 DTA = 2.0986E7 * (EXP( - 2.3046E - 02 * TA))
335 DTB = 2.0986E7 * (EXP( - 2.3046E - 02 * TB))
340 ACOB = (1. - XB) / ZB
345 AHYB = (M - XB) / ZB
350 AMEB = ( (FME / FCO) + XB) / ZB
```

```
355 SYA = (FUCA * ACOA * P) * ( (FUHA * AHYA * P) * * 2) - ( (FUMA * A
   1MEA * P) / AKOA)
360 RHYA = (ATA + (BTA * FUCA * ACOA * P) + (CTA * FUHA * AHYA * P) +
   1(DTA * FUMA * AMEA * P)) * * 3
365 RCOA = (SYA / RHYA) * ETTA
370 SYB = (FUCB * ACOB * P) * ( (FUHB * AHYB * P) * * 2) - ( (FUMB * A
   1MEB * P) / AKOB)
375 RHYB = (ATB + (BTB * FUCB * ACOB * P) + (CTB * FUHB * AHYB * P) +
   1(DTB * FUMB * AMEB * P)) * * 3
380 RCOB = (SYB / RHYB) * ETTA
385 RAV = ( (1. / RCOA) + (1. / RCOB)) / 2.
390 CPMA = 4.394 + (24.274E - 03 * TA) - (6.855E - 06 * (TA * * 2))
395 CPMB = 4.394 + (24.274E - 03 * TB) - (6.855E - 06 * (TB * * 2))
400 CPCA = 6.42 + (1.665E - 03 * TA) - (0.196E - 06 * (TA * * 2.))
405 CPCB = 6.42 + (1.665E - 03 * TB) - (0.196E - 06 * (TB * * 2.))
410 CPHA = 6.947 - (0.2E - 03 * TA) + (0.48E - 06 * (TA * * 2.))
415 CPHB = 6.947 - (0.2E - 03 * TB) + (0.48E - 06 * (TB * * 2.))
420 CPIA = 6.524 + (1.250E - 03 * TA) - (0.001E - 06 * (TA * * 2.))
425 CPIB = 6.524 + (1.250E - 03 * TB) - (0.001E - 06 * (TB * * 2.))
430 DELHA = - 48100. - (15.92 * TA) + (11.5045E - 03 * (TA * * 2)) - (
   12.53967E - 06 * (TA * * 3))
435 DELHB = - 48100. - (15.92 * TB) + (11.5045E - 03 * (TB * * 2)) - (
   12.53967E - 06 * (TB * * 3))
440 DELL = ( (FCO * DELX * RAV) / (ACR * ROB))
445 HRAV = (DELHA + DELHB) / 2.
450 FMEA = ZA * AMEA * CPMA * FCO
455 FMEB = ZB * AMEB * CPMB * FCO
460 FCOA = ZA * ACOA * CPCA * FCO
465 FCOB = ZB * ACOB * CPCB * FCO
470 FHYA = ZA * AHYA * CPHA * FCO
475 FHYB = ZB * AHYB * CPHB * FCO
480 FIA = FIN * CPIA
485 FIB = FIN * CPIB
490 FIAV = (FIA + FIB) / 2.
495 FMAV = (FMEA + FMEB) / 2.
500 FCAV = (FCOA + FCOB) / 2.
505 FHAV = (FHYA + FHYB) / 2.
510 CPK = 0.177
515 FLBK = ROB * DELL * ACR
520 FKAV = FLBK * CPK
525 DELT = ( - HRAV * FCO * DELX) / (FMAV + FHAV + FCAV + FIAV)
530 Q = ABS(DELT - BOLD)
    LB = LA + DELL
    IF (Q - 0.05) 535,535,545
535 CONTINUE
    XA = XB
    TA = TB
    LA = LB
    IF (TA - 673.16) 540,540,560
540 CONTINUE
    GOTO 550
545 GOTO 205
550 CONTINUE
555 FORMAT(10X,'TEMPERATURE AT EXIT',19X,F7.3,/10X,'STAGE LENGTH, CM.'
   1,20X,F8.3,/10X,'MOLE FRACTION METHANOL',18X,F7.5/)
560 WRITE(6,555)TA,LA,XA
    DIS = LA / 30.48
    WRITE(6,565)DIS
565 FORMAT(10X,'LENGTH OF REACTOR STAGE,FT.'13X,F7.3/)
    GOTO(570,600,615,630,645),JTEM
570 TB1 = TA
```

```
      XB1 = XA
      DIS1 = LA / 30.48
      FCO2 = FCO1 * (1. - XB1) + Q1 * FCOQ
      FME2 = FCO1 * XB1
      FHY2 = FHY1 + (Q1 * FHYQ) - (2. * FCO1 * (XB1))
      FIN2 = FIN1 + (Q1 * FINQ)
  575 FORMAT(10X,E12.4,10X,E12.4)
      GOTO 655
  580 TA2 = GEORG
      WRITE(6,585)
  585 FORMAT(20X,'SECOND REACTOR STAGE'/)
      WRITE(6,590)TA2
  590 FORMAT(10X,'TEMPERATURE AT INLET',20X,F9.5)
      XA2 = XB1 * FCO1 / (FCO1 + (Q1 * FCOQ))
      WRITE(6,595)XA2
  595 FORMAT(10X,'MOLE FRACTION METHANOL',19X,F7.5)
      GOTO 750
  600 TB2 = TA
      XB2 = XA
      DIS2 = LA / 30.48
      FCO3 = (FCO1 + (Q1 * FCOQ)) * (1. - XB2) + (Q2 * FCOQ)
      FME2 = (FCO1 + (Q1 * FCOQ)) * XB2
      FHY3 = FHY1 + ( (Q1 + Q2) * FHYQ) - (2. * ( (FCO1 + (Q1 * FCOQ)) *
     1(XB2)))
      FIN3 = FIN2 + (Q2 * FINQ)
      GOTO 655
  605 TA3 = GEORG
      WRITE(6,610)
  610 FORMAT(20X,'THIRD REACTOR STAGE'/)
      WRITE(6,590)TA3
      XA3 = XB2 * (FCO1 + (Q1 * FCOQ)) / (FCO1 + ( (Q1 + Q2) * FCOQ))
      WRITE(6,595)XA3
      GOTO 750
  615 TB3 = TA
      XB3 = XA
      DIS3 = LA / 30.48
      FCO4 = (FCO1 + ( (Q1 + Q2) * FCOQ)) * (1. - XB3) + (Q3 * FCOQ)
      FME4 = (FCO1 + ( (Q1 + Q2) * FCOQ)) * XB3
      FHY4 = FHY1 + ( (Q1 + Q2 + Q3) * FHYQ) - (2. * ( (FCO1 + (Q1 + Q2)
     1* FCOQ) * (XB3)))
      FIN4 = FIN3 + (Q3 * FINQ)
      GOTO 655
  620 TA4 = GEORG
      WRITE(6,625)
  625 FORMAT(1H1,20X,'FOURTH REACTOR STAGE'/)
      WRITE(6,590)TA4
      XA4 = XB3 * (FCO1 + ( (Q1 + Q2) * FCOQ)) / (FCO1 + ( (Q1 + Q2 + Q3
     1) * FCOQ))
      WRITE(6,595)XA4
      GOTO 750
  630 TB4 = TA
      XB4 = XA
      DIS4 = LA / 30.48
      FCO5 = (FCO1 + ( (Q1 + Q2 + Q3) * FCOQ)) * (1. - XB4) + (Q4 * FCOQ
     1)
      FME5 = (FCO1 + ( (Q1 + Q2 + Q3) * FCOQ)) * XB4
      FHY5 = FHY1 + FHYQ - (2. * ( (FCO1 + (Q1 + Q2 + Q3) * FCOQ) * (XB4
     1)))
      FIN5 = FIN4 + (Q4 * FINQ)
      GOTO 655
  635 TA5 = GEORG
```

```
      WRITE(6,640)
  640 FORMAT(20X,'FIFTH REACTOR STAGE'/)
      WRITE(6,590)TA5
      XA5 = XB4 * (FCO1 + ( (Q1 + Q2 + Q3) * FCOQ)) / (FCO1 + FCOQ)
      WRITE(6,595)XA5
      GOTO 750
  645 TB5 = TA
      XB5 = XA
      DIS5 = LA / 30.48.
      YTOT = DIS1 + DIS2 + DIS3 + DIS4 + DIS5
      WRITE(6,650)YTOT
  650 FORMAT(10X,'TOTAL LENGTH OF QUENCH REACTOR',10X,F10.5///)
      GOTO 755
  655 CONTINUE
      GOTO(660,665,670,675),ITO
  660 FCO = FCO2
      FHY = FHY2
      FME = FME2
      FIN = FIN2
      QUE = Q1
      TB = TB1
      GOTO 680
  665 FCO = FCO3
      FHY = FHY3
      FME = FME3
      FIN = FIN3
      QUE = Q2
      TB = TB2
      GOTO 680
  670 FCO = FCO4
      FHY = FHY4
      FME = FME4
      FIN = FIN4
      QUE = Q3
      TB = TB3
      GOTO 680
  675 FCO = FCO5
      FHY = FHY5
      FME = FME5
      FIN = FIN5
      QUE = Q4
      TB = TB4
      GOTO 680
  680 GCO = (FCO - (QUE * FCOQ))
      GHY = (FHY - (QUE * FHYQ))
      GIN = FIN - (QUE * FINQ)
      GME = FME
  685 EA = ( (GCO * ALPCO) + (GHY * ALPHY) + (FIN * ALPIN) + (GME * ALPM
     1E)) * (TB - TQ)
  690 EB = ( ( (GCO * BETCO) + (GHY * BETHY) + (FIN * BETIN) + (GME * BE
     1TME)) * ( (TB * * 2) - (TQ * * 2))) / 2.
  695 EC = ( ( (GCO * GAMCO) + (GHY * GAMHY) + (FIN * GAMIN) + (GME * GA
     1MME)) * ( (TB * * 3) - (TQ * * 3))) / 3.
  700 ENTH = EA + EB + EC
      GICO = (QUE * FCOQ) + GCO
      GIHY = (QUE * FHYQ) + GHY
      GIME = (QUE * FHYQ) + GME
      GIIN = (QUE * FINQ) + GIN
      ED = (GICO * ALPCO) + (GIHY * ALPHY) + (GIME * ALPME) + (GIIN * AL
     1PIN)
      EF = ( (GICO * BETCO) + (GIHY * BETHY) + (GIME * BETME) + (GIIN *
```

```
     1BETIN)) / 2.
      EG = ( (GICO * GAMCO) + (GIHY * GAMHY) + (GIME * GAMME) + (GIIN *
     1GAMIN)) / 3.
      DA = ENTH + (ED * TQ) + (EF * (TQ * * 2)) + (EG * (TQ * * 3))
      TR = 523.16
      YOLD = (ED * TR) + (EF * (TR * * 2)) + (EG * (TR * * 3)) - DA
      DELT = 100.0
      T = 523.16
  705 T = T + DELT
      IF (T - 773.) 710,710,745
  710 CONTINUE
  715 Y = (ED * T) + (EF * (T * * 2)) + (EG * (T * * 3)) - DA
      IF (Y * YOLD) 730,725,720
  720 YOLD = Y
      GOTO 705
  725 CONTINUE
      GOTO 745
  730 RU = ABS(Y)
      CU = ABS(YOLD)
      SU = ABS(RU - CU)
      IF (SU - 0.10) 745,745,735
  735 CONTINUE
      DELT = DELT / 2.
      IF (DELT - 0.002) 745,745,740
  740 CONTINUE
      T = T - DELT
      GOTO 715
  745 GEORG = T
      GOTO(580,605,620,635),KTO
  750 ITEM = ITEM + 1
      JTEM = JTEM + 1
      ITO = ITO + 1
      KTO = KTO + 1
      GOTO 100
  755 CONTINUE
      GOTO 10
  760 STOP
      END
```

```
      SUBROUTINE OUTPU
      COMMON TA1,TO,P,ACP,ROB,FO,Q1,Q2,Q3,Q4
      WRITE(6,20)
   20 FORMAT(1H1,30X,'INITIAL CONDITIONS'//)
      WRITE(6,8991)TA1
 8991 FORMAT(10X,'INLET TEMPERATURE',22X,F9.4/ )
      WRITE(6,8992)TO
 8992 FORMAT(10X,'QUENCH TEMPERATURE',21X,F9.4/ )
      WRITE(6,8993) P
 8993 FORMAT(10X,'REACTOR PRESSURE,ATM.',18X,F9.4/ )
      WRITE(6,8994)ACP
 8994 FORMAT(10X,'REACTOR CROSS SECTION,SQ. CM.',10X,F10.5/)
      WRITE(6,8995) ROB
 8995 FORMAT(10X,'CATALYST BULK DENSITY,GM/CU CM ',9X,F9.5/ )
      WRITE(6,30)FO
   30 FORMAT(10X,'QUENCH FRACTION OF TOTAL FEED',11X,F7.3 /)
      WRITE(6,40)Q1
   40 FORMAT(10X,'FRACTION OF QUENCH TO SECOND STAGE',6X,F7.3/ )
      WRITE(6,8996)Q2
 8996 FORMAT(10X,'FRACTION OF QUENCH TO THIRD STAGE',7X,F7.3 /)
      WRITE(6,8997)Q3
 8997 FORMAT(10X,'FRACTION OF QUENCH TO FOURTH STAGE',6X,F7.3 /)
      WRITE(6,8998)Q4
 8998 FORMAT(10X,'FRACTION OF QUENCH TO FIFTH STAGE',7X,F7.3)
      RETURN
      END
```

APPENDIX C

COMPARISON OF OTHER METHANOL REACTORS WITH A QUENCH REACTOR FOR 15 % CONVERSION

QUENCH REACTOR

LENGTH = 70.6 FEET

ISOTHERMAL REACTOR AT 395 °C

$$\frac{W}{F_{A0}} = \int_0^{.15} \frac{dx}{r_a}$$

FROM FIQURE 6

$$\int_0^{.15} \frac{dx}{r_a} = 1.889$$

F_{A0} = 2359.24 Kmoles / hr

W = 4455 Kg catalyst

$W = \rho_b \times A_{cr} \times L$

ρ_b = .82508 gm/cm^3

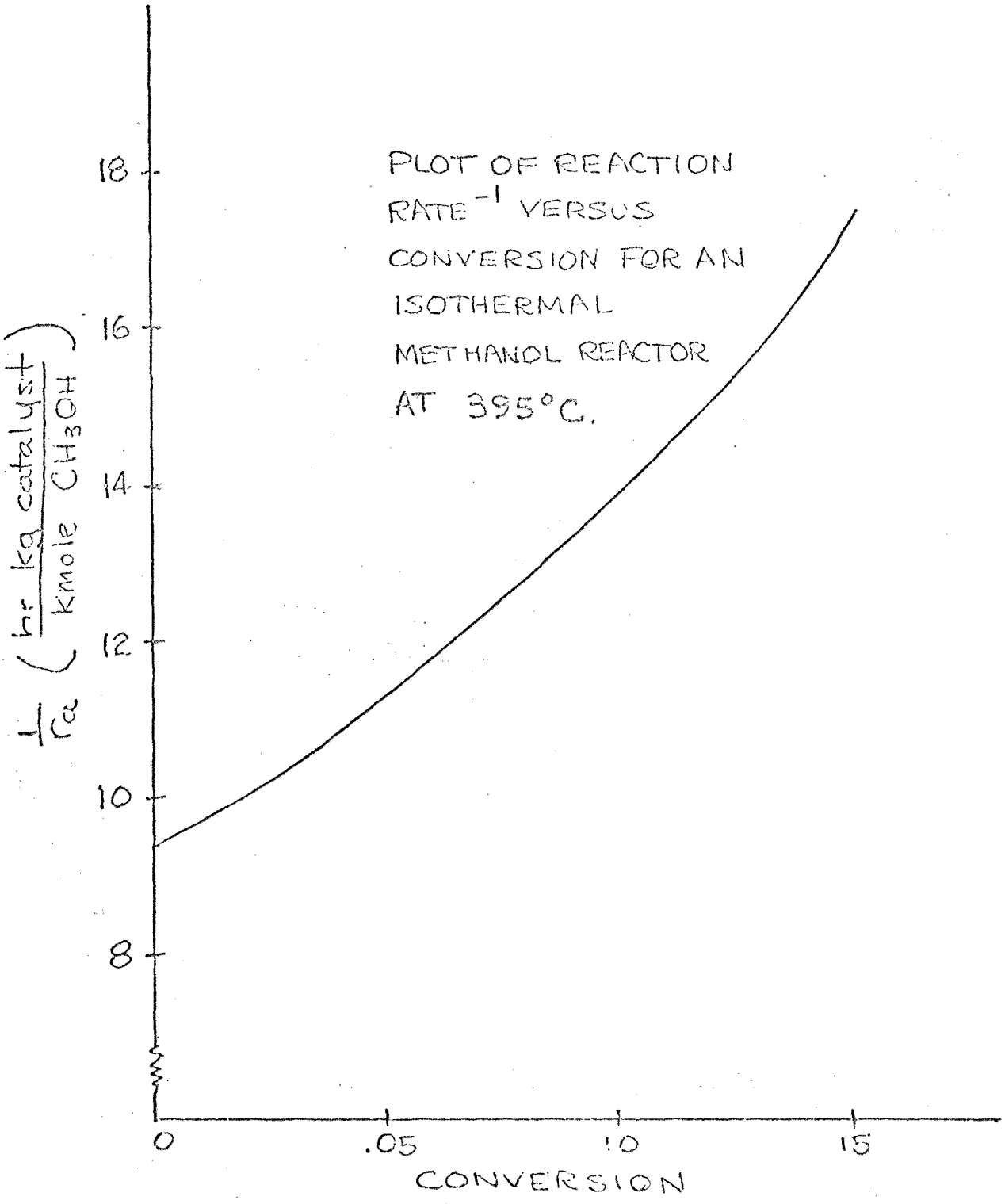
A_{cr} = 3848.45 cm^2

$$L = \frac{4.455 * 10^6}{.82508 * 3848.45 * 30.48}$$

L = 46.03 feet

LENGTH = 46.0 FEET

Figure 6


PLOT OF REACTION RATE^{-1} VERSUS CONVERSION FOR AN ISOTHERMAL METHANOL REACTOR AT 395°C.
$\frac{1}{r_a}\left(\frac{\text{hr. kg catalyst}}{\text{kmole } CH_3OH}\right)$
18
16
14
12
10
8
0
.05
.10
.15
CONVERSION

OPTIMUM REACTION RATE REACTOR

$$\frac{W}{F_{A0}} = \int_0^{.15} \frac{dx}{r_{a\,opt}}$$

FROM FIGURE 7

$$\int_0^{.15} \frac{dx}{r_{a\,opt}} = 1.175$$

$F_{A_0} = 2359.24$ K Moles / hr.

$W = 2772$ kg cat.

$W = \rho_b \times A_{cr} \times L$

$\rho_b = .82503$ gm / cm^3

$A_{cr} = 3848.45$ cm^2

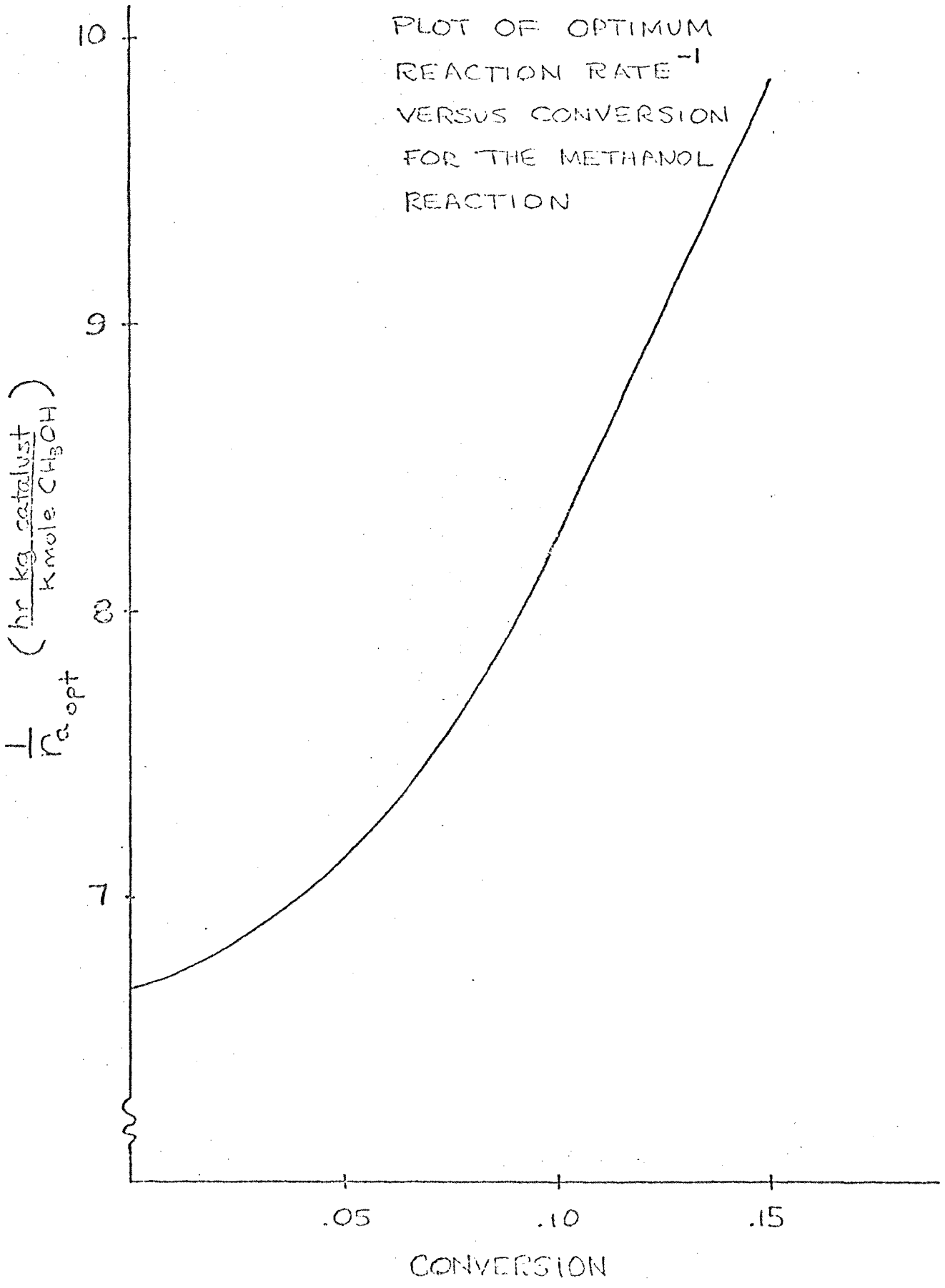
$L = 28.64$ feet (This assumes catalyst effectiveness factor of 1.0)

For catalyst effectiveness factor of 0.67

$L = 28.64 / 0.67$

LENGTH = 42.8 FEET

Figure 7


PLOT OF OPTIMUM REACTION RATE^{-1} VERSUS CONVERSION FOR THE METHANOL REACTION
10
9
8
7
$\frac{1}{r_{a\,opt}}$ $\left(\frac{\text{hr kg catalyst}}{\text{kmole } CH_3OH}\right)$
.05
.10
.15
CONVERSION

OPTIMUM TEMPERATURE PROFILE REACTOR

FROM WRAMPE

S_{opt} for 20% Conversion

$= 49,830 \frac{scfh}{ft^3 \text{ reactor vol.}}$

$$S = \frac{\text{Volumetric Flow Rate } (V_o)}{\text{Volume of Reactor } (V)}$$

FOR 300 TON/DAY PRODUCTION

$V_o = 3900$ lb moles/hr CO

$+ 11700$ lb moles/hr H_2

$+ 1700$ lb moles/hr Inerts

$= 17300$ lb moles/hr Reactor Feed

$$V = \frac{17300 * 359}{49,830}$$

$= 124.64$ ft^3 reactor volume

$A_{cr} = 4.142$ ft^2

$L = V / A_{cr}$

LENGTH = 30.1 FEET

APPENDIX D

Table IV

QUENCH FRACTION = 0.20

INLET TEMPERATURE	CONVERSION	REACTOR LENGTH
608.16	0.126	48.48
613.16	0.123	46.29
623.16	0.118	41.71
628.16	0.117	39.80
633.16	0.113	38.12
638.16	0.110	36.01

Table V

QUENCH FRACTION = 0.25

INLET TEMPERATURE	CONVERSION	REACTOR LENGTH
608.16	0.148	67.48
613.16	0.144	63.69
623.16	0.140	60.30
628.16	0.137	56.44
633.16	0.134	55.44
638.16	0.132	52.69

Table VI

QUENCH FRACTION = 0.30

INLET TEMPERATURE	CONVERSION	REACTOR LENGTH
608.16	0.150	84.75
613.16	0.150	85.17
623.16	0.151	81.34
628.16	0.150	80.74
633.16	0.151	78.17
638.17	0.150	77.80

Table VII

QUENCH FRACTION = 0.35

INLET TEMPERATURE	CONVERSION	REACTOR LENGTH
608.16	0.150	119.86
613.16	0.151	116.27
623.16	0.150	108.00
628.16	0.150	106.45
633.16	0.150	107.73
638.16	0.150	105.73

Table VIII

QUENCH FRACTION = 0.40

INLET TEMPERATURE	CONVERSION	REACTOR LENGTH
608.16	0.150	226.2
613.16	0.150	207.6
623.16	0.150	185.4
628.16	0.150	180.4
633.16	0.150	169.5
638.16	0.149	165.7

Table IX

QUENCH FRACTION = 0.17

QUENCH TEMPERATURE	CONVERSION	REACTOR LENGTH
313.16	0.112	38.44
317.16	0.110	37.40
321.16	0.110	37.39

QUENCH FRACTION = 0.18

QUENCH TEMPERATURE	CONVERSION	REACTOR LENGTH
313.16	0.115	40.25
317.16	0.115	40.15
321.16	0.113	39.50

QUENCH FRACTION = 0.19

QUENCH TEMPERATURE	CONVERSION	REACTOR LENGTH
313.16	0.120	43.25
316.16	0.120	42.79
317.16	0.118	42.01

Table X

QUENCH FRACTION = 0.20

QUENCH TEMPERATURE	CONVERSION	REACTOR LENGTH
313.16	0.123	46.29
323.16	0.121	44.42
333.16	0.119	43.11
353.16	0.114	39.90
373.16	0.110	37.82
393.16	0.105	34.62

Table XI

QUENCH FRACTION = 0.25

QUENCH TEMPERATURE	CONVERSION	REACTOR LENGTH
313.16	0.144	63.69
323.16	0.141	61.16
333.16	0.139	59.13
353.16	0.132	54.10
373.16	0.126	48.39
393.16	0.121	44.72
413.16	0.114	40.16
433.16	0.108	37.01

QUENCH FRACTION = 0.27

QUENCH TEMPERATURE	CONVERSION	REACTOR LENGTH
318.16	0.150	72.01
323.16	0.150	70.75

Table XII

QUENCH FRACTION = 0.275

QUENCH TEMPERATURE	CONVERSION	REACTOR LENGTH
313.16	0.151	74.99
323.16	0.149	72.37
328.16	0.149	70.60
333.16	0.148	69.36
353.16	0.141	62.64
373.16	0.138	56.50
393.16	0.128	50.19
413.16	0.121	45.13
433.16	0.113	40.50

Table XIII

QUENCH FRACTION = 0.30

INLET TEMPERATURE	CONVERSION	REACTOR LENGTH
313.16	0.151	85.18
323.16	0.149	80.94
333.16	0.150	78.30
353.16	0.150	72.73
373.16	0.144	64.67
393.16	0.135	56.78
413.16	0.127	50.38
433.16	0.121	45.74
453.16	0.112	40.23

Table XIV

QUENCH FRACTION = 0.40

QUENCH TEMPERATURE	CONVERSION	REACTOR LENGTH
313.16	0.150	207.61
333.16	0.151	154.26
353.16	0.150	125.05
373.16	0.151	104.34
393.16	0.151	93.93
413.16	0.151	82.15
433.16	0.145	71.57
453.16	0.134	59.78

Table XV

QUENCH FRACTION = 0.50

QUENCH TEMPERATURE	CONVERSION	REACTOR LENGTH
313.16	0.150	1328.6
333.16	0.151	714.8
353.16	0.150	436.0
373.16	0.150	270.2
393.16	0.151	180.0
413.16	0.151	134.4
433.16	0.151	109.3
453.16	0.150	91.37
473.16	0.141	74.21

Table XVI

OPTIMUM REACTOR FOR 12% CONVERSION
INITIAL CONDITIONS

INLET TEMPERATURE	613.1600
QUENCH TEMPERATURE	316.1600
REACTOR PRESSURE, ATM.	280.0000
REACTOR CROSS SECTION, SQ. CM.	3848.44775
CATALYST BULK DENSITY, GM/CU CM	0.82500
QUENCH FRACTION OF TOTAL FEED	0.100
FRACTION OF QUENCH TO SECOND STAGE	0.250
FRACTION OF QUENCH TO THIRD STAGE	0.250
FRACTION OF QUENCH TO FOURTH STAGE	0.250
FRACTION OF QUENCH TO FIFTH STAGE	0.250

FIRST REACTOR STAGE

INLET MOLES CARBON MONOXIDE	0.191093E 07
M RATIO	3.000000
TEMPERATURE AT EXIT	674.632
STAGE LENGTH, CM.	330.277
MOLE FRACTION METHANOL	0.03599
LENGTH OF REACTOR STAGE, FT.	10.835

SECOND REACTOR STAGE

TEMPERATURE AT INLET	633.12398
MOLE FRACTION METHANOL	0.03400
INLET MOLES CARBON MONOXIDE	0.189426E 07
M RATIO	3.035202
TEMPERATURE AT EXIT	676.084
STAGE LENGTH, CM.	206.664
MOLE FRACTION METHANOL	0.06000
LENGTH OF REACTOR STAGE, FT.	6.780

THIRD REACTOR STAGE

TEMPERATURE AT INLET	636.31002
MOLE FRACTION METHANOL	0.05685
INLET MOLES CARBON MONOXIDE	0.2013718 07
M RATIO	3.060283
TEMPERATURE AT EXIT	675.071
STAGE LENGTH, CM.	219.976
MOLE FRACTION METHANOL	0.08025
LENGTH OF REACTOR STAGE, FT.	7.184

FOURTH REACTOR STAGE

TEMPERATURE AT INLET	637.15841
MOLE FRACTION METHANOL	0.07682
INLET MOLES CARBON MONOXIDE	0.207453E 07
M RATIO	3.083217
TEMPERATURE AT EXIT	675.136
STAGE LENGTH, CM.	295.308
MOLE FRACTION METHANOL	0.10082
LENGTH OF REACTOR STAGE, FT.	8.376

FIFTH REACTOR STAGE

TEMPERATURE AT INLET	638.80636
MOLE FRACTION METHANOL	0.09603
INLET MOLES CARBON MONOXIDE	0.213267E 07
M RATIO	3.106237
TEMPERATURE AT EXIT	676.028
STAGE LENGTH, CM.	293.004
MOLE FRACTION METHANOL	0.12003
LENGTH OF REACTOR STAGE, FT.	9.612
TOTAL LENGTH OF QUENCH REACTOR	42.78973

Table XVII

OPTIMUM REACTOR FOR 15% CONVERSION

INITIAL CONDITIONS

INLET TEMPERATURE	613.1599
QUENCH TEMPERATURE	328.1599
REACTOR PRESSURE, ATM.	280.0000
REACTOR CROSS SECTION, SQ. CM.	3848.44751
CATALYST BULK DENSITY, GM/CU CM	0.82508
QUENCH FRACTION OF TOTAL FEED	0.275
FRACTION OF QUENCH TO SECOND STAGE	0.250
FRACTION OF QUENCH TO THIRD STAGE	0.250
FRACTION OF QUENCH TO FOURTH STAGE	0.250
FRACTION OF QUENCH TO FIFTH STAGE	0.250
FIRST REACTOR STAGE	
INLET MOLES CARBON MONOXIDE	0.171045E 07
M RATIO	3.000000
TEMPERATURE AT EXIT	674.630
STAGE LENGTH, CM.	295.600
MOLE FRACTION METHANOL	0.03600
LENGTH OF REACTOR STAGE, FT.	9.698
SECOND REACTOR STAGE	
TEMPERATURE AT INLET	614.32495
MOLE FRACTION METHANOL	0.03288
INLET MOLES CARBON MONOXIDE	0.181107E 07
M RATIO	3.053999
TEMPERATURE AT EXIT	673.876
STAGE LENGTH, CM.	376.983
MOLE FRACTION METHANOL	0.06888
LENGTH OF REACTOR STAGE, FT.	12.368
THIRD REACTOR STAGE	
TEMPERATURE AT INLET	617.77344
MOLE FRACTION METHANOL	0.06339
INLET MOLES CARBON MONOXIDE	0.190585E 07
M RATIO	3.067685
TEMPERATURE AT EXIT	675.536
STAGE LENGTH, CM.	444.232
MOLE FRACTION METHANOL	0.09939
LENGTH OF REACTOR STAGE, FT.	14.575

FOURTH REACTOR STAGE

TEMPERATURE AT INLET	622.70190
MOLE FRACTION METHANOL	0.09205
INLET MOLES CARBON MONOXIDE	0.199480E 07
M RATIO	3.101388
TEMPERATURE AT EXIT	675.671
STAGE LENGTH, CM.	486.525
MOLE FRACTION METHANOL	0.12605
LENGTH OF REACTOR STAGE, FT.	15.962

FIFTH REACTOR STAGE

TEMPERATURE AT INLET	625.94604
MOLE FRACTION METHANOL	0.11739
INLET MOLES CARBON MONOXIDE	0.208230E 07
M RATIO	3.132999
TEMPERATURE AT EXIT	674.485
STAGE LENGTH, CM.	548.452
MOLE FRACTION METHANOL	0.14939
LENGTH OF REACTOR STAGE, FT.	17.994
TOTAL LENGTH OF QUENCH REACTOR	70.59685

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