CHEMICAL PROCESS SIMULATION OF HEXANE ISOMERIZATION IN A FIXED-BED AND A CSTCR REACTOR

By

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PREFACE

In recent years, Chemical Reaction Engineering has developed to a science that uses complicated theoretical apparatus and sophisticated mathematical models to describe the behavior of reacting system. It is not simple to find a realistic approach to the application of the theory in practical technological research. The main purpose of this study is to develop a more reliable model to simulate chemical reactions which proceed in reactors. For this research work, the ideal plug flow reactor and CSTCR are chosen.

Many people have aided me in this research work, and it is impossible to adequately acknowledge their efforts except in a general way. I am deeply indebted to Dr. Arland H. Johannes who offered me numerous valuable suggestions and, who was the main promoter of this study. Also, Dr. Robert L. Robinson, Jr. and Dr. Khaled A. M. Gasem are most generous in the encouragement and cooperation. Financial support from the School of Chemical Engineering is appreciated.

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INTRODUCTION

Present isomerization applications in petroleum refining are used to provide additional feedstock for alkylation units or high-octane fractions for gasoline blending. Straight chain paraffins, such as n-butane, n-pentane or n-hexane can be converted to isomers by continuous, catalytic (aluminum chloride, antimony trichloride, etc.) processes.

Isomerization found initial commercial application during World War II for making high-octane aviation gasoline. Atlas Processing Company of Shreveport, La., was the first to install a hexane isomerization process (Penex) for the production of a motor-fuel blending component (1).

Licensed by the Pure Oil Company, a division of the Union Oil Company of California, Isomerate is another continuous isomerization process designed to convert pentanes and hexanes into highly branched isomers. A rugged dual-function catalyst is used in a fixed-bed reactor system (2). Another process licensed by British Petroleum Company, BP is a two fixed-bed-reactor (one for C_5 feed) process using high activity Platinum catalyst and external hydrogen (3). These processes will be described in more detail.

This study is devoted to model design and neglects the mechanical design and stability study of hexane isomerization reactors. To model a reactor it is necessary to write a set of mathematical equations which express the behavior of the reacting system under various operating conditions. For the fixed-bed reactor model, two ordinary differential equations (ODEs) are required to describe the reactor system. One is a reactor mass balance and the other is energy balance. For the perfectly mixed reactor model, two linear equations are also required to describe the reactor system. One is a reactor material balance and the other is a reactor energy balance. The two ODEs describing catalytic fixed-bed and the two linear equations describing perfectly mixed reactors must be solved simultaneously and can be solved by means of a computer.

There are various numerical methods which have been developed to solve systems of simultaneous ODEs. A modified fourth-order, Runge-Kutta algorithm will be utilized to obtain the solution of the initial-value ODEs encountered in fixed-bed reactor problems. Newton's method was used to solve the linear equations in the Continuously Stirred Tank Catalytic Reactor (CSTCR) model.

The fixed-bed reactor program is called HEXFI. The CSTCR model is called HEXCR. Both programs are written in the FORTRAN language and are listed in Appendix A and B.

CHAPTER II

LITERATURE REVIEW

The literature review will cover the following subjects:

1. Importance of Isomerization
2. Hexane Isomerization Kinetics
3. Catalytic Reactors
4. Process Descriptions and Catalysts

Importance of Isomerization

The demand of today's automobiles for high-octane gasolines has stimulated the use of catalytic reforming. Catalytic reformate furnishes approximately 45-55% of the United States gasoline requirements and with the increasing utilization of low-lead and lead-free gasolines, this can be expected to increase (4).

Catalytic reforming is a continuous process to upgrade low-octane virgin, or heavy catalytically cracked naphthas into high-octane components for motor or aviation fuel blending or petrochemical usage. The commercial processes available for use today can be broadly classified as moving-bed, fluidized-bed or fixed-bed types. The primary reaction mechanisms include in the followings (2):

(1) dehydrogenation of naphthenes
(2) dehydrocyclization of paraffins
(3) paraffin isomerization
(4) dehydroisomerization of naphthenes
(5) paraffin hydrocracking
(6) desulfurization
(7) olefin saturation

The petroleum processing industry is without doubt the largest user of catalysts in the chemical industry. The catalytic materials include both solids and liquids and range all the way from common clay to precious metals. Table I lists various catalytic processes commonly used in petroleum processing and the materials employed.

To understand the significance of catalytic reforming in refinery operations, the use of the octane number as a standard for gasoline quality must be understood. Octane rating has been used for years to measure the antiknock performance of gasoline. The higher the octane number, the less the tendency for a gasoline to produce a knocking sound in an automobile engine.

In 1923, a standard was established for measuring the octane number of gasoline. The straight-chain paraffin, n-heptane, was assigned an octane number of zero, and a branched-chain paraffin, iso-octane (2,2,4-trimethyl pentane), was assigned an octane number of 100. The octane number of a gasoline is determined by comparing its anti-

TABLE I

[a]ISOMERIZATION CATALYSTS

Low-temperature processes	Catalyst	Selectivity
Vapor phase:		
Anglo-Jersey	Impreg. bauxite	95
Phillips	Impreg. bauxite	95
Shell	Impreg. bauxite	95
Liquid phase:		
UOP	Complex on quartz	97
Standard Oil	Liquid complex	97

High-temperature processes	Catalyst	Regeneration
Butamer	Platinum	None required
Iso Kel	Precious metal	Regenerable
Isomerate	Nonnoble metal	Infrequent
Penex	Platinum	None required

[a]REFERENCE (2)

knock engine performance with various blends of n-heptane and iso-octane under specified laboratory conditions. Automotive engineers fix compression ratios for particular engine designs. Engines with higher compression ratios require higher-octane-number fuel than those with lower ratios.

Two methods of determining motor fuel octane number are now in use (5):

1) the research method, ASTM D-2699, a laboratory simulation of engine performance at low speed (reported as RON, research octane number).
2) the motor method, ASTM D-2700, a laboratory simulation of engine performance at high speed (reported as MON, motor octane number).

Road testing a number of different autos under varying conditions and gasolines have shown that the average of the RON and MON, (R+M)/2, gives an acceptable number for rating gasolines. This average is now a specification on gasoline and is the octane number displayed on the pumps at service stations. In the U.S., most service stations offer three gasoline choices: leaded regular, unleaded regular and unleaded premium. Leaded regular at service stations has an octane rating of 88-89. Unleaded regular has an octane rating of 87-88 and unleaded premium is 91-92.

A few examples of octane number of individual hydrocarbons and some selected refinery motor fuel blend stocks are shown in Table II. Note C_5^+ reformate (pentane and heavier) from a reformer is the only gasoline stock that varies in octane number. Reformate octane number can be varied from 1 to 25 or more. That flexibility is what makes the catalytic reformer so useful to the petroleum refiner.

There is one thing I would like to mention here about tetraethyl lead (TEL) in TABLE II. First introduced in 1922, its effect in improving the octane number of motor gasoline is well established, the response varying with the hydrocarbon composition of the gasoline. In spite of much research work, the exact mechanism by which TEL works to suppress knock is not known. It is visualized that the compound is decomposed by heat in the combustion chamber. This gives rise to particles which then influence the chemical reactions involved in the combustion of the fuel. This promotes smooth combustion to the exclusion of knock. However, TEL has certain well-recognized disadvantages such as tending to increase deposits in the combustion chamber, tending to inverse exhaust valve burning, and tending to foul spark plugs (6).

Isomerization Kinetics

The isomerization of n-hexane to its isomeric forms has been the subject of a great deal of study (7-10). Various postulations related to the reaction paths have been made and rate constants for the mathematical model have been determined. There are some possible models which describe

TABLE II

OCTANE NUMBERS OF SELECTED HYDROCARBONS AND REFINERY BLEND STOCKS[a]

	Research ml TEL/gal[b]		Motor ml TEL/gal		Octane Rating (R + M)/2
	0.0	3.0	0.0	3.0	
n-Butane	94.0	104.0	89.0	104.7	91.5
i-Butane	102.0	118.0	97.0	—	99.5
n-Pentane	61.8	84.6	83.2	84.8	72.5
i-Pentane	93.0	104.9	89.7	107.3	91.4
n-Octane	—	24.8	—	28.1	—
2,2,4-TMP[c]	100.0	115.5	100.0	115.5	100.0
Cyclohexane	84.0	96.6	77.6	87.4	80.8
Alkylate	93.0	104.0	92.0	106.0	91.0
C_5^+ reformate	90.0	98.0	81.0	89.0	85.5
C_5^+ reformate	95.0	101.0	85.0	93.0	90.0
C_5^+ reformate	100.0	104.5	90.0	94.0	95.0

[a] REFERENCE (5)

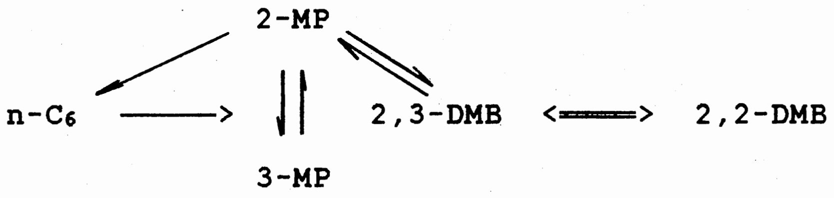
[b] To convert milliliters of tetraethyl lead per gallon(ml TEL/gal) to grams Pb/gal, multiply ml TEL/gal by 1.057

[c] Trimethylpentane

the reaction kinetics:

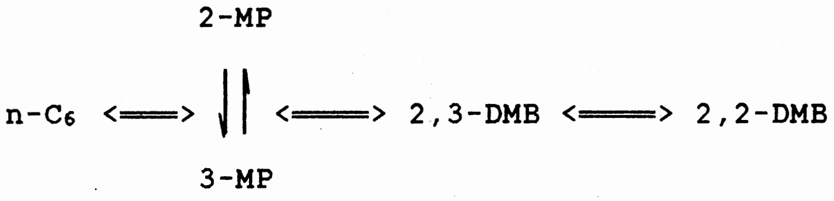
Frölich (11) and Evering (9) deduced from experimental data that the isomerization of n-hexane proceeded stepwise according to the scheme.

Model I:



Note that for this model, they used $AlCl_3$-HCl catalyst. Frölich and Evering also found that the rate determining step for isomerizing n-hexane to 2,2-dimethylbutane (2,2-DMB) was the last step in Model I. Later on, Evering proposed another mathematical model (9) based on graphical analysis of his experimental data.

Model II:



To simplify calculation of the reaction kinetics, a slightly different reaction mechanism was proposed by Cull and Brenner (12). First-order reactions were assumed and the system was described by differential equations given in the following:

Model III:

$$n\text{-}C_6 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 3\text{-MP} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} 2\text{-MP} \underset{k_6}{\overset{k_5}{\rightleftharpoons}} 2,3\text{-DMB} \underset{k_8}{\overset{k_7}{\rightleftharpoons}} 2,2\text{-DMB}$$

$$\frac{d(n\text{-}C_6)}{dt} = k_2(3\text{-MP}) - k_1(n\text{-}C_6)$$

$$\frac{d(3\text{-MP})}{dt} = k_1(n\text{-}C_6) + k_4(2\text{-MP}) - (k_2+k_3)(3\text{-MP})$$

$$\frac{d(2\text{-MP})}{dt} = k_3(3\text{-MP}) + k_6(2,3\text{-DMB}) - (k_4+k_5)(2,3\text{-DMB})$$

$$\frac{d(2,3\text{-DMB})}{dt} = k_5(2\text{-MP}) + k_8(2,2\text{-DMB}) - (k_6+k_7)(2,3\text{-DMB})$$

$$\frac{d(2,2\text{-DMB})}{dt} = k_7(2,3\text{-DMB}) - k_8(2,2\text{-DMB})$$

To test this model, data were obtained from batch runs and a nonlinear regression technique was applied to determine the rate constants.

Catalytic Reactors

Choosing a suitable reactor for a gas-solid reaction is a question of matching the characteristics of the reaction system, especially the reaction kinetics, with the characteristics of the reactors under consideration.

There is a wide choice of contacting methods and equipment for gas-solid reaction. These reactors include : fixed-bed reactor, Carberry reactor and fluidized-bed reactor. Each of these reactors has different key features and are discussed below.

Fixed-bed reactors consist of one or more tubes packed with catalyst particles and are typically operated in a vertical position. The catalyst particles may be a variety of sizes and shapes: granular, pelleted, cylinders, spheres, etc.. Because of the necessity of removing or adding heat, it may not be possible to use a single large-diameter tube packed with catalyst. In this event the reactor may be built of a number of tubes encased in a single body, such as is illustrated in Figure 1. The energy exchange with the surroundings is obtained by circulating, or boiling, a fluid in the space between the tubes. For an exothermic reaction, heat evolved due to reaction is much often greater than that can be transferred to the cooling fluid. This leads to a maximum temperature somewhere in the reactor, and is called a "hot spot" (13).

The construction of this type of reactor is straightforward. In general, unsteady operation results due to catalyst aging. The reactor is, not very useful for gathering kinetic data when the catalyst decays rapidly (14). Leva (15) reported the calculation of pressure drop along the fixed bed, and Nauman (16) suggests using the Ergun equation to calculate the pressure drop in this type of reactor.

The rotating-basket reactor (often known as the Carberry reactor) has been widely used for gas-solid

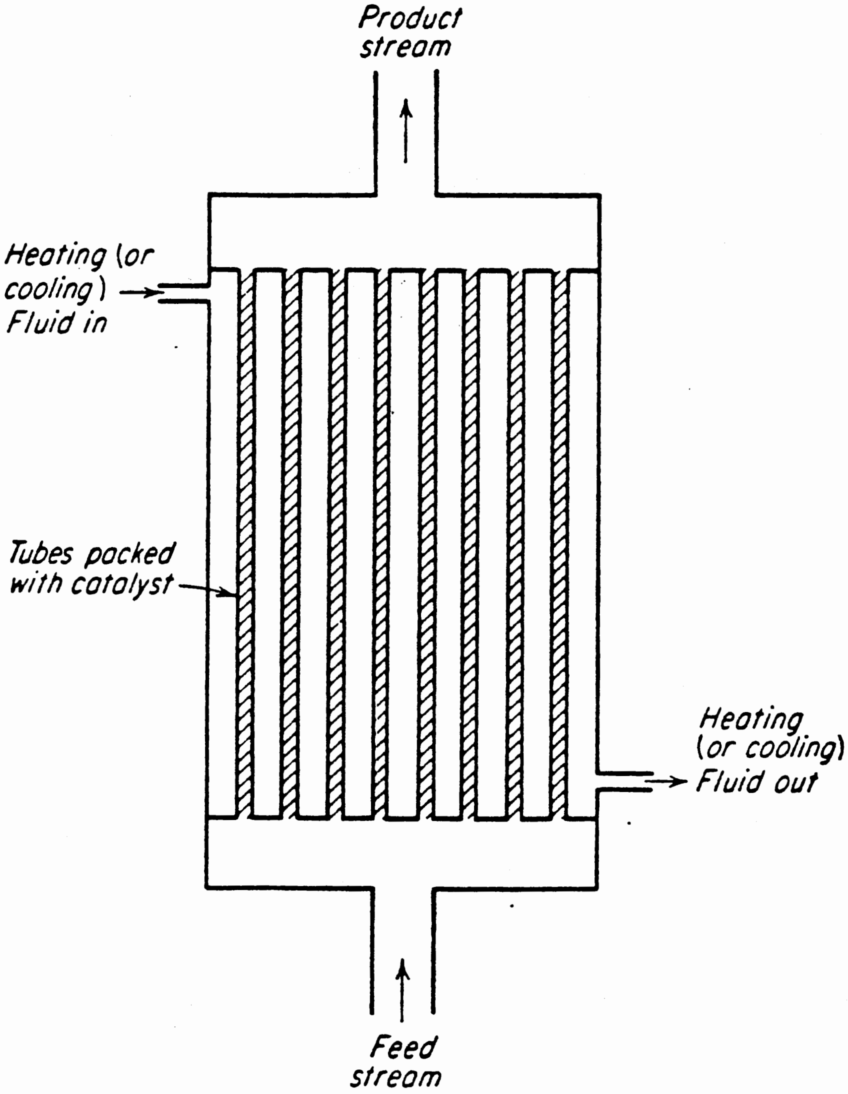


Figure 1. Multitube Reactor, Fixed-Bed; adapted from Smith (1970).

catalytic reactions. The construction is not very difficult, but it is more complex and expensive to build than a batch or fixed-bed reactor. The catalyst baskets can be attached to a stirrer or they can be used as the stirrer paddles. The reactor is operated under transient conditions if the catalyst decays rapidly. Otherwise, steady-state operation is obtained. Baffles can be installed to obtain better contact (17). Figure 2 sketches the main features of an experimental reactor.

This type of reactor has several disadvantages. Erosion of the catalyst may occur under sever agitation and it can be a problem to keep powered catalyst in the baskets. The surface temperature of the catalyst is very difficult to measure and it is often erroneously assumed to be equal to the bulk temperature. For these reasons, the use of very small catalyst particle size is not recommended.

Fluidized-bed reactors are catalyst particles supported by an upflow of gas as a fluid bed (18). A mechanical advantage is also gained by the relative ease with which solids may be conveyed and, because of solids mixing, the gas in the reactor is at approximately the same temperature. Another important advantage of the fluidized-bed reactor over the fixed-bed type is that the catalyst can be externally regenerated without disturbing the operation of the reactor. A disadvantage of the fluidized-bed reactors is that the equipment is large. To avoid the solid particles from being blown out the top of the reactor, the

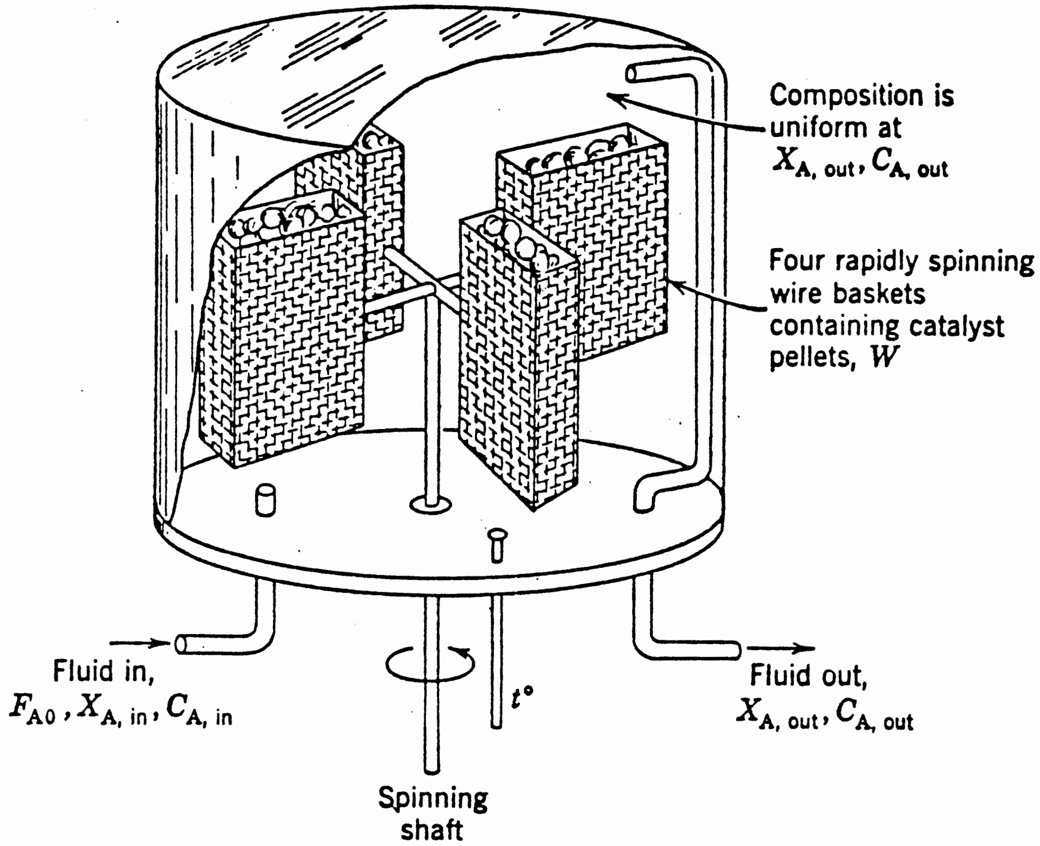


Figure 2. CSTCR; adapted from Levenspiel (1972).

gas velocity must be low. This means that we need to design large-diameter vessels and this increases the initial cost. There are also losses of catalyst fines from the reactor, necessitating expensive dust-collection equipment in the exit streams.

LHSV and Hydrogen-to-Hydrocarbon Ratio

LHSV

Space velocity is an important variable in refinery because it is interchangeable with reaction temperature. Space velocity has to do with the length of time of contact between the reactants and the catalyst. Refiners choose an easily accessible parameter of residence time in either liquid hourly space velocity (LHSV) or in weight hourly space velocity (WHSV).

LHSV is the volume per hour of reactor charge per volume of catalyst. The higher the LHSV, the greater the volume of feed charge per hour over a given amount of catalyst. Therefore, contact time with catalyst is less. Normally, in most isomerization process, LHSVs are controlled between 1.5 - 2.5 (19).

Hydrogen-to-Hydrocarbon Ratio

The main purpose of hydrogen recycle is to increase hydrogen partial pressure in the reactors. The hydrogen react with coke precursors, removing them from the catalyst before they can form polycyclic aromatics which ultimately deactivate the catalyst. Also, hydrogen can inhibit side reactions such as cracking. Most of the present processes control the ratio between 2 - 1 (3,20).

Process Descriptions

Many papers have published information about their isomerization processes and operating conditions. These processes such as Penex, Isomerate and BP are now applied in commercial processes.

Penex

Licensed by Universal Oil Products, Penex is a nonregenerative C_5 and/or C_6 isomerization process. The reaction takes place in the presence of hydrogen and a platinum catalyst. The Penex process may be applied to many feedstocks by varying the fractionating system. Mixed feed may be split into pentane and hexane fractions, and respective isofractions separated from each other. Reactor temperatures range from 500 - 900 °F; pressures from 300 - 1000 psig. Hydrogen requirements are low — (49 scf/bbl) for pentane isomerization and slightly higher for hexane isomerization (21,22,23).

Isomerate

Licensed by the Pure Oil Company, Isomerate is a continuous isomerization process designed to convert pentanes and hexanes into highly branched isomers. A rugged dual-function catalyst is used in a fixed-bed reactor system. Operating conditions include reactor temperatures and pressures which are less than 750 °F and 750 psig, respectively (24,25).

BP

Licensed by British Petroleum Company, BP is a two fixed-bed-reactor isomerization process. It uses very high activity, regenerable Platinum catalyst and hydrogen. Pentanes, hexanes or mixtures of the two from catalytic reforming or solvent extraction may be processed. Operating temperatures are typical less than 320 °F , pressure is about 250 psig, LHSV is around 1 to 2 and hydrogen to hydrocarbon mole ratio is 2:1.

A typical simplied flow diagram is shown in Figure 3 (1,3).

Catalysts

The platinum-based catalysts used for isomerization are similar to those used in catalytic reforming but the conditions are much less severe. A catalyst promoter such as hydrogen chloride is added continuously to maintain high catalyst activity but catalyst deactivation occurs so slowly that catalyst regeneration is not necessary except at long intervals (generally greater than one year). Hydrogen is used to minimize carbon deposits on the catalyst but

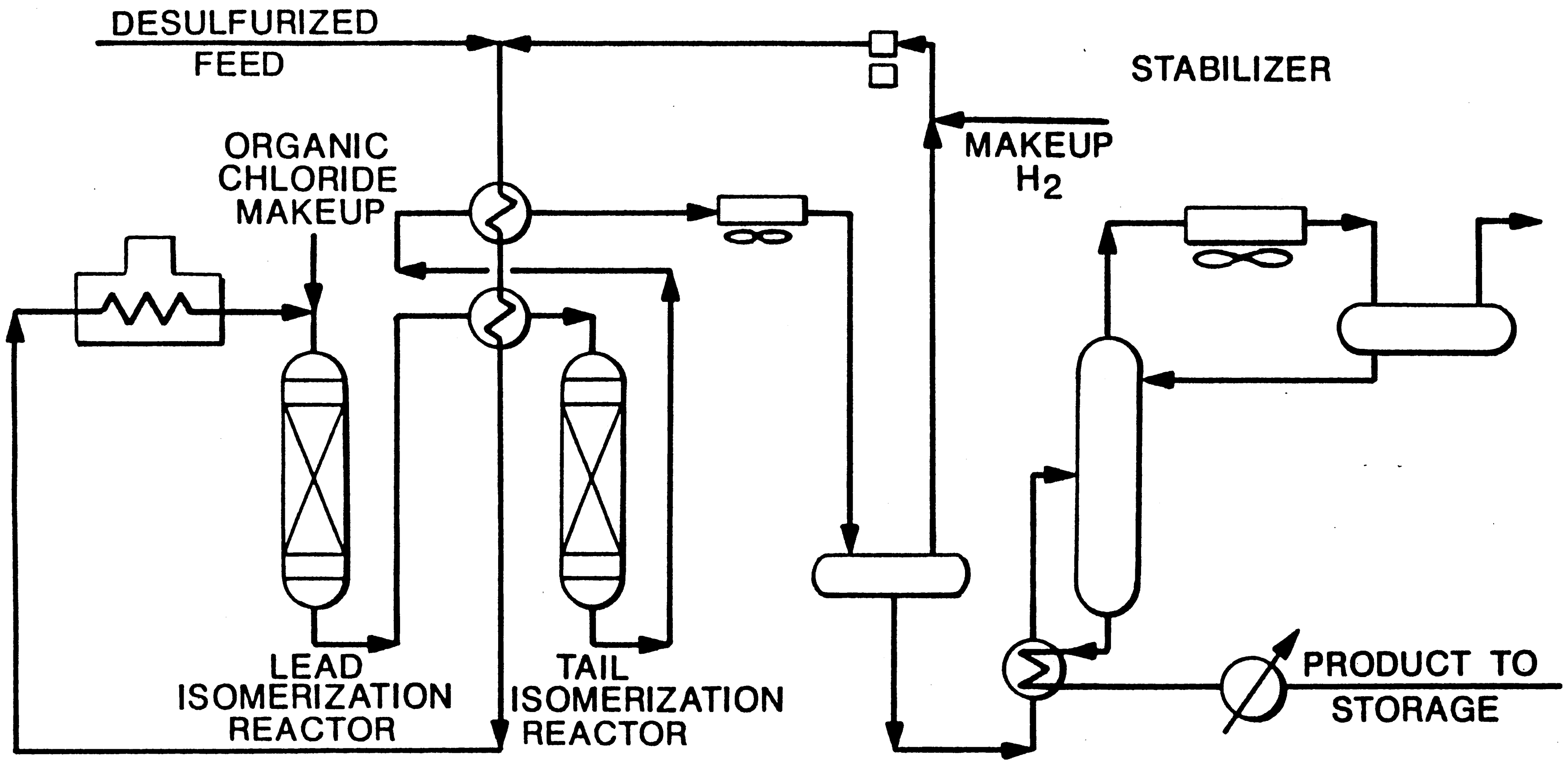


Figure 3. Hexane Isomerization Flow Diagram

hydrogen consumption is negligible (19). Table I lists the catalysts used in some commercial processes. Supported metal catalysts have been developed for use in high-temperature processes which operate in the range 700 - 900 °F and 300 to 750 psig. Aluminum chloride plus hydrogen chloride are universally used in the low-temperature processes.

Deactivation

Most often catalysts are employed to speed up reactions that are sluggish or will not proceed at all. They may also allow operation at a lower operating temperature level, influence the product distributions, or more rarely, slow down a reaction.

During the chemical process the properties of the catalyst gradually deteriorate . There may be several reasons for this (27):

Catalytic Poisoning Catalysts become poisoned when feed stream contains impurities which are deleterious to the activity of the catalyst. Particularly strong poisons are substances whose molecular structure contains lone electron pairs capable of forming covalent bonds with catalyst surfaces. For instance, catalytic poisons for metals are compounds containing sulphur, arsenic and nitrogen. Acidic catalyst poisons are all normally basic compounds. Catalytic poisons most often come from impurities present in raw materials, but sometimes may be present in the material used for preparation of the catalyst itself.

Catalyst Fouling Reactions involving organic compounds are inevitably accompanied by decomposition of the materials to carbon or possibly the formation of high-molecular weight compounds. These gradually cover the surface of the pellets and block access the active surface (20).

CHAPTER III

FIXED-BED REACTOR AND CSTCR DESIGN PRINCIPLES

Fixed-Bed Reactors

Beecher, and Voorhies (28) reported that hexane isomerization was obtained under plug flow (tubular flow) conditions in a fixed-bed reactor. In a plug-flow reactor specific assumptions are usually made about the extent of mixing: no mixing in the axial direction, complete mixing in the radial direction and uniform velocity across the radius. The absence of longitudinal mixing is the special characteristic of this type of reactor (29).

Derivation of Mass Balance Equation

The performance equation for a steady state plug flow reactor is:

$$R_p \, dW = F \, dx \qquad (3-1)$$

where

W = mass of catalyst, kg

F = molar flow rate of reactant, kgmole/hr

x = conversion of reactant

R_p = global rate of reaction per unit mass of catalyst, kgmole/(kg of cat -hr)

Equation (3-1) is based on a material balance and is derived by several authors (29,30).

Although equation (3-1) is the general form for tubular-flow reactor packed with catalyst pellets, it does not meet our requirements. Therefore, it was converted into the following form which can be utilized for this study:

$$\Sigma\ (-r_{ij}\ R_j)\ dW = F_{io}\ dx_i \qquad (3\text{-}2)$$

Rearranging,

$$\frac{dW}{F_{io}} = \int \frac{dx_i}{\Sigma(-r_{ij}R_j)}$$

Integrating,

$$\frac{W}{F_{io}} = \int \frac{dx_i}{\Sigma(-r_{ij}R_j)}$$

Since,

$$F_i = F_{io}\ (1-x_i)$$

then,

$$dF_i = -F_{io}\ dx_i$$

and,

$$dx_i = \frac{dF_i}{-F_{io}}$$

Therefore,

$$\frac{W}{F_{io}} = \int \frac{(-dF_i/F_{io})}{\Sigma(-r_{ij}R_j)}$$

or,

$$\frac{W}{1} = \int \frac{dF_i}{\Sigma(r_{ij}R_j)}$$

taking derivatives of both sides, it becomes

$$dW = \frac{dF_i}{\Sigma(r_{ij}R_j)}$$

or,

$$dF_i = (dW)\ \Sigma(r_{ij}R_j) \qquad (3\text{-}3)$$

If we assume the reactor tube has a diameter, D, then:

$$dW = \rho_b A_c dZ = \rho_b \frac{\pi D^2}{4} dZ \qquad (3\text{-}4)$$

Substituting equation (3-4) into equation (3-3) gives:

$$dF_i = (\rho_b \frac{\pi D^2}{4} dZ)\ \Sigma(r_{ij}R_j)$$

or,

$$\frac{dF_i}{dZ} = \rho_b \frac{\pi D^2}{4}\ \Sigma(r_{ij}R_j) \qquad (3\text{-}5)$$

This is the final mass balance equation utilized in my design.

where

F_i = the molar flow rate of species i, kgmole/hr

r_{ij} = stoichiometric coefficient of the ith component in the jth reaction.

R_j = reaction rate of the jth reaction, kgmole/(kg of cat -hr)

ρ_b = the bulk density of the bed, kg/m^3

D = the diameter of the tube, m

Z = the length of the reactor, m

Derivation of Energy Balance Equation

If the enthalpy of the reaction per unit mass above a base state is H at the entrance to an element and H+ΔH at the exit, a standard energy balance can be written as:

$$F_t H \Delta t - F_t (H+\Delta H)\ t + U(\Delta A_h)(T_s - T)\Delta t = 0$$

or

$$-F_t \Delta H + U(\Delta A_h)(T_s - T) = 0 \qquad (3\text{-}6)$$

where

F_t = total molar-flow rate, kgmole/hr

U = overall heat transfer coefficient, kj/(m^2-hr-K)

ΔH = enthalpy change due to reaction, kj/kgmole

ΔA_h = heat transfer area, m^2

Δt = time interval, hr

T_s = surrounding temperature, K

T = bulk temperature in reactor, K

but,

$$\Delta H = C_{pt} \Delta T + \Sigma\ (\Delta H_{Rj})\ x_{ij}\ \frac{F_i}{F_t}$$

Using this expression for ΔH in equation (3-6) and simplifying yields

$$-F_t C_{pt} \Delta T - \Sigma F_i \Delta H_{Rj} \Delta x_{ij} + U(\Delta A_h)(T_s - T) = 0$$

If we divide each term by ΔW, and take the limit as $\Delta W \longrightarrow 0$, we obtain;

$$F_t C_{pt} \frac{dT}{dW} = U(T_s - T) \frac{dA_h}{dW} + \Sigma\ F_i (-\Delta H_{Rj}) \frac{dx_{ij}}{dW}$$

Combining with,

$$F_i\ dx_{ij} = R_j\ dW$$

gives,

$$F_t C_{pt} \frac{dT}{dW} = U(T_s - T) \frac{dA_h}{dW} + \Sigma(-\Delta H_{Rj}) R_j$$

or,

$$(\Sigma F_i C_{pi})\ dT = U(T_s - T) dA_h + \Sigma(-\Delta H_{Rj}) R_j dW \qquad (3\text{-}7)$$

and,

$$dT = \frac{U(T_s - T)\pi D dZ + \Sigma(-\Delta H_{Rj}) R_j \rho_b A_c dZ}{\Sigma\ F_i C_{pi}}$$

since,

$$dA_h = \pi D dZ$$

$$dW = \rho_b A_c dZ$$

Substituting into equation (3-7) gives equation (3-8)

$$\frac{dT}{dZ} = \frac{U(T_s - T)\pi D + \frac{\pi D^2}{4} \rho_b \Sigma\ R_j(-\Delta H_{Rj})}{\Sigma\ F_i C_{pi}} \qquad (3\text{-}8)$$

Equations (3-5) and (3-8) are the two basic equations which will be used to model a fixed-bed reactor.

Pressure Drop Prediction

For the calculation of the pressure drop for a catalyst bed, Ergun (31) recommends the following equation:

$$\frac{dP\rho}{G_o^2}\;\frac{d_p}{L}\;\frac{\epsilon^3}{1-\epsilon} = 150\,\frac{(1-\epsilon)\,\mu}{d_p\;G_o} + 1.75 \qquad (3\text{-}9)$$

where

ϵ = void fraction of the bed, dimensionless

d_p = effective diameter of particles, m

L = height of the bed, m

dP = pressure drop, Pa

μ = viscosity of fluid, Pa-s = kg/(m-s)

G_o = superficial mass velocity, kg/(m^2-s)

ρ = density of fluid, kg/m^3

For turbulent region, characterized by:

$$R_E = \frac{d_p\;G_o}{\mu(1-\epsilon)} > 100$$

Hence, equation (3-9) may be simplified to:

$$dP = 1.75L\rho V_o^2(1-\epsilon)/(d_p\epsilon^3)$$

As I mentioned before, there are numerous correlations in the literature for the calculation of pressure drop (15), the Ergun equation is probably the best.

Model Simulation

In Chapter 2, it was mentioned that there were three existing types of theoretical models. The mechanism proposed by Cull and Brenner (12) is one of the simplest possible mechanisms involving all five hexane isomers and requires estimation of a minimum number of kinetic parameters, ie., eight rate constants. This mechanism can be written as:

$$n\text{-}C_6 \underset{k_{1r}}{\overset{k_{1f}}{\Longleftrightarrow}} 3\text{-MP} \underset{k_{2r}}{\overset{k_{2f}}{\Longleftrightarrow}} 2\text{-MP} \underset{k_{3r}}{\overset{k_{3f}}{\Longleftrightarrow}} 2,3\text{-DMB} \underset{k_{4r}}{\overset{k_{4f}}{\Longleftrightarrow}} 2,2\text{-DMB}$$

The following assumptions were made to simplify the kinetic model:

1. Reactions from n-C_6 to 2,3-DMB occur very fast and were modeled as being equilibrium controlled.
2. Total moles of hexane in the reactor are conserved down the reactor. That is, no appreciable side reactions such as hydrocracking occur.
3. The reactor operates in plug flow.
4. The reaction of 2,3-DMB to neo-hexane is the rate controlling step.

With these assumptions, we can eliminate rate constants k_{1r} through k_{3r} and k_{1f} through k_{3f}. Reaction coordinates can be used to solve for the equilibrium mole fractions of n-hexane, 3-MP and 2-MP.

Numerical Approach

Computer-implemented numerical methods are now commonly used for solving system of ordinary differential equations. In order to calculate the equilibrium mole fraction of n-C_6, 3-MP, 2-MP, and 2,3-DMB, three linear simultaneous equations were required to solve for the reaction coordinates. A numerical method was used to solve these equations, followed by a fourth order Runge-Kutta method to approximate the two ordinary differential equations (equations (3-5) and (3-8)). The detailed approach will be discussed in the following chapter.

Design Equations for a CSTCR

Another approach uses a Continuously Stirred Tank Catalytic Reactor (CSTCR) to carry out the isomerization. Carberry (17) introduced this type of reactor, which consists of a rotating basket of catalyst particles. This reactor also accommodates commercial-size pellets and extruded catalysts. Levenspiel (30) also refers to this kind of catalytic reactor as a basket-type mixed reactor.

In the theory of continuous stirred tank reactors, an important basic assumption is that the contents of the tank are well mixed (32). This means that the compositions in the tank are everywhere uniform and that the product stream leaving the tank has the same composition as the mixture within the tank.

Derivation of Mass Balance Equation

Assume the following hypothetical reaction occurs in a CSTCR

$$A \underset{k_r}{\overset{k_f}{\longleftrightarrow}} B$$

where

k_f = forward rate constant

k_r = reverse rate constant

A CSTCR is used for this reaction system. The volumetric feed to the reactor is Q, the catalyst weight W, and the total flow rate is Fto. Since a CSTCR is designed to operate at steady-state, a steady-state mole balance defines the performance of the system. The following mole balance can be constructed:

	OUT	=	IN	+	GENERATION	-	CONSUMPTION
(component A)	$C_A Q$	=	$C_{Ao} Q$	+	$R_r W$	-	$R_f W$
(component B)	$C_B Q$	=	$C_{Bo} Q$	+	$R_f W$	-	$R_r W$

Assuming simple first order reaction,

$R_f = k_f C_A$

$R_k = k_r C_B$

Substituting the rate expressions and rearranging results in the following set of linear equations:

$$F_1 = -C_A + C_{Ao} + \frac{W}{Q} (k_r C_B - k_f C_A) = 0 \tag{3-10}$$

$$F_2 = -C_B + C_{BO} + \frac{W}{Q} (k_f C_A - k_r C_B) = 0 \qquad (3\text{-}11)$$

Note that the only unknowns are C_A and C_B. These equations can be solved using Newton's method and the final concentrations of C_A and C_B can be calculated.

The performance equation of a mixed reactor can then be utilized to calculate the conversion. It appears below:

$$\frac{W}{F_{AO}} = \frac{X_{AOUT}}{-R'_{AOUT}} \qquad (3\text{-}12)$$

where

F_{AO} = the molar flow rate of species i, kgmole/hr

X_{AOUT} = conversion of reactant

R'_{AOUT} = reaction rate, kgmole/(kg of cat -hr)

W = weight of catalyst, kg

Equation (3-12) is derived by Levenspiel (30).

Derivation of Energy Balance Equation

Consider a mixed flow reactor, in which conversion is X_A, and T_1 is the a temperature on which the enthalpies and heats of reactions are based.

enthalpy of entering feed:

$H'_1 = Cp'(T_1 - T_1) = 0$

enthalpy of leaving system:

$H''_2 X_A + H'_2(1-X_A) = Cp''(T_2-T_1)X_A + Cp'(T_2-T_1)(1-X_A)$

energy released by reaction:

$\Delta H_{R1} X_A$ at T_1

At steady state the energy balance is:

input = output + accumulation + released by reaction

or,

$$0 = [\ Cp''(T_2 - T_1)X_A + Cp'(T_2 - T_1)(1 - X_A)\ ] + \Delta H_{R1} X_A$$

rearranging,

$$\begin{aligned} 0 &= (Cp''T_2 - Cp''T_1)X_A + Cp'(T_2 - T_1 - T_2X_A + T_1X_A) + \Delta H_{R1}X_A \\ &= X_A Cp''T_2 - X_A Cp''T_1 + Cp'T_2 - Cp'T_1 - Cp'T_2X_A \\ &\quad + Cp'T_1X_A + \Delta H_{R1}X_A \\ &= T_2\ (X_A Cp'' + Cp' - Cp'X_A) - X_A Cp''T_1 - Cp'T_1 + Cp'T_1X_A \\ &\quad + \Delta H_{R1}X_A \end{aligned}$$

$$T_2 = \frac{-\Delta H_{R1}X_A + T_1(Cp''X_A + Cp' - Cp'X_A)}{Cp''X_A + Cp' - Cp'X_A} \qquad (3\text{-}13)$$

where subscripts 1,2 refer to temperatures of entering and leaving streams and,

Cp', Cp'' = mean specific heat of unreacted feed stream and of completely converted product stream per kgmole of entering reactant A.

H', H'' = enthalpy of unreacted feed stream and of completely converted product stream per kgmole of entering reactant A.

ΔH_R = heat of reaction per kgmole of entering reactant A.

Equations (3-12) and (3-13) are the two basic equations which will be used for modeling a CSTCR.

Model Simulation

For the CSTCR it was also assumed that the model proposed by Cull and Brenner (12) was valid and the assumptions made previously were still valid.

Numerical Approach

A program for simulating CSTCR performance called "HEXCR" was written in the FORTRAN language. Newton's method was applied to solve two linear equations containing two unknowns. The detailed procedures will be discussed in the next chapter.

CHAPTER IV

PROGRAM DESCRIPTIONS AND TESTING

The main purpose of this research is to simulate chemical reactions in a fixed bed reactor and a CSTCR. HEXFI and HEXCR are the names of programs developed for simulating the fixed-bed reactor and the CSTCR, respectively. The HEXFI program offers users two kinds of simulation, one is optimized model, the other is fixed-length model. The optimized model calculates the equilibrium mole fractions of hexane isomers at specified condition and outputs the required reactor length. However, in the fixed-length model, it calculates mole fractions at specified reactor length. Both programs provide users the option to simulate isothermal or adiabatic operation. Both models allow users to see the effects of changing the reactor operating conditions, such as temperature, pressure, catalyst weight, etc.. All models were using the FORTRAN language.

Software Applied

In order to simulate real control panels in the chemical industry, IBM software (EZVU) was used. This software can create panels which connect design variables and users together. Users can easily manipulate different operating conditions from the panels and outputs will be shown on the panels simultaneously. This software is very user friendly to the persons who are undertaking simulations.

Program Organization and Subroutine Descriptions

Figures 4,5 show the FORTRAN flow diagrams for the fixed-bed and the CSTCR, respectively. A short description of the program subroutines follows.

Fixed-Bed Reactor

DATAN

This subroutine is used in HEXFI and HEXCR. The function of DATAN is to defined stoichiometric coefficients, feed conditions, and it is called at the beginning of each simulation run.

ARRAY

Subroutine ARRAY also appears in both HEXFI and HEXCR. It calculates the heat capacities of each isomer, the heats of reactions, and the Gibbs free energies of reactions at T K. Heat capacities and Gibbs free energies can be expressed as polynomials in terms of temperature. Table III and IV which appear on the next pages are the data sources. A Cubic Spline polynomial approximation was applied to

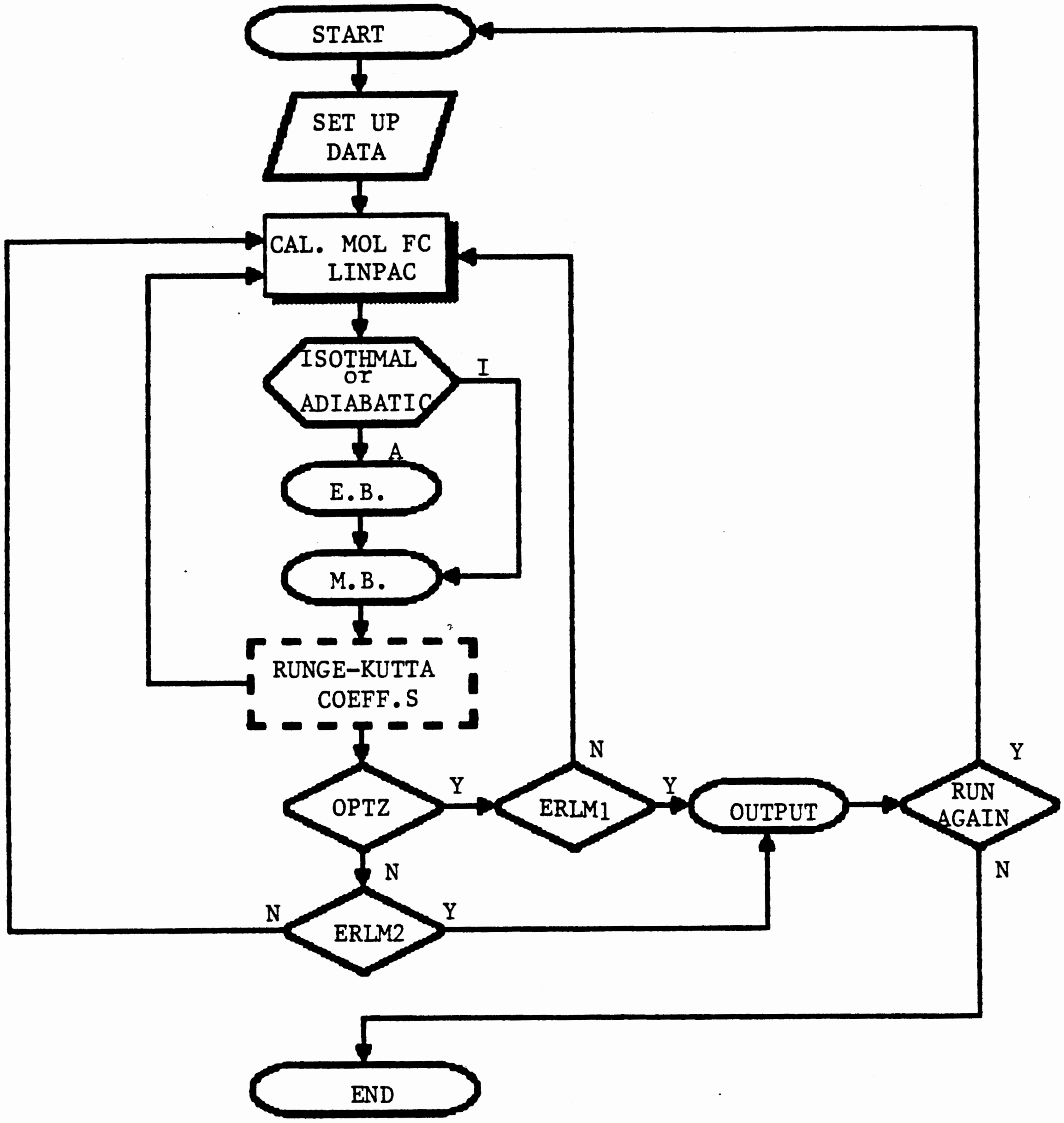


Figure 4. Program Organization of HEXFI

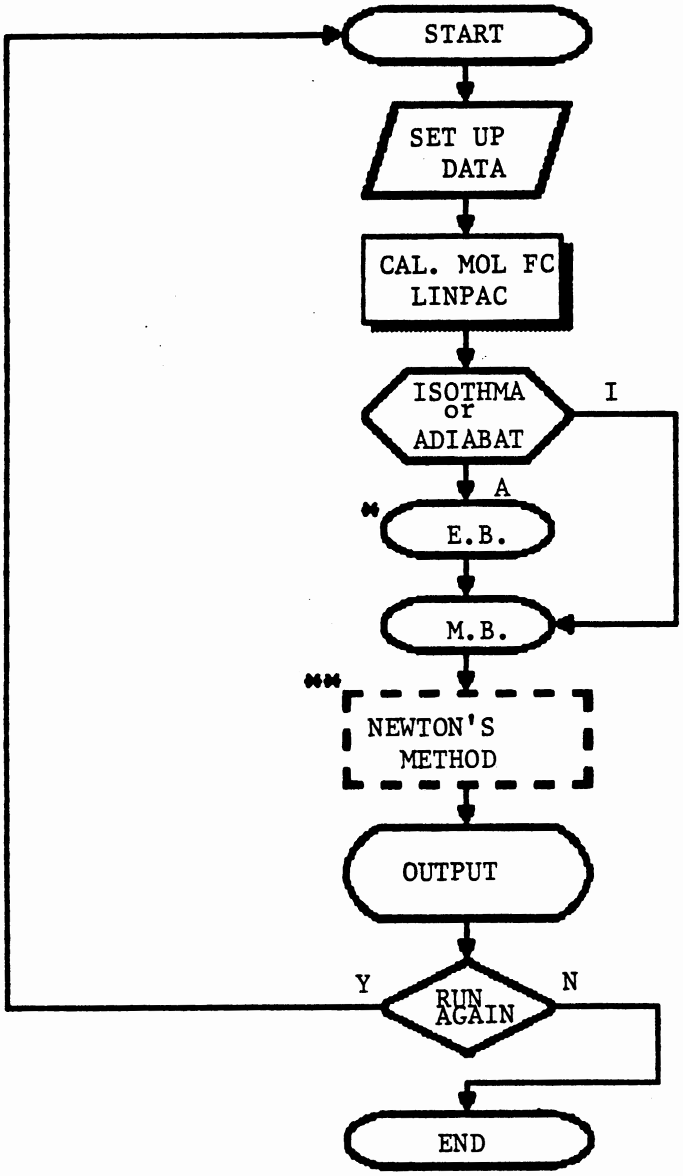


Figure 5a. Program Organization of HEXCR

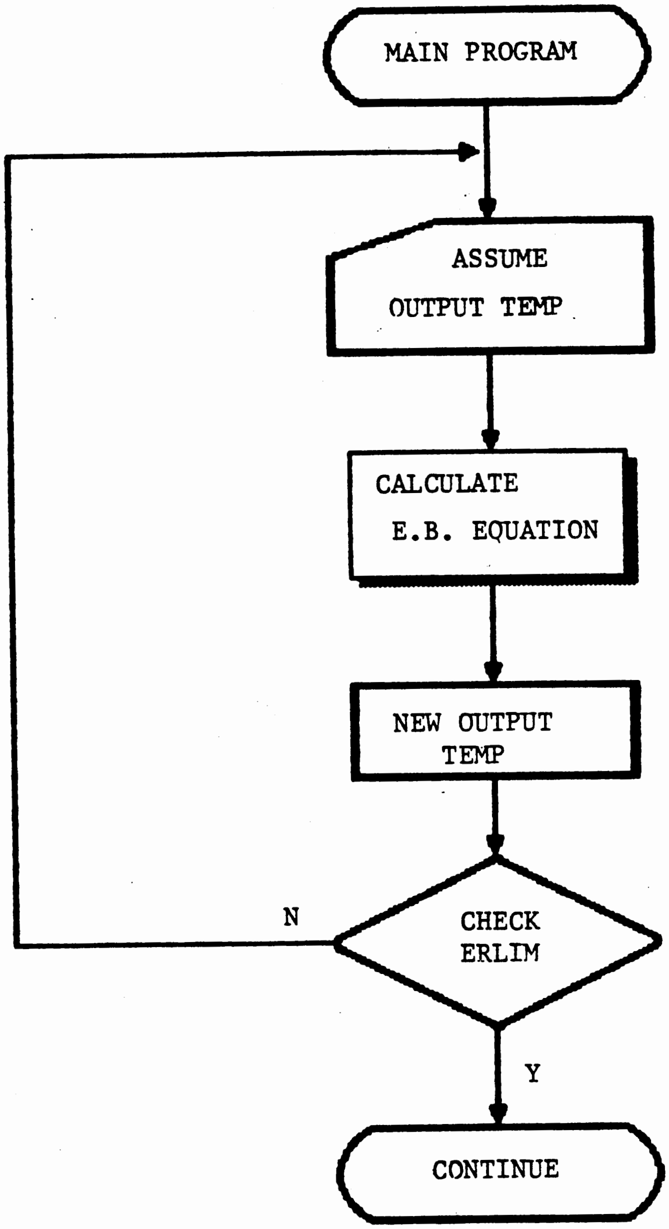


Figure 5b. Program Organization of Energy Balance

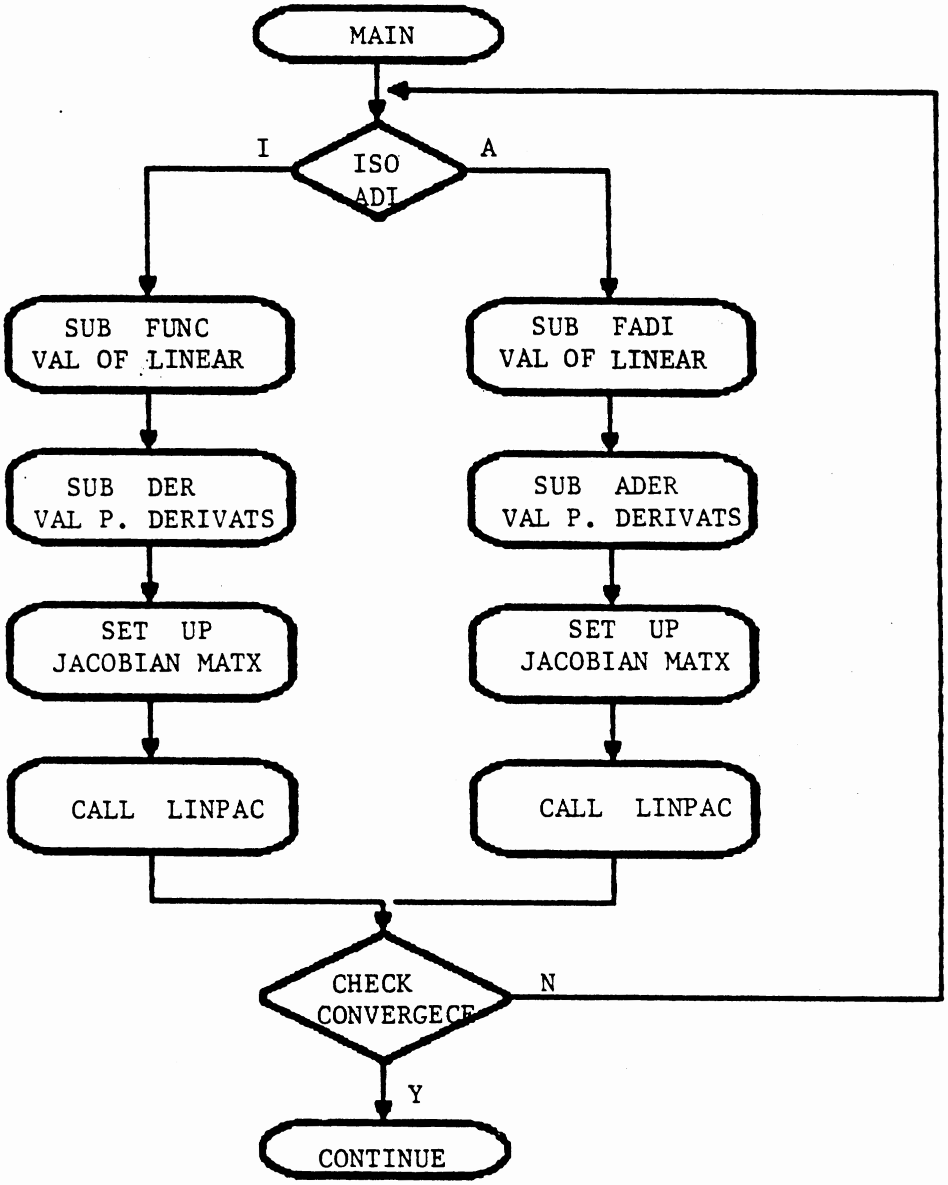


Figure 5c. Program Organization of Newton's Method

*TABLE III

HEAT CAPACITY FOR THE IDEAL GAS STATE

Compound Name	Temperature in K						
	298.15	400	500	600	700	800	1000
	Heat Capacity $Cp^{\circ}(T)$ in $J\ K^{-1}\ mol^{-1}$						
n-Hexane	142.59	181.54	217.28	248.11	274.05	296.23	331.37
[a]2-M.P.	142.21	183.51	219.83	251.04	277.40	300.41	337.23
[b]3-M.P.	140.12	181.17	217.48	248.95	275.73	298.74	335.98
[c]2,2-DMB	141.46	183.13	220.33	253.13	281.58	306.69	348.11
[d]2,3-DMB	139.41	181.71	218.36	250.20	277.40	301.67	340.58

[a] 2-methylpantane
[b] 3-methylpantane
[c] 2,2-dimethylbutane
[d] 2,3-dimethylbutane

*TRC TABLE (1985)

*TABLE IV

GIBBS ENERGY OF FORMATION FOR IDEAL GAS STATE

Compound Name	Temperature in K						
	298.15	400	500	600	700	800	1000
	Gibbs Energy of Formation $\Delta G(T)$, in KJ mol^{-1}						
n-Hexane	0.15	58.87	118.96	180.51	243.15	306.28	433.73
[a] 2-M.P.	-5.14	54.42	115.20	177.52	241.25	304.56	433.09
[b] 3-M.P.	-3.17	56.15	116.88	179.14	242.25	305.71	434.67
[c] 2,2-DMB	-8.52	53.30	116.41	180.99	246.28	312.59	445.06
[d] 2,3-DMB	-2.90	58.21	120.61	184.56	249.47	314.70	446.49

[a] 2-methylpentane
[b] 3-methylpentane
[c] 2,2-dimethylbutane
[d] 2,3-dimethylbutane

*TRC TABLE (1985)

fit the data. Heat capacities and the Gibbs free energies at any specified temperature can then be easily approximated. Function CP and function GF are included in this subroutine predict these values. To reduced program execution time, ninety points between 298 and 1000 K were to evaluate heat capacities and Gibbs free energies and the data was stored in vector form. Therefore, in order to predict the heat capacities and the Gibbs free energies at any temperatures, subroutine PROP was used to look up a pre-calculated value.

FNC

Subroutine FNC is the heart of HEXFI and it includes several additional subroutines. Basically, it contains two differential equations (O.D.E.s). One is the mass balance equation, the other is the energy balance equation. In order to evaluate these two equations, it also needs to call additional subroutines. These subroutines are PROP, EQCON, SLTRES, RXN. These subroutines have different functions to calculate the terms appearing in the differential equations. After finishing calculations, this subroutine will transfer the values of the two differential equations to the main program and use the Runge-Kutta method to evaluate the function values.

PROP

Subroutine PROP calculates the heats of reactions, heat capacities and Gibbs free energies at any temperatures between 298 and 1000 K. As mentioned previously in subroutine ARRAY, ninety points were calculated by Cubic Spline approximation in terms of temperature. Other points between any two known points were evaluated by linear interpolation.

EQCON

Subroutine EQCON handles the calculation of equilibrium constants and forward and reverse rate constants. From subroutine PROP, we can get Gibbs free energies of each isomers at specified temperatures. Then the following equations applied:

$$\Delta G_R{}^\circ = -R_g T \ln K$$

$$\ln K = \frac{-\Delta G_R{}^\circ}{R_g T}$$

$$K = \exp\left(\frac{-\Delta G_R{}^\circ}{R_g T}\right)$$

where

R_g = gas constant, 8.314 kj/kgmole-K

T = temperature, K

$\Delta G_R{}^\circ$ = standard Gibbs free energy, kj/kgmole

Equilibrium constants for all the reactions in the mechanism can be evaluated.

By definition, the equilibrium constant is the ratio of forward rate constant to reverse rate constant. That is:

$$K = \frac{k_f}{k_r}$$

or,

$$k_f = K * k_r$$

where

k_r = reverse rate constant, $m^3/(kg\ of\ cat\ -hr)$

k_f = forward rate constant, $m^3/(kg\ of\ cat\ -hr)$

The reverse rate constant it is always expressed in Arrhenius form:

$$k = k_0 \exp\left(- \frac{E}{R_g T} \right)$$

where

E = activation energy, kj/kgmole-K

k_0 = frequency factor

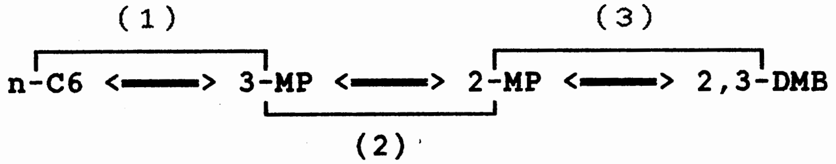
R_g = gas constant, 8.314 kj/kgmole-K

T = temperature, K

If the reverse rate constant has been determined from experimental data, the forward rate constant is fixed.

SLTRES

Subroutine SLTRES calculates the thermodynamic equilibrium mole fractions of the following reactions:



Assume the reaction coordinates for the first, second and third reactions are ϵ_{I}, ϵ_{II}, ϵ_{III}, respectively. For example, assume the initial feed compositions is 50% n-hexane and 50% 3-MP. Nauman (17) proposed an equation to solve reaction coordinates; i.e.,

$$N - N_0 = \mu\, \epsilon \tag{4-1}$$

where N and N_0 are vectors (N*1 matrices) giving the final and initial number of moles of each component, μ is the matrix of stoichiometric coefficients, and ϵ is the reaction coordinate vector (M*1 matrix). In more explicit form,

$$\begin{bmatrix} N_A \\ \cdot \\ \cdot \\ \cdot \end{bmatrix} - \begin{bmatrix} N_A \\ \cdot \\ \cdot \\ \cdot \end{bmatrix}_0 = \begin{bmatrix} \mu_{A,I} & \mu_{A,II} & \cdots \\ \mu_{B,I} & \mu_{B,II} & \\ \cdot & \cdot & \\ \cdot & \cdot & \\ \cdot & \cdot & \end{bmatrix} \begin{bmatrix} \epsilon_{I} \\ \epsilon_{II} \\ \cdot \\ \cdot \\ \cdot \end{bmatrix}$$

converting equation (4-1) into our case, it has the following form:

$$\begin{bmatrix} n\text{-}C_6 \\ 3\text{-MP} \\ 2\text{-MP} \\ 2,3\text{-DMB} \end{bmatrix} - \begin{bmatrix} 0.5 \\ 0.5 \\ 0.0 \\ 0.0 \end{bmatrix} + \begin{bmatrix} -1 & 0 & 0 \\ 1 & -1 & 0 \\ 0 & 1 & -1 \\ 0 & 0 & 1 \end{bmatrix} + \begin{bmatrix} \epsilon_{I} \\ \epsilon_{II} \\ \epsilon_{III} \end{bmatrix}$$

or

$N_{n-C6} = 0.5 - \epsilon_I$

$N_{3-MP} = 0.5 + \epsilon_I - \epsilon_{II}$

$N_{2-MP} = 0.0 + \epsilon_{II} - \epsilon_{III}$

$N_{2,3-DMB} = 0.0 + \epsilon_{III}$

Using equilibrium constants to solve reaction coordinates for reaction I, it becomes:

$$K_1 = \frac{(0.5 + \epsilon_I - \epsilon_{II}) * P_T}{(0.5 - \epsilon_I) * P_T} \qquad (4\text{-}2)$$

for reaction II, it becomes:

$$K_2 = \frac{(\epsilon_{II} - \epsilon_{III}) * P_T}{(0.5 + \epsilon_I + \epsilon_{II}) * P_T} \qquad (4\text{-}3)$$

for reaction III, it becomes:

$$K_3 = \frac{(\epsilon_{III} + 0.0) * P_T}{(\epsilon_{II} - \epsilon_{III}) * P_T} \qquad (4\text{-}4)$$

From subroutine EQCON, we have evaluated equilibrium constants K_1, K_2, K_3. Hence, equations (4-2), (4-3) and (4-4) will turn out to be three simultaneous equations with three unknowns ϵ_I, ϵ_{II} and ϵ_{III}. Subroutine LINPAC then solves handle these equations for specified condition.

RXN

Subroutine RXN calculates the globe rate of the final reaction.

$$2,3\text{-DMB} \underset{k_r}{\overset{k_f}{\Longleftrightarrow}} 2,2\text{-DMB}$$

$$\text{Rate}_{2,2\text{-DMB}} = k_f * C_{2,3\text{-DMB}} - k_r * C_{2,2\text{-DMB}}$$

When the rate is determined it is substituted into equations (3-5) and (3-8) for calculating the value of the two differential equations.

LINPAC

This subroutine was written by individuals at Argonne National Laboratory. It uses partial pivoting and matrix decomposition with Gaussian elimination to very efficiently solve large sets of linear equations (33).

CSTCR

NEWTN

Subroutine Newtn is one of the biggest difference when comparing CSTCR with the fixed-bed design. This subroutine employs Newton's method in order to solve a set of two linear equations containing two unknowns. It includes subroutines DER, FUNC, ADER and FADI. First of all, let me explain its algorithm and all the functions of the subroutines.

The algorithm for this case is a two-dimensional problem and may be represented as simultaneous solution of the following equations:

$$\left.\frac{\partial f_1(\mathbf{X})}{\partial x_1}\right|_{\mathbf{x}^{(j)}} d_1^{(j)} + \left.\frac{\partial f_1(\mathbf{X})}{\partial x_2}\right|_{\mathbf{x}^{(j)}} d_2^{(j)} + f_1(\mathbf{x}^{(j)}) = 0$$

$$\left.\frac{\partial f_2(\mathbf{X})}{\partial x_1}\right|_{\mathbf{x}^{(j)}} d_1^{(j)} + \left.\frac{\partial f_2(\mathbf{X})}{\partial x_2}\right|_{\mathbf{x}^{(j)}} d_2^{(j)} + f_2(\mathbf{x}^{(j)}) = 0$$

where

$$x_1^{(j+1)} = x_1^{(j)} + d_1^{(j)}$$

and

$$x_2^{(j+1)} = x_2^{(j)} + d_2^{(j)}$$

Note that the superscript (j) or (j+1) indicates the number of linear approximations that have been used in searching for the roots. The coefficient matrix for this system of two linear equations contains all the possible combinations of partial derivatives of functions, $f_k(\mathbf{x})$, with respect to each independent variable, x_i. This coefficient matrix is called the **Jacobian matrix**. For the isothermal case, the two linear equations are equations (3-10) and (3-11). Hence, the partial derivatives of these two equations are:

$$\frac{\partial f_1}{\partial C_A} = -1 - \frac{W}{Q} k_f$$

$$\frac{\partial f_1}{\partial C_B} = k_r \frac{W}{Q}$$

$$\frac{\partial f_2}{\partial C_A} = k_f \frac{W}{Q}$$

$$\frac{\partial f_2}{\partial C_B} = -1 - \frac{W}{Q} k_r$$

the above equations are inputed in subroutine DER.

ENGBALS

Subroutine ENGBALS performs the energy balance in a CSTCR. The energy balance equations are constructed for the following reactions:

$$n\text{-}C_6 \Longleftrightarrow 3\text{-MP} \Longleftrightarrow 2\text{-MP} \Longleftrightarrow 2,3\text{-MP}$$

As I mentioned previously, it was assumed to reach thermodynamic equilibrium very fast. So the energy balance equations are:

$$\underline{\text{INPUT}} = \underline{\text{OUTPUT}} + \underline{\text{ACCUMULATION}} + \underline{\text{DISAPPEARANCE}}$$

The reference temperature was picked to be the same as the feed temperature.

input term:

$$Fto * \Sigma\ [YI(i) * Cp(i) * (T_0 - T_0)] = 0$$

energy released by reaction:

$$Fto * \Sigma\ [EXC(i) * \Delta H(i)]$$

output term:

assuming an output temperature of T_1, the equation becomes:

$$Fto * \Sigma\ \{YF(i) * Cp(i) * (T_1 - T_0)\}$$

Replacing these quantities in the energy balance gives,

$$\begin{aligned} &\Sigma\ \{YF(i) * Cp(i) * (T_1 - T_0)\} \\ = &- \Sigma\ [EXC(i) * \Delta H(i)] \end{aligned} \tag{4-5}$$

In the above equation, T_0, EXC(i) and also dH(i), Cp(i) are function of temperature. In order to satisfy both sides in equation (4-5), a trial and error method is applied to find the temperature T_1. Another energy balance for the final reaction is then required.

$$\underset{(I)}{\text{2,3-DMB}} \quad \Longleftrightarrow \quad \underset{(II)}{\text{2,2-DMB}}$$

$$\begin{array}{lccccccccl} & \underline{\text{OUT}} & = & \underline{\text{IN}} & + & \underline{\text{GENERATION}} & - & \underline{\text{CONSUMPTION}} & \\ (I) & H_2 C_I Q & = & H_1 C_{I0} Q & + & H_2 R_r W & - & H_2 R_f W & (a) \\ (II) & H'_2 C_{II} Q & = & H'_1 C_{II0} Q & + & H'_2 R_f W & - & H'_2 R_r W & (b) \end{array}$$

converting (a) and (b) into the following set of linear equations:

$$f_1 = -H_2 C_I + H_1 C_{I0} + \frac{W}{Q} (H_2 R_r - H_2 R_f) = 0 \tag{c}$$

$$f_2 = -H'_2 C_{II} + H'_1 C_{II0} + \frac{W}{Q} (H'_2 R_f - H'_2 R_r) = 0 \tag{d}$$

Substituting the rate expressions into (c) and (d) and taking derivatives of each equations with respect to each variable is done in subroutine FADI.

$$\frac{\partial f_1}{\partial C_I} = -H_2 - \frac{W}{Q} (H_2 k_f) \tag{4-6}$$

$$\frac{\partial f_1}{\partial C_{II}} = \frac{W}{Q} (H_2 k_r) \tag{4-7}$$

$$\frac{\partial f_2}{\partial C_I} = \frac{W}{Q} (H'_2 k_f) \tag{4-8}$$

$$\frac{\partial f_2}{\partial C_{II}} = -H'_2 - \frac{W}{Q} (H'_2 k_r) \tag{4-9}$$

Equations (4-6) to (4-9) are the coefficients of Jocobian matrix for adiabatic case. After setting up the Jocobian matrix, we can apply LINPAC to solve for the roots (i.e., concentrations at some temperature).

THEQ

Subroutine THEQ is similar to subroutine FNC in HEXFI. It also contains several subroutines, such as PROP, EQCON, SLTRES and ENGBALS. The main difference between THEQ and FNC is the subroutine ENGBALS. However, the basic function of this subroutine are similar to what was calculated in FNC.

Testing and Results

Overview

The programs developed in this study were tested using the model proposed by Cull and Brenner (12). However, their experimental data was based on results from data in a batch reactor and were not suitable verification use. Other literature, listed in references did not supply parameters and constants related to their experiments. Because of the above reasons, it was impossible to proceed using this data. Finally, a copy of operating data from a proprietary source was obtained and this data was used to validate the model. The results of the numerical solutions are close to the proprietary data.

Testing

In industry, there are several isomerization processes licensed by the Pure Oil Company, British Petroleum and Phillips Petroleum Company. Generally speaking, their operating conditions are:

1. isothermal reaction
2. LHSV = 1 - 20
3. reactor charge = 3000 barrels per stream day, (bpsd)
4. bulk density of catalyst = 40 lb/ft^3
5. hydrogen-to-hydrocarbon ratio = 2 : 1

Basically, HEXFI was designed for industrial simulation. However, adiabatic operation was added in this study to compare the benefits and shortcomings of each. Another option supplied allows users to select one of two objective functions, optimized or fixed-length models. A few examples are shown below to demonstrate design. Units used in HEXFI were all converted into the metric system.

Control panels of some cases are all listing in Appendix C.

Optimized Model

Figures 18 and 19 in Appendix C show the control panels for fixed-bed reactor design. Original inputs were set to be zero. The following operating conditions were then used as inputs:

Case I

1. isothermal reaction
2. flow rate = 153.5 kgmole/hr
3. feed temperature = 408 K
4. system pressure = 35 ATM
5. tube diameter = 0.05 m
6. number of tubes = 150
7. bulk density of the catalyst = 640 kg/m^3
8. opz = 'Y'
9. pure n-hexane as feedstock

The final results from the computer monitor are shown in Figures 20 and 21 in Appendix C. Figure 6 shows that hexane isomers mole fraction distributions with respect to reactor length. From this figure, it is evident that if the reaction reaches equilibrium conditions, it needs 12.1 m of reactor length. Comparison of the simulation outputs with the proprietary source, shows that both sets of data have similar trends. The equilibrium prediction from HEXFI model for final mole percent of neo-hexane is 37.69 % which is very close to the experimental value of 36.25 %.

Case II

operating conditions:

1. system pressure = 61 ATM
2. other factors are the same as Case I

For this case the pressure was increased to 61 atm and results are shown in Figure 7. The equilibrium value from the proprietary data for neo-hexane is 36.25 % which is close to the model prediction of 37.69 %. Comparing flow trends of both sets of data shows that the simulation curves closely resemble the experimental curves. From Case I and II, we find that pressure effect does not influence the mole fraction of neo-hexane. Slightly lower temperature cases were also tested and shown in Figures 8 and 9. The results are summaried in Table V. From this table, it can be summaried that higher temperatures do not favor isomerization reaction.

Besides the isothermal reaction, HEXFI can also simulate adiabatic reactors. Case III is a typical case of adiabatic operations.

Case III

operating conditions:

1. adiabatic reaction
2. other factors are the same as Case I

Results are shown in Figure 10. Comparing Case III

TABLE V

RESULTS OF THE COMPARISON OF EXPERIMENTAL DATA WITH MODEL PREDICTIONS FOR AN ISOTHERMAL FIXED-BED REACTOR

CASE NO.	T (K)	P (ATM)	MODEL PREDICTION[1]	EXPERIMENTAL DATA
1.	408.0	35.0	37.69 %	36.25 %
2.	408.0	61.0	37.69 %	36.05 %
3.	366.5	35.0	46.84 %	42.75 %
4.	366.5	61.0	46.84 %	41.25 %

1. product mole percentage of neo-Hexane

with Case I, we notice that the adiabatic reactor has a lower 2,2-DMB formation than that of the isothermal reactor. This is because hexane isomerization equilibrium is favored at lower temperatures.

Other adiabatic conditions were also tested and are plotted in Figures 11 - 13. From these figures, it can be concluded that although adiabatic reactors give lower mole fractions of 2,2-DMB, they also require a shorter reactor length than for isothermal conditions. In general the initial cost for building an adiabatic reactor is less than that required to build an isothermal reactor. Furthermore, Figure 14 through 17 show the difference in temperature profiles inside a reactor during adiabatic operation. At the beginning of the reactors, the slopes of the curves are quite steep. This means that the reactions release a large amount of heat. After some reactor length, reactions gradually approach equilibrium and then the temperatures remain constant.

Fixed-Length Model

In addition to the optimized-model, HEXFI can also simulate a Fixed-Length reactor. The reason for this model is sometimes room is available to build a long reactor or information is required to know the conversion of a reactor of specified length.

Case IV

1. specified reactor length = 3.0 m

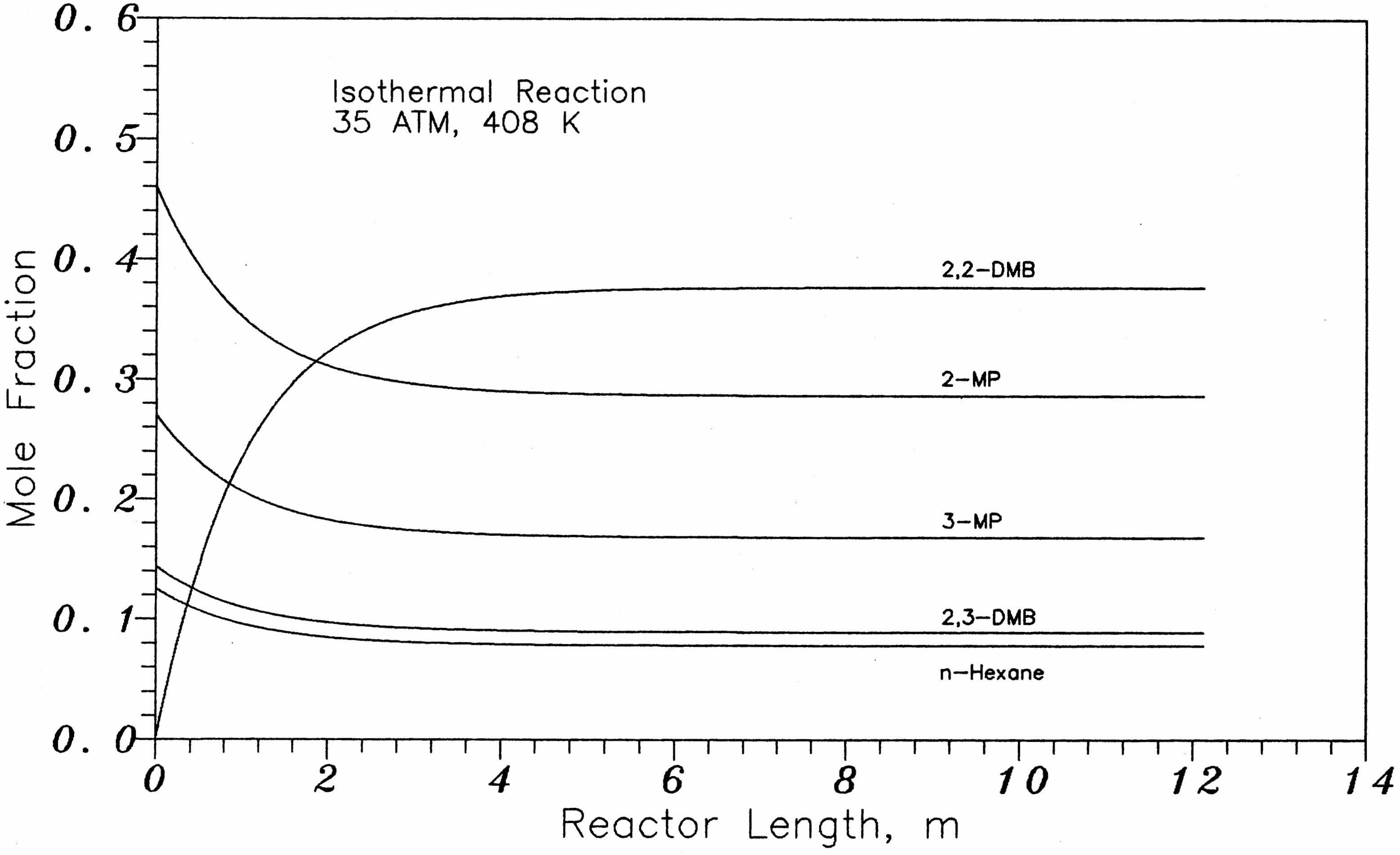


Figure 6. Mole Fraction Distributions of Hexane Isomerization

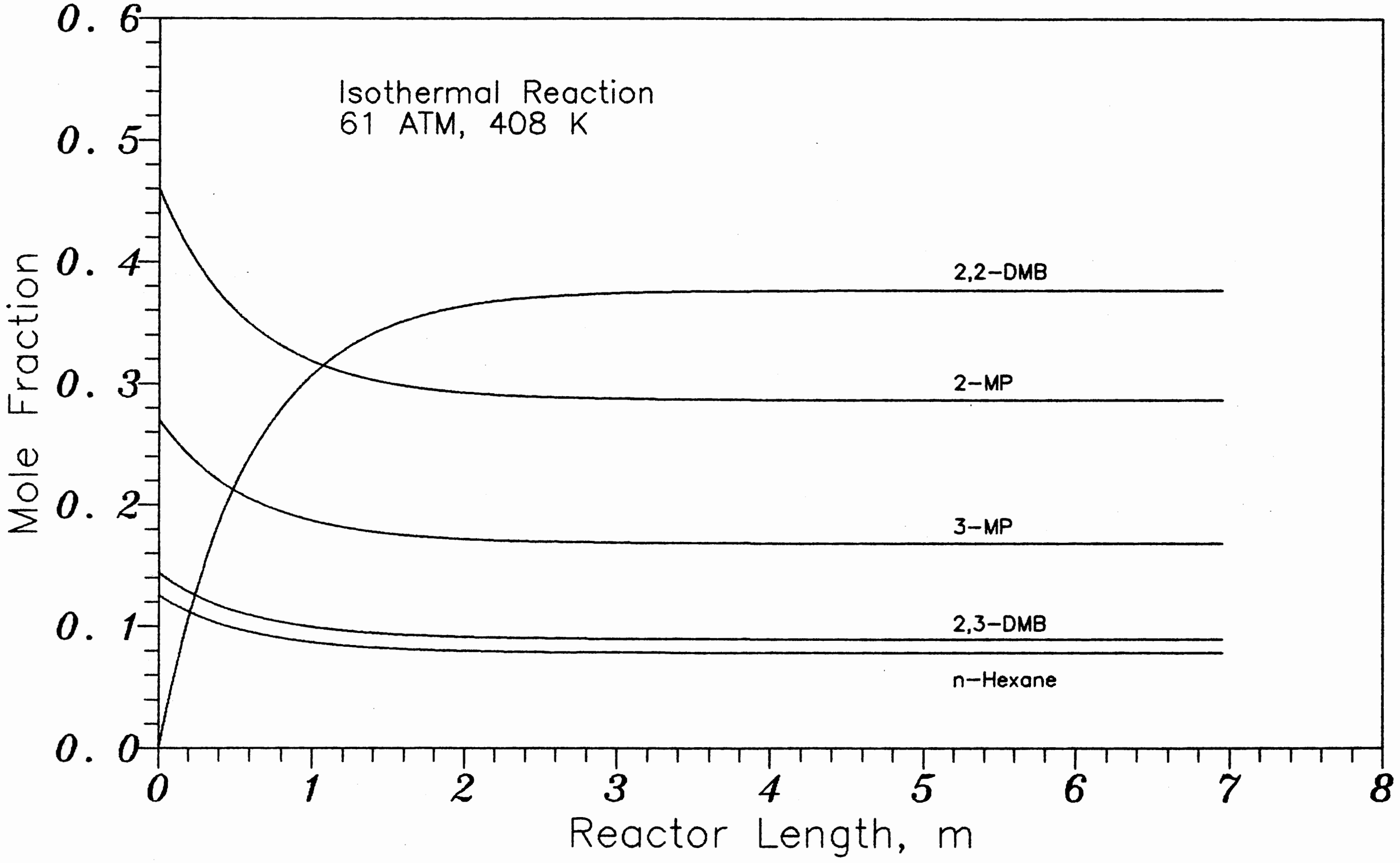


Figure 7. Mole Fraction Distributions of Hexane Isomerization

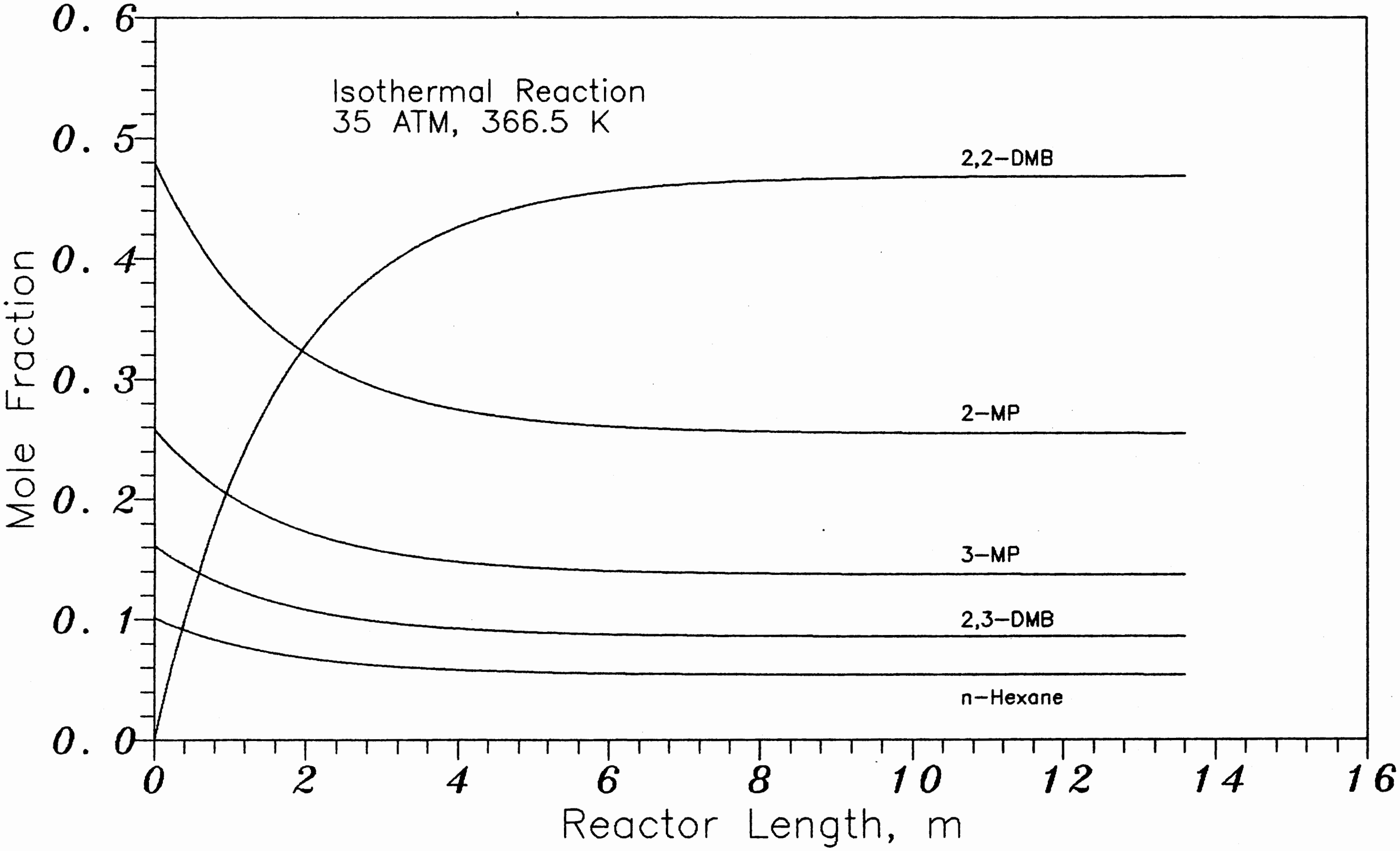


Figure 8. Mole Fraction Distributions of Hexane Isomerization

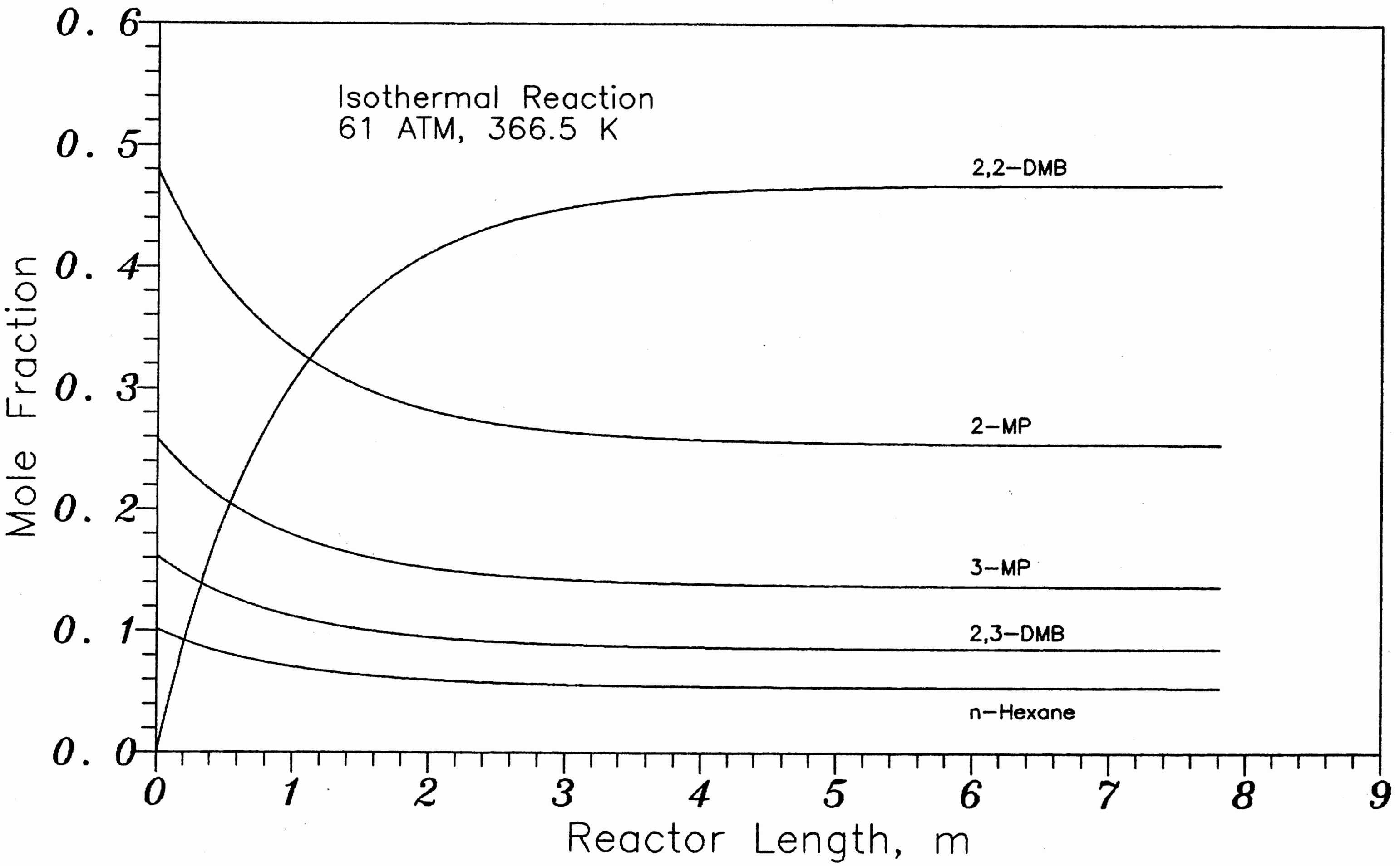


Figure 9. Mole Fraction Distributions of Hexane Isomerization

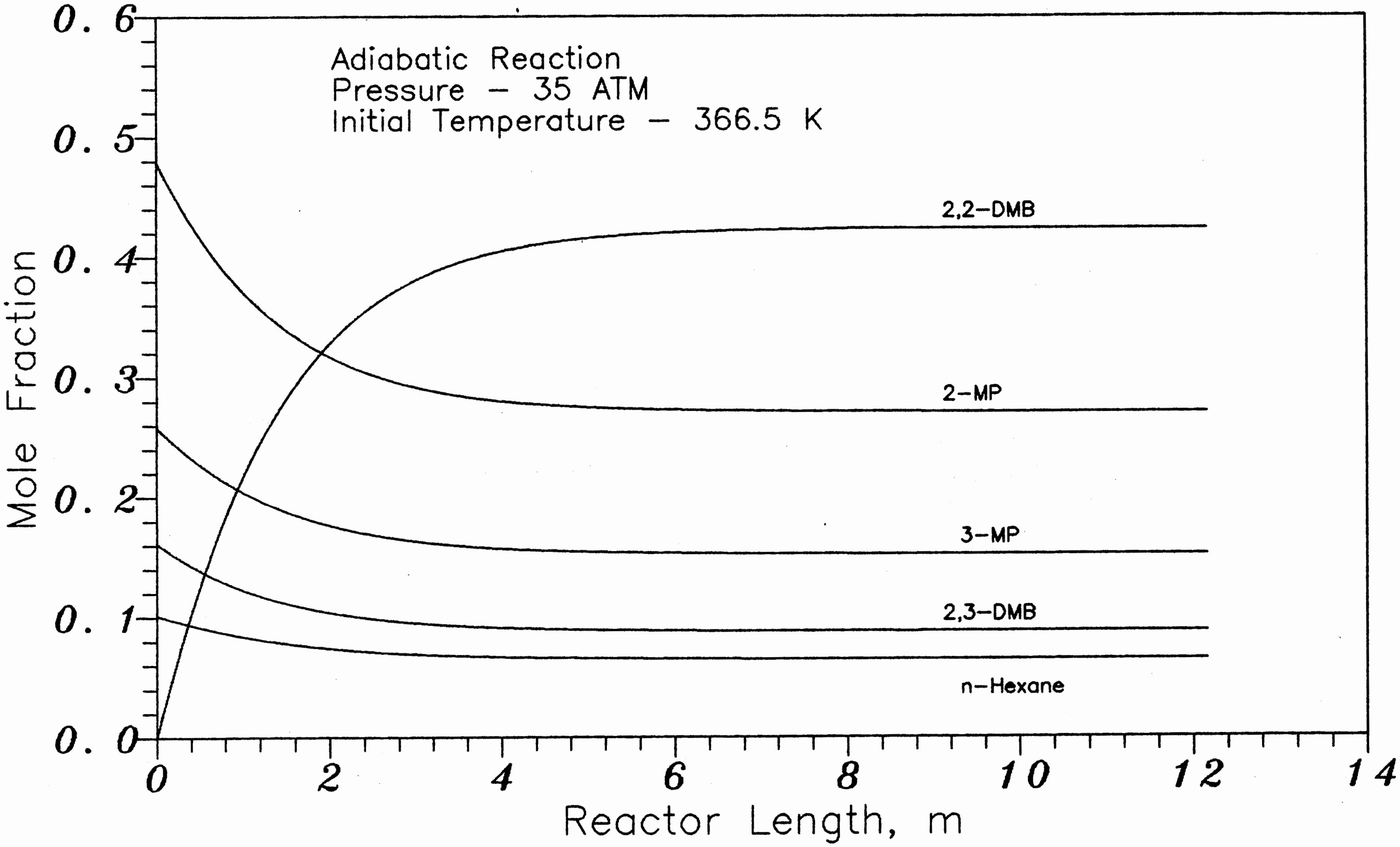


Figure 10. Mole Fraction Distributions of Hexane Isomerization

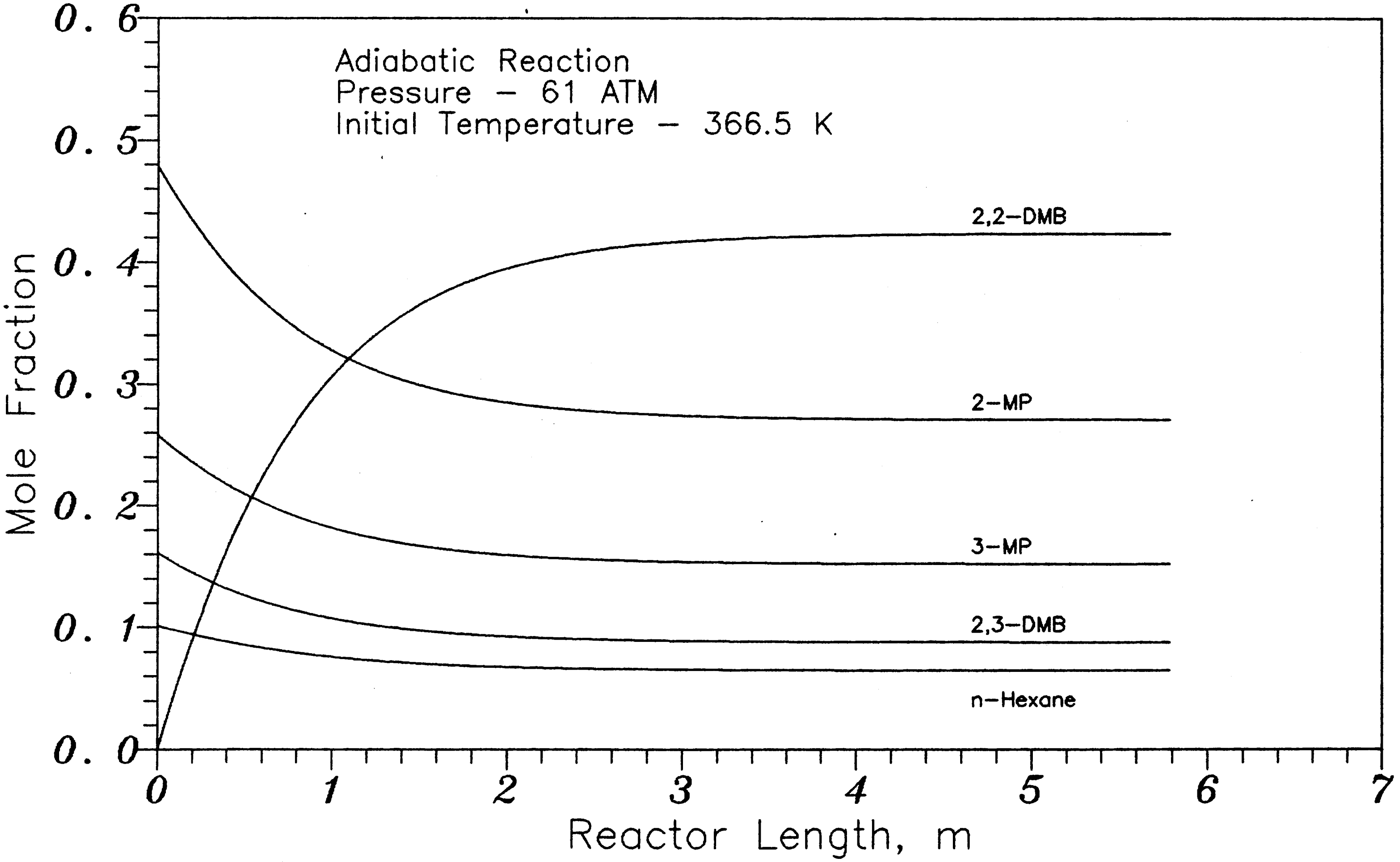


Figure 11. Mole Fraction Distributions of Hexane Isomerization

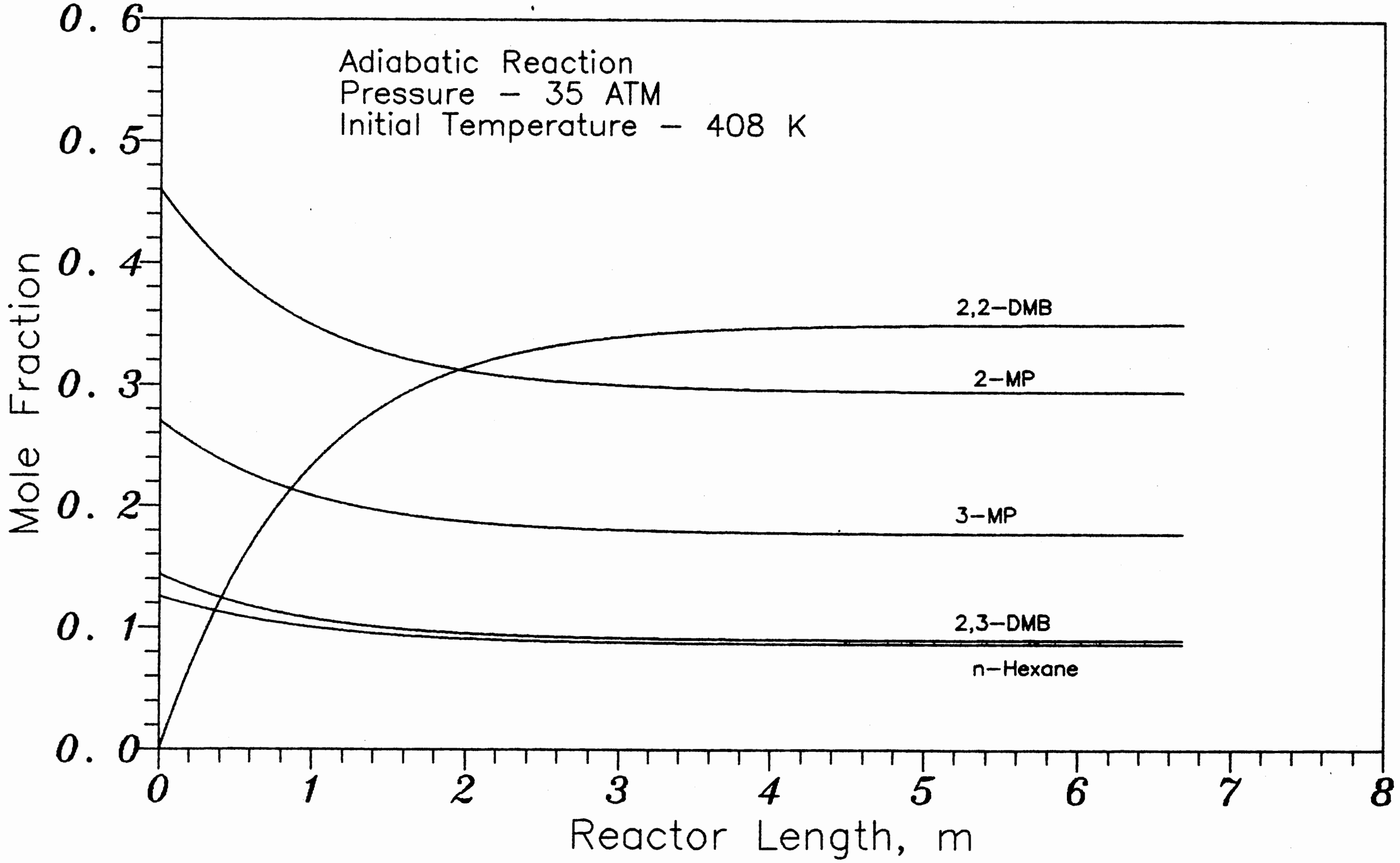


Figure 12. Mole Fraction Distributions of Hexane Isomerization

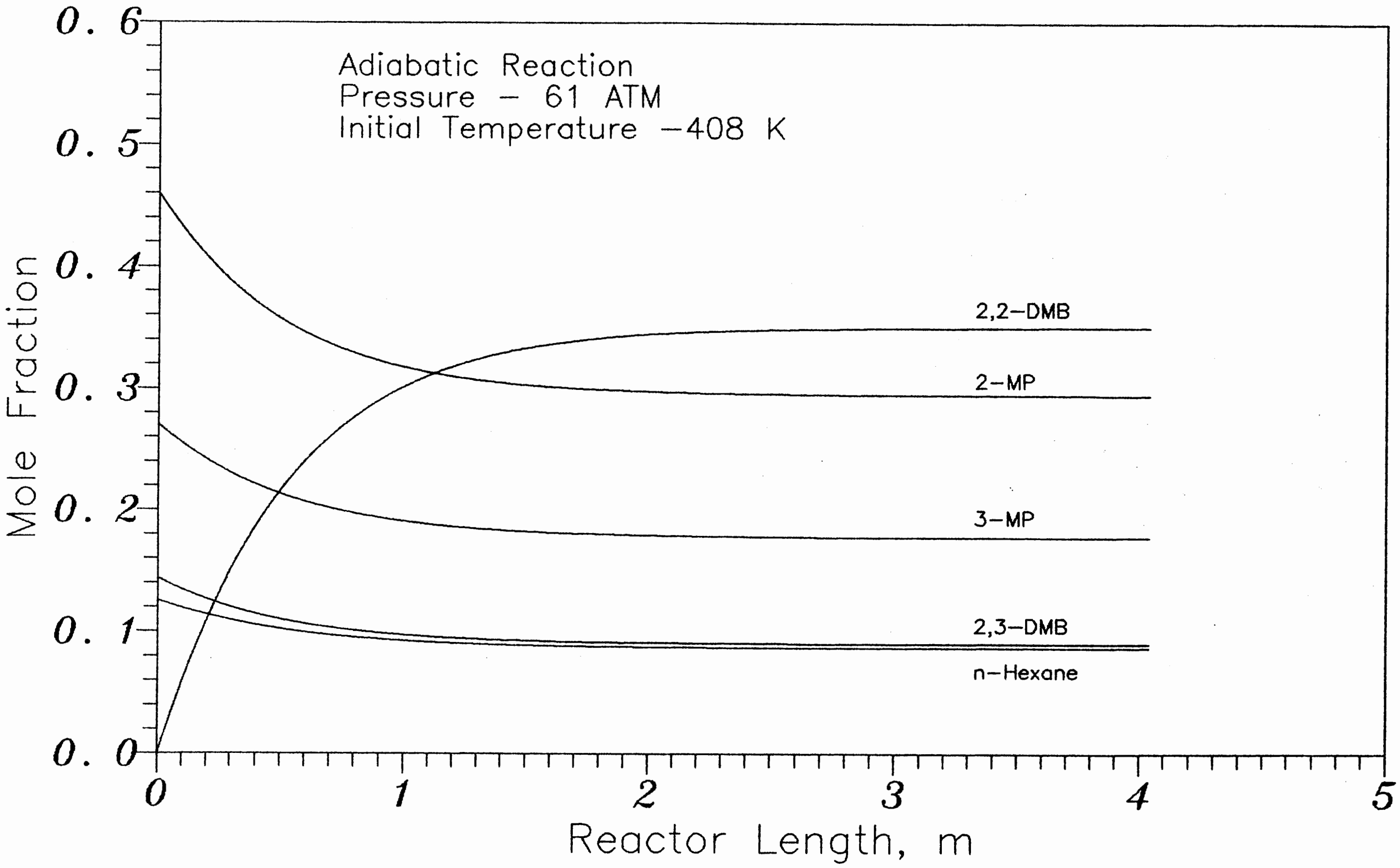


Figure 13. Mole Fraction Distributions of Hexane Isomerization

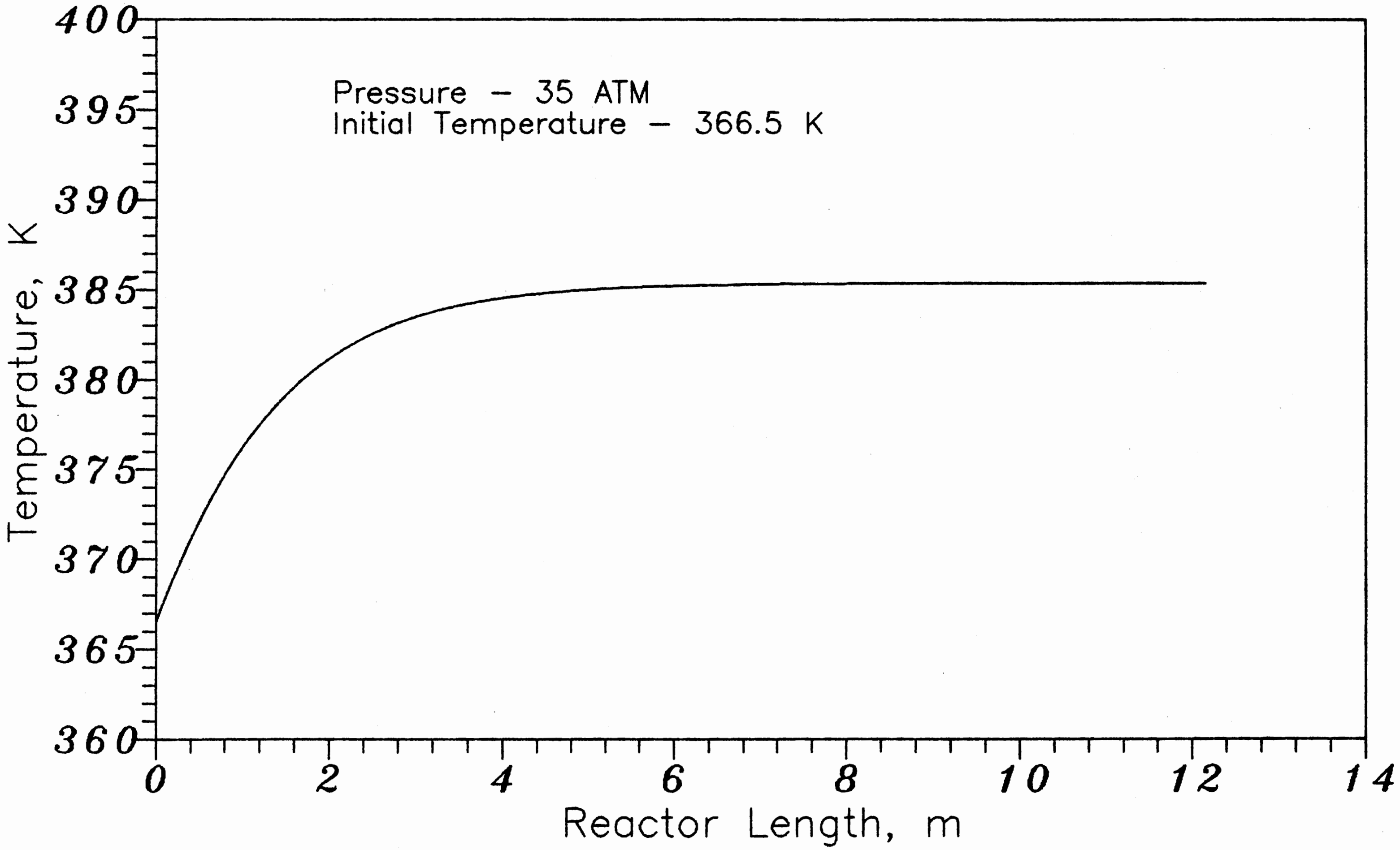


Figure 14. Temperature Profile vs Reactor Length of Hexane Isomerization

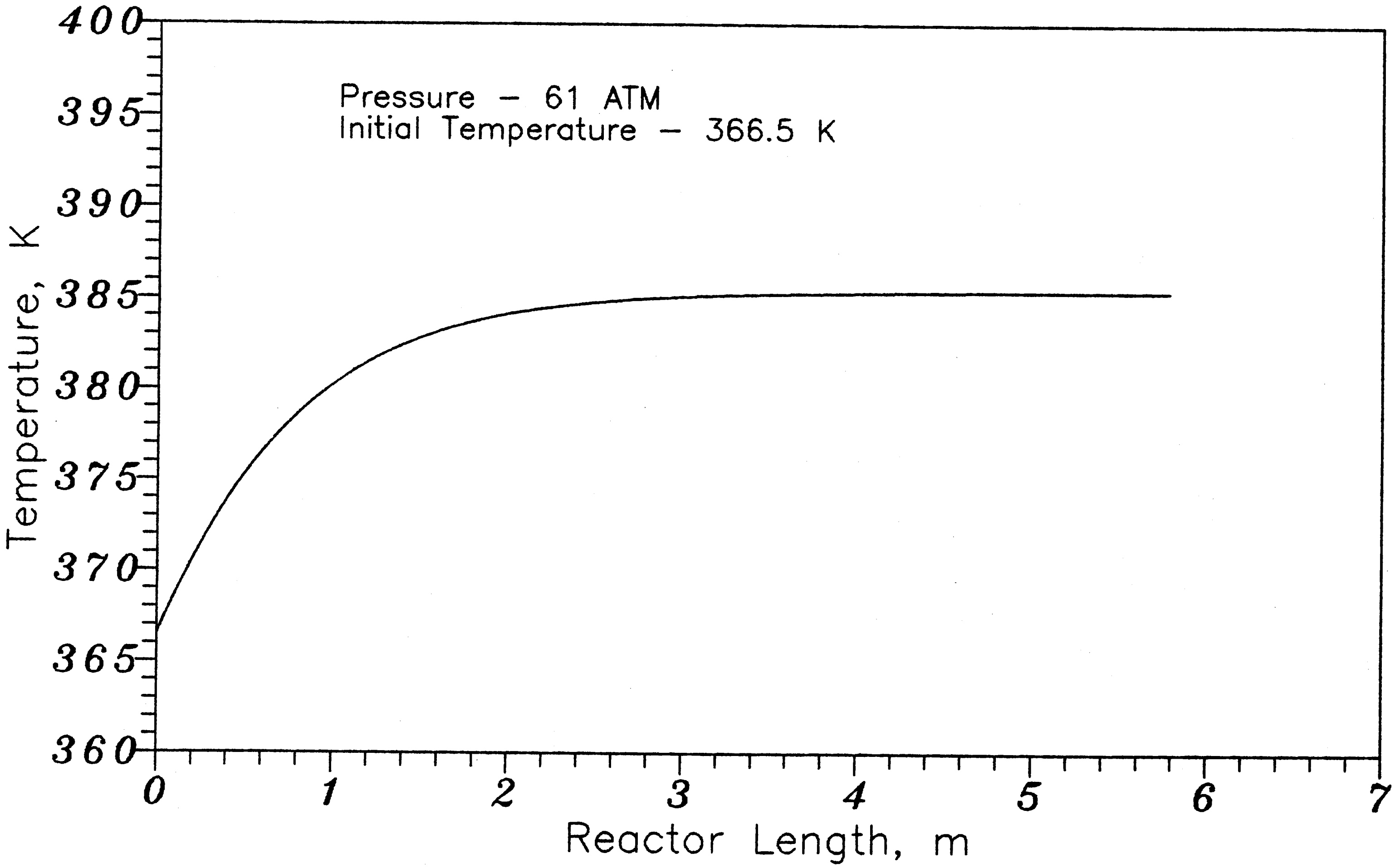


Figure 15. Temperature Profile vs Reactor Length of Hexane Isomerization

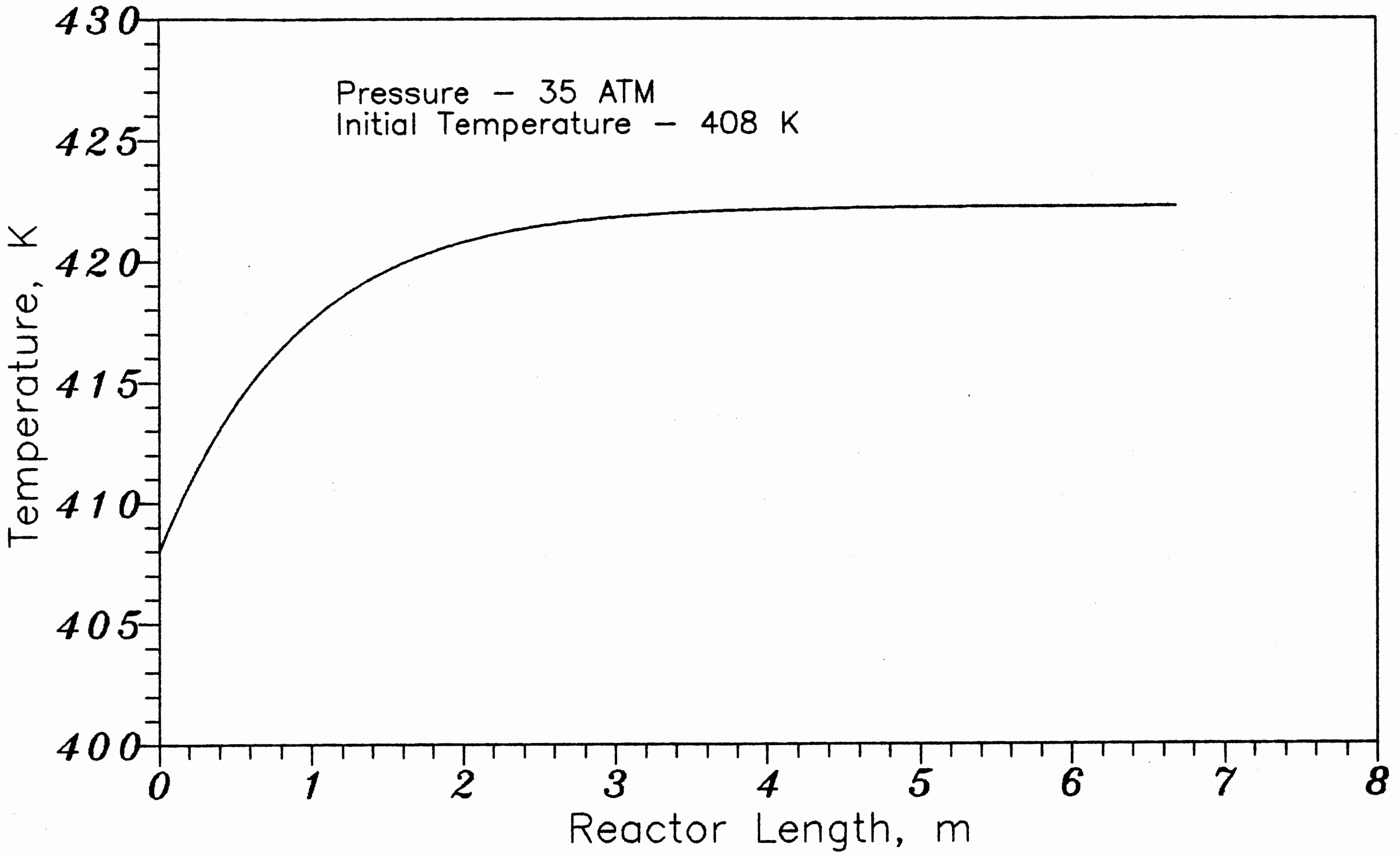


Figure 16. Temperature Profile vs Reactor Length of Hexane Isomerization

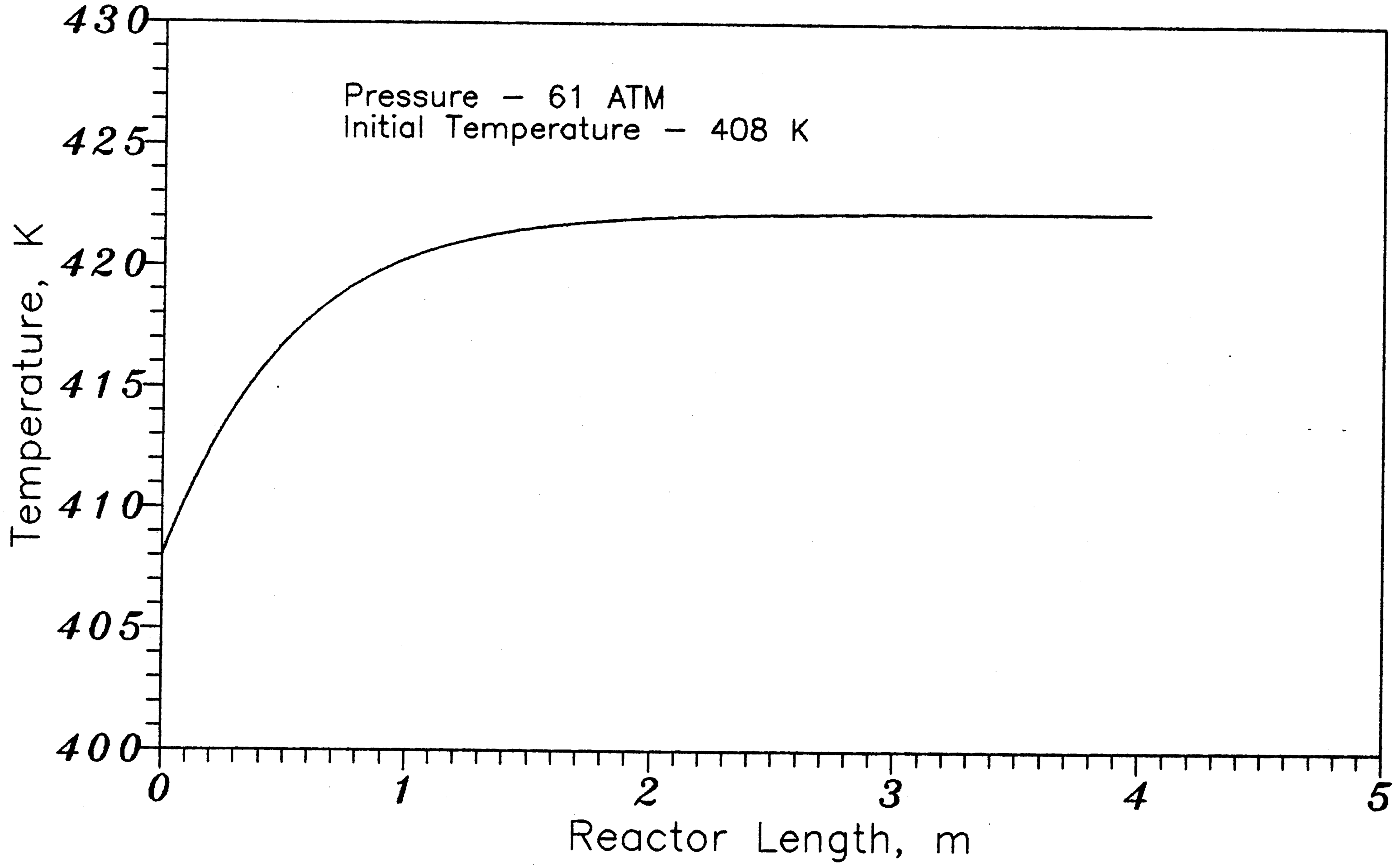


Figure 17. Temperature Profile vs Reactor Length of Hexane Isomerization

2. opz = 'N'
3. other factors are the same as Case I

Final results are shown in Figures 22 and 23 in Appendix C. The mole percentage of 2,2-DMB is 35.64 % at 3.0 m compared with a mole percentage of 37.69 % at 12.1 m.

Comparing the outputs for these cases, the following conclusions can be reached:

1. At the same initial temperature and system pressure, isothermal reaction can reach higher neo-Hexane mole fractions than the adiabatic case.
2. Higher temperature does not favor the yield of neo-hexane. For isothermal conditions a reactions, a reactor temperature decrease of 1 K, increases the mole percentage of 2,2-DMB by 0.2 %. For adiabatic operation, an initial temperature decrease of 1 K, increase the mole percentage of 2,2-DMB by 0.16 %.
3. Pressure has a very little influence on the conversion of neo-hexane but does affect the reactor length. Comparing Case I with Case II, the reactor length in Case II decreases almost 42 % over that of Case I.

HEXCR

At present, CSTCRs still are used mainly in the laboratory. This is because it is more complex and expensive to build than a batch or fixed-bed reactor. Further, the mole fraction of neo-hexane is generally lower than that of the fixed-bed reactor. The program for simulating a CSTCR was called HEXCR and supplies two choices to the user, isothermal or adiabatic operation. At this time, no published papers and no data is available that shows that hexane isomerization in a CSTCR. Two basic simulation runs are illustrated below.

Figures 24 and 25 in Appendix C are the control panels for the CSTCR.
Initial values of the parameters are set to zero.

Case I.

operating conditions:

1. isothermal reaction
2. reactor charge = 153 kgmole/hr
3. feed temperature = 408 K
4. volumetric flow rate = 125 m^3/hr
5. weight of catalyst = 2200 kg
6. pure n-hexane as feedstock

For these parameters, results are shown in Figures 26 and 27 in Appendix C. The mole fraction of neo-hexane is significantly lower than that of a fixed-bed reactor using same amount of catalyst.

Case II.

operating conditions:

1. adiabatic reaction
2. other conditions are the same as Case I

Results for the two cases are shown in Table VI. From this table, we find that isothermal reaction gives higher mole fractions of neo-hexane than that of adiabatic operation. This is because higher temperature does not favor the formation of neo-hexane.

From the above cases, the following conclusions can be made:

1. For isothermal operation, a temperature decrease of 1 K, increases the mole fraction of neo-hexane by 0.04 %. For adiabatic operation, a temperature decrease of 1 K, increases the mole fraction of neo-hexane by 0.03 %.
2. A CSTCR requires more catalyst than fixed-bed reactor.
3. If we have equal catalyst weight a large number of CSTCRs connected in series will behave as a plug flow reactor.
4. If the volumetric flow rate increases, the final mole fraction of neo-hexane decreases. This is a function of reactor residence time.

TABLE VI

RESULTS OF THE COMPARISON OF ISOTHERMAL AND ADIABATIC OPERATION OF A CSTCR

CASE	T_i (K)	T_f (K)	MODEL PREDICTION[1]
Isothermal	366.5	366.5	13.14 %
Isothermal	408.0	408.0	11.37 %
Adiabatic	366.5	435.1	11.39 %
Adiabatic	408.0	469.1	10.07 %

1. product mole percentage of neo-hexane

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The purpose of this study is to simulate an ideal plug flow reactor and a CSTCR for hexane isomerization. An isomerization catalyst, $Pt\text{-}Al_2O_3$ and proprietary data were used to validate the model. In actual operation, hydrogen and chloride are added to the reactors in order to prevent hydrocracking and keep the activity of the catalyst.

In summary, the models developed in this study can perform the following:

1. The optimized-length model of a fixed-bed reactor predicts that the distribution of hexane isomers optimal and the optimal length under specified operating conditions.
2. The fixed-length model of a fixed-bed reactor predicts the distributions of hexane isomers at specified reactor length.
3. The CSTCR model evaluates the distribution of hexane isomers at different input conditions.

In this study several conclusions can be made from model output data.

1. High temperature does not favor the isomerization process and isothermal operation gives higher yields of neo-hexane than that for adiabatic reaction for both optimized and fixed-length models.
2. Pressure does not affect the yield of neo-Hexane, but does influence the optimal reactor length.
3. Pressure drop in most fixed-bed reactors will be small compared to total system pressure and therefore can be neglected.

Recommendations

1. The ideal gas law was used in both reactor models to evaluate concentrations, however, since this system operates at high pressure, the gases do not behave as ideal gases. Therefore, it is suggested that a more accurate equation of state such as Redlich-Kwong or Peng-Robinson be used instead of the ideal gas law. Generally speaking, equilibrium constants are defined in terms of fugacities or activities and are not dependent upon the pressure. The behavior is explained in Appendix D.
2. This study did not consider any side reactions. It is recommended that these reactions be included in future work to more realistically model the hexane isomerization process.
3. It is recommended that additional experimental data be obtained to test the model for other catalysts.

This model can not be generalized until additional kinetic data is generated for a specific catalyst.

4. The equilibrium assumptions of the first three reactions are probably reasonable, but should be verified with experimental data.

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APPENDIXES

APPENDIX A

COMPUTER PROGRAM FOR HEXFI

```
$debug
C______________________ ABSTRACT ____________________
C
C    THIS PROGRAM CAN BE USED TO DESIGN A FIXED BED REACTOR
C  IN WHICH THERE ARE MULTIPLE REACTIONS OCCURING UNDER
C  ISOTHERMAL CONDITION OR ADIABATIC CONDITION.  THIS MODEL
C  ASSUMES PLUG FLOW AND NEGLECTS AXIAL DISPERSION AND
C  RADIAL TEMPERATURE GRADIANTS WITHIN THE BED.  THE DESIGN
C  EQUATIONS ARE INTEGRATED USING A FOURTH ORDER RUNGE-KUTTA
C  METHOD WITH A VARYING STEP SIZE.  THE STEP SIZE IS SET
C  SUCH THAT THERE IS A CERTAIN CHANGE IN THE TEMPERATURE OR
C  MOLE FRACTIONS OF THE REACTANTS.
C____________________ NOMENCLATURE ____________________
C_____________________________________________________
C
C  D    -  THE DIAMETER OF THE REACTOR TUBE, M
C  P    -  THE SYSTEM PRESSURE, ATM
C  Q    -  THE VOLUMETRIC FLOW RATE, M³/HR
C  T    -  TEMPERATURE, K
C  W    -  CATALYST WEIGHT, KG
C  Z1   -  THE LENGTH OF THE REACTOR TUBE, M
C  ZSP  -  REACTOR LENGTH SPECIFIED BY USER, M
C  ID   -  FLAG WHICH DETERMINES REACTION TYPE
C  NC   -  THE NUMBER OF CHEMICAL COMPONENTS
C  NR   -  THE NUMBER OF CHEMICAL REACTIONS
C  DZ   -  THE AXIAL STEP SIZE, M
C  DZT  -  THE AXIAL STEP SIZE BASED UPON A 10 K TEMPERATURE
C  FTO  -  THE TOTAL MOLAR FLOW RATE AT THE INLET FLOW RATE,
C             KGMOLES/HR
C  FTR  -  FLOW RATE IN A SINGLE TUBE, KGMOLE/HR
C  TNT  -  NO OF TUBES IN REACTOR
C  F(I)   -  FOR I=5, THE MOLAR FLOW RATE OF THE I-TH
C               COMPONENT, KGMOLES/HR); FOR I=6, THE REACTOR
C               TEMPERATURE, K
C  R(I)   -  THE RATE OF THE I-TH REACTION, KGMOLES/(KG OF
C               CAT-HR)
C  B(I)   -  THE CONSTANT TERM IN THE ITH EQUATION
C  FMP1   -  FEED MOLE PERCENTAGE OF n-HEXANE
C  FMP2   -  FEED MOLE PERCENTAGE OF 3-METHYLPANTANE
C  FMP3   -  FEED MOLE PERCENTAGE OF 2-METHYLPANTANE
C  FMP4   -  FEED MOLE PERCENTAGE OF 2,3 DIMETHYLBUTANE
C  FMP5   -  FEED MOLE PERCENTAGE OF 2,2 DIMETHYLBUTANE
C  FMP6   -  FEED MOLE PERCENTAGE OF INERT GAS
C  PMP1   -  PRODUCT MOLE PERCENTAGE OF n-HEXANE
C  PMP2   -  PRODUCT MOLE PERCENTAGE OF 3-METHYLPANTANE
C  PMP3   -  PRODUCT MOLE PERCENTAGE OF 2-METHYLPANTANE
C  PMP4   -  PRODUCT MOLE PERCENTAGE OF 2,3-DIMETHYLBUTANE
C  PMP5   -  PRODUCT MOLE PERCENTAGE OF 2,2-DIMETHYLBUTAME
C  PMP6   -  PRODUCT MOLE OF INERT GAS
C  THCAP   -  THE TOTAL HEAT CAPACITY OF THE REACTION MIXTURE
C                ,KJ/K
C  YO(I)   -  THE MOLE FRACTION OF THE I-TH COMPONENT IN THE
C                FEED
```

```
C  CP(J)  -  THE HEAT CAPACITY OF THE J-TH COMPONENT AT
C              TEMPERATURE T, KJ/(KGMOLE-K)
C  FP(I)  -  THE DERIVATIVE OF F(I) WITH RESPECT TO Z1
C  CA(I)  -  THE HEAT CAPACITY OF THE I-TH COMPONENT,
C              KJ/(KGMOLE-K)
C  BULDEN  -  THE BULK DENSITY OF THE BED, KG/M³
C  TDHRXN  -  THE NET HEAT OF REACTION, KJ/M³-HR)
C  EXC(I)  -  REACTION COORDINATE, I=1,3
C  A(I,J)  -  THE COEFICIENT OF THE JTH VARIABLE IN THE ITH
C               EQUATION
C  CAY1(I)--+
C  CAY2(I)  |--->  THE K'S USED IN THE RUNGE-KUTTA METHOD
C  CAY3(I)  |
C  CAY4(I)--+
C  FSAVE(I)  -  A VECTOR WHICH SAVE THE VALUES OF F(I)
C  GAM(I,J)  -  THE STOICHIOMETRIC COEFFICIENT OF THE I-TH
C                 COMPONENT IN THE J-THE REACTION
C  GFERV(I)  -  THE GIBBS FREE ENERGY OF THE I-TH REACTION,
C                 KJ/KGMOLE
C  CPV(I,J)  -  A VECTOR CONTAINING HEAT CAPACITIES OF
C                 COMPONENT I AT DiSCRETE VALUE OF
C                 TEMPERATURE, KJ/(KGMOLE-K)
C  DHRXN(I)  -  THE HEAT OF REACTION OF THE I-TH REACTION
C                 KJ/KGMOLE
C  DHRXV(I,J)  -  A VECTOR CONTAINING THE HEAT OF REACTION
C                   OF THE I-TH REACTION AT DISCRETE VALUES
C                   OF TEMPERATURE, KJ/KGMOLE
C-------------------------------------------------------------
C +------------- INPUT FORMAT DESCRIPTION -------------+
C |                                                    |
C |    INPUT DATA FOR HEXANE ISOMERIZATION AND SET UP CPV |
C |  AND HEAT OF REACTION.                             |
C +----------------------------------------------------+

C
C  +---------------------------------+
C  |  THIS FILE CONTAINS ALL THE SCREEN |
C  | INPUT VAULES AND DEFINITIONS     |
C  +---------------------------------+

$STORAGE:2
      INTEGER RC
      DOUBLE PRECISION FP(10),FSAV(10),TS
      DOUBLE PRECISION CAY1(10),CAY2(10),CAY3(10),CAY4(10)
      COMMON /DHRX/ DHRXN(4),T,YO(10)
      COMMON /DATA6/ P,GAM(5,4),D
      COMMON /DATA5/ NC,FTO,F(10),NR
      COMMON /CATAP/ BULDEN
      DIMENSION YF(10)
C
C +----------------------------------------------------+
C |  THIS PROGRAM APPLIES SOFTWARE EZVU DEVELOPED BY IBM |
C |   DEFINE INPUT AND OUTPUT VARIABLES FOR SCREEN      |
C |                HEX1,HEX2,HEX3                       |
C +----------------------------------------------------+
```

```
      RC=0
      CALL ISPFFV(4,'T F7',RC,T,4)
      CALL ISPFFV(4,'P F5',RC,P,4)
      CALL ISPFFV(4,'D F5',RC,D,4)
      CALL ISPFFV(5,'OPZ C',RC,OPZ,4)
      CALL ISPFFV(5,'Z1 F7',RC,Z1,4)
      CALL ISPFFV(5,'AI F1',RC,AI,4)
      CALL ISPFFV(6,'OPZ1 C',RC,OPZ1,4)
      CALL ISPFFV(6,'ZSP F7',RC,ZSP,4)
      CALL ISPFFV(6,'FTO F7',RC,FTO,4)
      CALL ISPFFV(7,'TEMP F7',RC,TEMP,4)
      CALL ISPFFV(7,'FMP1 F6',RC,FMP1,4)
      CALL ISPFFV(7,'FMP2 F6',RC,FMP2,4)
      CALL ISPFFV(7,'FMP3 F6',RC,FMP3,4)
      CALL ISPFFV(7,'FMP4 F6',RC,FMP4,4)
      CALL ISPFFV(7,'FMP5 F6',RC,FMP5,4)
      CALL ISPFFV(7,'FMP6 F6',RC,FMP6,4)
      CALL ISPFFV(7,'PMP1 F6',RC,PMP1,4)
      CALL ISPFFV(7,'PMP2 F6',RC,PMP2,4)
      CALL ISPFFV(7,'PMP3 F6',RC,PMP3,4)
      CALL ISPFFV(7,'PMP4 F6',RC,PMP4,4)
      CALL ISPFFV(7,'PMP5 F6',RC,PMP5,4)
      CALL ISPFFV(7,'PMP6 F6',RC,PMP6,4)
      CALL ISPFFV(9,'BULDEN F6',RC,BULDEN,4)

C
C     SET FUNCTION KEYS
C

      ZF10='QUIT'
      ZCMD='    '
      ZATR='WRI'
C
C     SET INITIAL VALUES OF
C        FUNCTION KEYS
C

      CALL ISPFFV(6,'ZATR C',RC,ZATR,4)
      CALL ISPFFV(6,'ZF01 C',RC,ZF01,4)
      CALL ISPFFV(6,'ZF02 C',RC,ZF02,4)
      CALL ISPFFV(6,'ZF03 C',RC,ZF03,4)
      CALL ISPFFV(6,'ZF10 C',RC,ZF10,4)
      CALL ISPFFV(6,'ZCMD C',RC,ZCMD,4)

C
C     INPUT VARIABLES FOR SCREEN HEX1,HEX2,HEX3
C        GET DEFAULT VALUES FROM PROFILE
C

      CALL ISPFF(8,'VGET D P',RC)
      CALL ISPFF(8,'VGET P P',RC)
      CALL ISPFF(8,'VGET T P',RC)
      CALL ISPFF(9,'VGET Z1 P',RC)
```

```
      CALL ISPFF(10,'VGET OPZ P',RC)
      CALL ISPFF(10,'VGET FTO P',RC)
      CALL ISPFF(10,'VGET ZSP P',RC)
      CALL ISPFF(11,'VGET TEMP P',RC)
      CALL ISPFF(11,'VGET FMP1 P',RC)
      CALL ISPFF(11,'VGET FMP2 P',RC)
      CALL ISPFF(11,'VGET FMP3 P',RC)
      CALL ISPFF(11,'VGET FMP4 P',RC)
      CALL ISPFF(11,'VGET FMP5 P',RC)
      CALL ISPFF(11,'VGET FMP6 P',RC)
      CALL ISPFF(11,'VGET PMP1 P',RC)
      CALL ISPFF(11,'VGET PMP2 P',RC)
      CALL ISPFF(11,'VGET PMP3 P',RC)
      CALL ISPFF(11,'VGET PMP4 P',RC)
      CALL ISPFF(11,'VGET PMP5 P',RC)
      CALL ISPFF(11,'VGET PMP6 P',RC)
      CALL ISPFF(11,'VGET OPZ1 P',RC)
      CALL ISPFF(13,'VGET BULDEN P',RC)
C
C    START SCREEN INPUTS
C

      CALL ISPFF(14,'DISPLAY OPTION',RC)
      IF((OPZ1.EQ.'a').OR.(OPZ1.EQ.'A')) GOTO 777
      IF((OPZ1.EQ.'b').OR.(OPZ1.EQ.'B')) GOTO 101

  101 ZCMD='    '
      CALL ISPFF(10,'VGET ZSP P',RC)
      ZF01='HEX1'
      ZF02='HEX2'
      ZF03='HEX3'
      CALL ISPFF(13,'DISPLAY KEYS1',RC)
      CALL ISPFF(12,'DISPLAY HEX1',RC)
        IF(ZCMD.EQ.'QUIT') CALL EXIT
        IF(ZCMD.EQ.'HEX2') GOTO 200
        IF(ZCMD.EQ.'HEX3') GOTO 300
        IF(OPZ.EQ.'N') GOTO 777
        IF(OPZ.EQ.'n') GOTO 777
        GOTO 102

  200 ZCMD='    '
      CALL ISPFF(13,'DISPLAY KEYS2',RC)
      CALL ISPFF(12,'DISPLAY HEX2',RC)
        IF(ZCMD.EQ.'QUIT') CALL EXIT
        IF(ZCMD.EQ.'HEX1') GOTO 101
        IF(ZCMD.EQ.'HEX3') GOTO 300
        GOTO 102

  300 ZCMD='    '
      CALL ISPFF(13,'DISPLAY KEYS3',RC)
      CALL ISPFF(12,'DISPLAY HEX3',RC)
        IF(ZCMD.EQ.'QUIT') CALL EXIT
```

```
        IF(ZCMD.EQ.'HEX2') GO TO 200
        IF(ZCMD.EQ.'HEX1') GO TO 101
        GOTO 102

  777 CONTINUE
      CALL ISPFF(9,'VGET Z1 P',RC)
        ZF01='HEF1'
        ZF02='HEX2'
        ZF03='HEF3'
        ZCMD='   '
      CALL ISPFF(13,'DISPLAY KEYS1',RC)
      CALL ISPFF(12,'DISPLAY HEF1',RC)
        IF(ZCMD.EQ.'QUIT') CALL EXIT
        IF(ZCMD.EQ.'HEX2') GOTO 201
        IF(ZCMD.EQ.'HEF3') GOTO 301
        IF(OPZ.EQ.'Y') GOTO 101
        if(OPZ.EQ.'y') GOTO 101
        GOTO 102

  201 ZCMD='   '
      CALL ISPFF(13,'DISPLAY KEYS2',RC)
      CALL ISPFF(12,'DISPLAY HEX2',RC)
        IF(ZCMD.EQ.'QUIT') CALL EXIT
        IF(ZCMD.EQ.'HEF1') GOTO 777
        IF(ZCMD.EQ.'HEF3') GOTO 301
        GOTO 102

  301 ZCMD='   '
      CALL ISPFF(13,'DISPLAY KEYS3',RC)
      CALL ISPFF(12,'DISPLAY HEF3',RC)
        IF(ZCMD.EQ.'QUIT') CALL EXIT
        IF(ZCMD.EQ.'HEF1') GOTO 777
        IF(ZCMD.EQ.'HEX2') GOTO 201
        GOTO 102

  102 ZCMD='    '
C +++++++++++++++++++++++++++++++++++++++
C +        STARTING MAIN PROGRAM        +
C +++++++++++++++++++++++++++++++++++++++
C
C      SET UP INITIAL DATA INFORMATION
C           1. ADIABATIC (ID=1)
C           2. ISOTHERMAL(ID=2)
C

      ID=1
      IF (AI.GT.1.5) ID=2
C
C  INPUT REACTOR TEMPERATURE, K
C

      T=TEMP
```

```
C
C  FLOW RATE IN A SINGLE TUBE
C

      FTR = FTO/TNT
C
C    INPUT INITIAL MOLE FRACTION
C        OF  N-HEXANE ... YO(1)
C            3-MP ....... YO(2)
C            2-MP ....... YO(3)
C            2,3-DMB .... YO(4)
C            2,2-DMB .... YO(5)
C            INERT ...... YO(6)
C

      YO(1)=FMP1/100.
      YO(2)=FMP2/100.
      YO(3)=FMP3/100.
      YO(4)=FMP4/100.
      YO(5)=FMP5/100.
      YO(6)=FMP6/100.
C
C    SET UP DATA FOR REACTOR MODEL
C

      CALL DATAN
C
C  CALCULATE HEAT CAPACITIES AND REACTION HEATS
C

      CALL ARRAY
C
C  INITIALIZE  REACTOR DISTANCE, Z1 (METER)
C

      Z1=0.0
C
C    INITIALLY ASSUME MOLE FRACTION OF
C           NEO-HEXANE
C

      COC1=0.0
C *************************************
C *      BEGIN INTEGRATION LOOP       *
C *************************************

  1   CALL FNC (F,FP,YO,ID)
      TS=0.0D0
C
C    CALCULATE NEW STEP SIZE
C
```

```
C
C          ISOTHERMAL CASE
C    —> USING CONCENTRATION CHANGES
C

      RT=ABS(FP(5)/FTR)
      IF (RT.GT.TS) TS=RT
      DZ=2.5E-4/TS
      IF (ID.EQ.2) GOTO 35
C
C          ADIABATIC CASE
C    —> USING TEMPERATURE CHANGE
C

      DZT=10.0/ABS(FP(6))
      IF(DZT.LT.DZ) DZ=DZT
      IF(DZ.GT.1) DZ=0.010
C >>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>
C >     STARTING RUNGE-KUTTA          >
C >>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>

   35 DO 3 I=5,6
    3 FSAV(I)=F(I)
C
C   SET UP CAY1(I)
C

      DO 4 I=5,6
    4 CAY1(I)=FP(I)
      DO 5 I=5,6
    5 F(I)=FSAV(I)+0.50*DZ*CAY1(I)
      CALL FNC(F,FP,YO,ID)
C
C   SET UP CAY2(I)
C

      DO 6 I=5,6
    6 CAY2(I)=FP(I)
      DO 7 I=5,6
    7 F(I)=FSAV(I)+0.50*DZ*CAY2(I)
      CALL FNC(F,FP,YO,ID)
C
C   SET UP CAY3(I)
C

      DO 8 I=5,6
    8 CAY3(I)=FP(I)
      DO 9 I=5,6
    9 F(I)=FSAV(I)+DZ*CAY3(I)
      CALL FNC(F,FP,YO,ID)
C
C   SET UP CAY4(I)
C
```

```
      DO 10 I=5,6
   10 CAY4(I)=FP(I)
C
C      CALCULATE THE NEW VALUES
C          OF F(I) AT Z1+DZ
C

      DO 11 I=5,6
   11 F(I)=FSAV(I)+DZ/6.0*(CAY1(I)+2.0*CAY2(I)
     &+2.0*CAY3(I)+CAY4(I))
C<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<
C     END OF RUNGE-KUTTA METHOD !!!
C<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<

C\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\
C           IF USER CHOOSE OPTIMIZED MODEL
C  CHECK WHETHER REACTION REACHES EQUILIBRIUM OR NOT
C\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\

      IF((OPZ.EQ.'y').OR.(OPZ.EQ.'Y')) THEN
        COC2=F(5)/FTR
        ERLIM=(COC2-COC1)*FTR
        COC1=COC2
        IF(ERLIM.LT.0.0001) GOTO 100
      ENDIF
C
C      CALCULATE NEW MOLE FRACTION OF NEO-HEXANE AND
C        NEW MOLE FRACTION OF 2,3-DIMETHYLBUTANE
C
C
C     NEW MOLE FRACTION OF NEO-HEXANE
C

      YF(5)=F(5)/FTR
C
C     NEW MOLE FRACTION OF 2,3-DMB
C

      YO(4)=YO(4)-(YF(5)-YO(5))
C
C     ASSIGN  YF  TO  YO
C

      YO(5)=YF(5)
C
C     MOLE FRACTION OF INERT GAS
C

      YF(6)=YO(6)
C
C     CALCULATE THE REACTOR LENGTH, METER
C
```

```
      Z1=Z1+DZ
C    ________________________________
C   | DETERMINE WHETHER THE REACTOR  |
C   |  LENGTH OVER THE  SPECIFIED    |
C   |      LENGTH OR NOT             |
C   |________________________________|

      IF((OPZ.EQ.'n').OR.(OPZ.EQ.'N')) THEN
        ERLIN=ZSP-Z1
        IF(ERLIN.LT.0.0) GOTO 100
      ENDIF
C    ____________________
C   | ITERATE RUNGE-KUTTA|
C   |____________________|

      GOTO 1
C    ________________________
C   | ***  FINAL OUTPUTS  ***|
C   |________________________|

 100  CONTINUE
C    ___________________________
C   |MOLE PERCENTAGE            |
C   |     OF N-HEXANE ..... PMP1|
C   |        3-MP ......... PMP2|
C   |        2-MP ......... PMP3|
C   |        2,3-DMB ...... PMP4|
C   |        2,2-DMB ...... PMP5|
C   |        INERT ........ PMP6|
C   |___________________________|

      PMP1=YO(1)*100.
      PMP2=YO(2)*100.
      PMP3=YO(3)*100.
      PMP4=YO(4)*100.
      PMP5=YO(5)*100.
      PMP6=YO(6)*100.
C    ______________________________
C   |FINAL REACTOR TEMPERATURE, K  |
C   |______________________________|

      T=F(6)

      IF((OPZ.EQ.'y').OR.(OPZ.EQ.'Y')) GOTO 101
      IF((OPZ.EQ.'n').OR.(OPZ.EQ.'N')) GOTO 777

      STOP
      END
C ++++++++++++++++++++++++++++++++++++++++
C +        END !  of MAIN Program        +
C ++++++++++++++++++++++++++++++++++++++++
```

```
C   ┌──────────────────────────────────────────────────────┐
C   │   THIS SUBROUTINE SUPPLIES THE MAJORITY OF THE DATA  │
C   │ FOR THE FIXED-BED REACTOR MODEL.  THIS SUBROUTINE IS │
C   │ USER SUPPLIED AND PROVIDES DATA, FEED CONDITIONS,    │
C   │ STOICHIOMETRIC COEFFICIENTS, HEATS OF REACTIONS,     │
C   └──────────────────────────────────────────────────────┘

      SUBROUTINE DATAN
      COMMON /DHRX/ DHRXN(4),T,YO(10)
      COMMON /DATA5/ NC,FTR,F(10),NR
      COMMON /DATA6/ P,GAM(5,4),D
      COMMON /CATAP/ BULDEN
C   ┌───────────────────────────┐
C   │ THE NUMBER OF REACTIONS   │
C   └───────────────────────────┘

      NR=4
C   ┌──────────────────────────────────────┐
C   │      NUMBER OF COMPONENTS,           │
C   │ (EXCEPT THE INERT GAS BECAUSE IT     │
C   │ DOESN'T REACT WITH OTHER REACTANTS)  │
C   └──────────────────────────────────────┘

      NC=5
C   ┌──────────────────────────────────────┐
C   │ THE STOICHIOMETRIC COEFICIENTS       │
C   │  **  INITIALIZE GAM(I,J) **          │
C   └──────────────────────────────────────┘

      DO 1 I=1,NC
      DO 1 J=1,NR
    1 GAM(I,J)=0.0
C   ┌────────────────────────────────────────────┐
C   │(1)n-HEXANE <──────> (1)  3-methylpantane   │
C   │ │                     │                    │
C   │ └───>GAM(1,1)         └───>GAM(2,1)        │
C   └────────────────────────────────────────────┘

      GAM(1,1)=-1.0
      GAM(2,1)=1.0
C   ┌────────────────────────────────────────────────────┐
C   │(1) 3-methylpantane <──────> (1) 2-methylpantane    │
C   │ │                            │                     │
C   │ └────>GAM(2,2)               └──────>GAM(3,2)      │
C   └────────────────────────────────────────────────────┘

      GAM(2,2)=-1.0
      GAM(3,2)=1.0
C   ┌───────────────────────────────────────────────────────┐
C   │(1) 2-methylpantane <──────> (1) 2,3-dimethylbutane    │
C   │ │                            │                        │
C   │ └────>GAM(3,3)               └──────>GAM(4,3)         │
C   └───────────────────────────────────────────────────────┘
```

```
      GAM(3,3)=-1.0
      GAM(4,3)=1.0
C
C   (1) 2,3-dimethylbutane <----> (1) 2,2-dimethylbutane
C    |                             |
C    +------>GAM(4,4)              +------>GAM(5,4)
C

      GAM(4,4)=-1.0
      GAM(5,4)=1.0
C
C      CALCULATE THE INLET
C   MOLAR FLOW RATES, (KGMOLE/HR)
C

      DO 2 I=1,NC
    2 F(I)=YO(I)*FTR
C
C     SET F(6) STANDS FOR
C   THE TEMP IN THE SYSTEM
C

      F(NC+1)=T

      RETURN
      END
C *********************************************************
C *   THIS SUBROUTINE CALCULATES THE HEAT CAPACITIES OF *
C *  EACH SPECIES AND THE HEATS OF REACTIONS AT T (K).  *
C *********************************************************

      SUBROUTINE ARRAY
      COMMON /DATA5/ NC,FTR,F(10),NR
      COMMON /DATA6/ P,GAM(5,4),D
      COMMON /DHRX/ DHRXN(4),T,YO(10)
      COMMON /VECTR/ DHRXV(4,150),CPV(5,150),GFERV(4,150)
      DOUBLE PRECISION SUM
C
C     DECIDE THE INTEGRATION INTERVAL,
C   (TEMP RANGE FROM 298.15 to 1000 K)
C

      TI=298.15
      DT=(1000.-TI)/90.
C
C   REACTION HEAT (KJ/KGMOLE)  AT 298.15 K
C
C   n-HEXANE <----> 3-METHYLPENTANE (3-MP)
C

      DHRXV(1,1)=-5.050*1000.
```

```
C
C   REACTION HEAT (KJ/KGMOLE) AT 298.15 K
C   3-METHYLPENTANE <-------> 2-METHYLPENTANE
C

      DHRXV(2,1)=-2.580*1000.
C
C   REACTION HEAT (KJ/KGMOLE) AT 298.15 K
C   2-METHYLPENTANE <-------> 2,3-DIMETHYLBUTANE
C

      DHRXV(3,1)=-2.250*1000.
C
C   REACTION HEAT (KJ/KGMOLE) AT 298.15 K
C   2,3-DIMETHYLBUTANE <-------> 2,2-DIMETHYLBUTANE
C

      DHRXV(4,1)=-7.880*1000.
C-----------------------------------------------------------
C
C   CALCULATE REACTION HEAT AT EVERY DT, (KJ/KGMOLE)
C----------       From T=298.15 K TO 1000 K       ------
C
C  For example: 1st reaction
C
C        n-Hexane <-----> 3-Methylpantane
C
C                 ⌠T2
C                 ⎮  (Cp'-Cp)dT = heat of reaction
C                 ⌡T1
C
C        where  Cp'= heat capacity of 3-MP
C               Cp = heat capacity of n-Hexane
C
C  p.s. 1st reaction: I=1
C                     TI=298.15 K (referance temp)
C                     sum=0.0
C                     K=2
C     we want to evaulate reaction heat at 305.98 K (TI+DT)
C        sum=0.0+DT*GAM(1,1)*Cp(1,305.98)=-DT*Cp(1,305.98)
C        sum=sum+DT*GAM(2,1)*Cp(2,305.98)=-DT*Cp(1,305.98)
C                                   +DT*1*Cp(2,305.98)
C        sum=sum+DT*GAM(3,1)*Cp(3,305.98)=-DT*Cp(1,305.98)
C                     +DT*Cp(2,305.98)+DT*0.0*Cp(3,305.98)
C           =-DT*Cp(1,305.98)+DT*Cp(2,305.98)
C        sum=sum+DT*GAM(4,1)*Cp(4,305.98)
C           =-DT*Cp(1,305.98)+DT*Cp(2,305.98)
C        sum=sum+DT*GAM(5,1)*Cp(5,305.98)
C           =-DT*Cp(1,305.98)+DT*Cp(2,305.98)
C
C      Therefore, heat of reaction with respect to referance
C      temp is  delta H= DT*( Cp(2,305.98)-Cp(1,305.98))
C------------------------------------------------------------
```

```
      DO 4 I=1,NR
      TI=298.15
      SUM=0.0D0
      DO 5 K=2,91
      TI=TI+DT
      DO 6 J=1,NC
      SUM=SUM+DT*GAM(J,I)*CP(J,TI)
  6   CONTINUE

      IF (TI.GT.1000.) GOTO 4
C
C    NEW VALUE OF REACTION HEAT
C    AT (T+dT) with respect to 298.15 K
C

      DHRXV(I,K)=DHRXV(I,K-1)+SUM

  5   SUM=0.0D0
  4   CONTINUE
C ----------------------------------------------------------
C +CALCULATE THE GIBBS ENERGY OF FORMATION OF EACH REACTION+
C -------------     GFERV(I,J), (KJ/KGMOLE)   --------------
C  For example: 1st reaction
C               referance temp=298.15 K
C               DT=7.8 K
C               new temp to evaulate : 305.9 K
C               suml=0.0
C
C               n-Hexane <------> 3-methylpantane
C
C   show steps: suml=GAM(1,1)*GF(1,305.9)+suml
C                   =-1*GF(1,305.9)+0.0
C                suml=GAM(2,1)*GF(2,305.9)+suml=
C                    =1*GF(2,305.9)-GF(1,305.9)
C               suml=GAM(3,1)*GF(3,305.9)+suml=GF(2,305.9)-
C                      GF(1,305.9)
C               suml=GAM(4,1)*GF(4,305.9)+suml=GF(2,305.9)-
C                      GF(1,305.9)
C               suml=GAM(5,1)*GF(5,305.9)+suml=GF(2,305.9)-
C                      GF(1,305.9)
C
C       Therefore, Gibbs energy of formation of 1st reaction
C    at t+dt GFERV(1,305.9)=suml
C
C-----------------------------------------------------------

      DO 34 I=1,NR
      TI=298.15
      SUM1=0.0
      DO 35 K=2,91
      TI=TI+DT
      DO 36 J=1,NC
```

```
      SUM1=GAM(J,I)*GF(J,TI)+SUM1
   36 CONTINUE
      IF (TI.GT.1000.) GO TO 34
      GFERV(I,K)=SUM1
   35 SUM1=0.0
   34 CONTINUE
C
C   SET UP CPV(I,J) --->> CONVERT EVERY
C   VALUE OF Cp(i,ti) INTO VECTOR IN
C   ORDER TO USE LINEAR INTERPOLATION
C

      DO 10 I=1,NC
      TI=298.15
      DO 11 J=1,90
      CPV(I,J)=CP(I,TI)
   11 TI=TI+DT
   10 CONTINUE
      RETURN
      END
C *****************************************
C *  THIS FUNCTION CALCULATES THE HEAT    *
C *  CAPCAITY OF EACH SPECIES             *
C *  FROM 200-1000 (K) (KJ/KGMOLE-K)      *
C *****************************************

      FUNCTION CP(I,T)
      IF (I.EQ.1) GOTO 1
      IF (I.EQ.2) GOTO 2
      IF (I.EQ.3) GOTO 3
      IF (I.EQ.4) GOTO 4
      IF (I.EQ.5) GOTO 5

    1 CP=(-1.0540+1.39E-1*T-7.449E-5*T²+1.551E-8*T³)*4.184
      RETURN
    2 CP=(-0.570+1.359E-1*T-6.854E-5*T²+1.202E-8*T³)*4.184
      RETURN
    3 CP=(-2.5240+1.477E-1*T-8.533E-5*T²+1.931E-8*T³)*4.184
      RETURN
    4 CP=(-3.489+1.469E-1*T-8.063E-5*T²+1.629E-8*T³)*4.184
      RETURN
    5 CP=(-3.973+1.503E-1*T-8.314E-5*T²+1.636E-8*T³)*4.184
      RETURN
      END
C *******************************************
C *  THIS FUNCTION CALCULATE THE GIBBS FREE *
C *  ENERGY OF FORMATION OF HEXANE ISOMERS  *
C *  FROM 200-1000 K, KJ/KGMOLE             *
C *******************************************

      FUNCTION GF(I,T)
      IF (I.EQ.1) GOTO 1
      IF (I.EQ.2) GOTO 2
```

```
      IF (I.EQ.3) GOTO 3
      IF (I.EQ.4) GOTO 4
      IF (I.EQ.5) GOTO 5

  1   GF=-0.000087*T³+0.219336*T²+453.119366*T-151738.80896
      RETURN
  3   GF=-0.000092*T³+0.225563*T²+458.412884*T-158998.25354
      RETURN
  2   GF=-0.000085*T³+0.216435*T²+460.331617*T-156934.60254
      RETURN
  5   GF=-0.000092*T³+0.224945*T²+481.313618*T-169166.74548
      RETURN
  4   GF=-0.000091*T³+0.22493*T²+473.536175*T-161194.52295

      RETURN
      END
C *******************************************************
C *   THIS SUBROUTINE CALCULATE THE DERIVATIVE OF F(I)   *
C *   WITH RESPECT TO Z.  THE DERIVATIVES ARE CALCULATED *
C *   FROM MATERIAL BALANCE WHEN F(I) IS THE MOLAR FLOW  *
C *   RATE OF A COMPONENT AND FROM ENERGY BALANCE WHEN   *
C *   F(I) IS THE TEMPERATURE.                           *
C *******************************************************

      SUBROUTINE FNC(F,FP,YO,ID)
      COMMON /CATAP/ BULDEN
      COMMON /DATA5/ NC,FTR,Y(10),NR
      COMMON /DATA6/ P,GAM(5,4),D
      DIMENSION F(10),EK(4),FK(4),RK(4),YO(10)
      DOUBLE PRECISION FP(10),CA(5),DHRXN(4),R(4),GFERN(4)
      DOUBLE PRECISION TDHRXN,THCAP,CONC(5),EXC(3)
C
C    REACTOR PRESSURE, (ATM)
C

      PO=P
C
C    REACTOR TEMPERATURE, K
C

      T=F(6)
C
C    CALCULATE THE VOLUMETRIC FLOW RATE, (M³/HR)
C          Using Ideal Gas Law, PV=nRT
C

      QO=FTO*22.4*T/273.15/PO
C
C     CALCULATE THE HEATS OF REACTIONS, HEAT
C    CAPACITIES AND GIBBS ENERGIES AT ANY TEMP
C    BETWEEN, 298 -1000 K
C       Using linear interpolation
C
```

```
      CALL PROP(T,DHRXN,CA,GFERN)
C
C        CALCULATE THE EQUILIBRIUM CONSTANTS
C     ,FORWARD AND REVERSE RATE CONSTANTS
C

      CALL EQCON(EK,FK,RK,F,GFERN)
C
C          CALCULATE THE EQUILIBRIUM MOLE
C         ,FRACTIONS OF HEXANE ISOMERS.
C       Using 'LINPAC' To Solve Reaction Coordinates
C

      CALL SLTRES(EK,YO,EXC)
C
C     CALCULATE THE CONCENTRATION OF
C     2,3-DMB AND NEOHEXANE, KGMOLE/M3
C

      DO 80 I=4,5
   80 CONC(I)=FTO*YO(I)/QO
C
C     CALCULATE THE GLOBE RATE OF FORTH REACTION
C

      CALL RXN(R,CONC,FK,RK)
      R(4)=R(4)*BULDEN
C
C     ID=2, ie.  ISOTHERMAL CONDITION
C

      IF (ID.EQ.2) GOTO 75
C
C      CALCULATE THE NET HEAT DUE TO REACTION, KJ/KGMOLE
C
C      by energy balance equation:
C
C            dT/dZ = (πD²/4)* Σ(bulk(-dH)) / Σ(Fi*Cpi)
C                             |<-------->|  |<--->|
C                                part A      part B
C                     |<--------------------------->|
C                                 part C
C
C
C              part A
C

      SRXN=0.0
      DO 77 I=1,3
 77   SRXN=EXC(I)*FTR*DHRXN(I)+SRXN
      SRXN=SRXN*BULDEN
      TDHRXN=SRXN+R(4)*DHRXN(4)
```

```
C
C          part B
C

      THCAP=0.0D0
      DO 3 I=1,NC
    3 THCAP=THCAP+FTR*YO(I)*CA(I)
C
C  PERFORM THE ENERGY BALANCE (K/M)
C               part C
C

      FP(6)=(-TDHRXN*3.14159D0*D*D/4.D0)/THCAP
C
C  PERFORM THE MATERIAL BALANCE, (KGMOLE/HR/M)
C
C    dFi/dZ= BULK*(πD²/4)* ΣRi
C

 75   FP(5)=R(4)*3.14159*D*D/4.0D0

      RETURN
      END
C ************************************************************
C *      THIS SUBROUTINE CALCULATES THE HEAT CAPACITY AND  *
C *   THE HEATS OF REACTIONS FOR A GIVEN TEMPERATURE BY     *
C *   LINERALY INTERPOLATING BETWEEN VALUES OF CPV(I,J) AND*
C *   DHRXV(I,J), RESPECTIVELY.                            *
C ************************************************************

      SUBROUTINE PROP(T,DHRXN,CA,GFERN)
      DOUBLE PRECISION DHRXN(4),CA(5),GFERN(4)
      COMMON /VECTR/ DHRXV(4,150),CPV(5,150),GFERV(4,150)
      COMMON /DATA5/ NC,FTR,F(10),NR

      DT=(1000.-298.15)/90.
      I=IFIX((T-298.15)/DT)+1
      PRO=(T-298.15-DT*FLOAT(I-1))/DT
C
C    CALCULATE THE HEATS OF REACTIONS
C    AT SPECIFIED TEMP, KJ/KGMOLE
C

      DO 1 J=1,NR
    1 DHRXN(J)=DHRXV(J,I)+PRO*(DHRXV(J,I+1)-DHRXV(J,I))
C
C  CALCULATE THE HEAT CAPACITIES OF
C  ISOMERS AT SPECIFIED TEMP, KJ/KGMOLE-K
C

      DO 2 J=1,NC
    2 CA(J)=CPV(J,I)+PRO*(CPV(J,I+1)-CPV(J,I))
```

```
C
C      CALCULATE THE GIBBS ENERGIES
C      AT SPECIFIED TEMP, (KJ/KGMOLE)
C

      DO 3 J=1,NR
  3   GFERN(J)=GFERV(J,I)+PRO*(GFERV(J,I+1)-GFERV(J,I))

      RETURN
      END
C ********************************************************
C *     THIS SUBROUTINE CALCULATES THE EQULIIBRIUM        *
C *  CONSTANTS OF EACH REACTION AND THE FORWARD AND REVERSE*
C *  REACTION RATE CONSTANTS.                              *
C ********************************************************

      SUBROUTINE EQCON(EK,FK,RK,F,GFERN)
      DIMENSION EK(4),FK(4),RK(4),F(10)
      DOUBLE PRECISION GFERN(4)

C--  REACTOR TEMPERATURE  --

      T=F(6)
C
C    CALCULATE EQUILIBRIUM CONSTANT OF NORMAL
C    HEXANE TO IT'S ISOMERS
C      delta G=-RT*lnK
C

      DO 5 I=1,4
  5   EK(I)=EXP(-GFERN(I)/(8.314*T))
C
C    CALCULATE REVERSE REACTION RATE CONSTANTS,
C    (FT³/LB of CAT-HR)
C             kr=k'exp(-E/RT)
C

      TR=9./5.*(T-273.15)+32.+459.67
      RK(4)=5.24*1000.* EXP(-9.55*1000./10.7302/TR)
C
C     CALCULATE FORWARD REACTION
C     RATE CONSTANTS, (FT³/LB-HR)
C        K=kf/kr ———> kf=K*kr
C

      FK(4)=RK(4)*EK(4)
C
C    CONVERT FORWARD AND REVERSE
C    RATE CONSTANTS TO, M³/KG-HR)
C
      FK(4)=FK(4)*0.06243
      RK(4)=RK(4)*0.06243
```

```
      RETURN
      END
C *************************************************************
C *  THIS SUBROUTINE CALCULATES THE RATES OF EACH REACTION *
C * GIVEN THE COMPOSITION AND TEMPERATURE.  THE DEFINITION *
C * AND UNITS OF THE VARIABLES CAN BE FOUND IN THE         *
C * NOMENCLATURE SECTION OF THE MAIN PROGRAM.              *
C *************************************************************

      SUBROUTINE RXN(R,CONC,FK,RK)
      COMMON /DATA5/ NC,FTR,Y(10),NR
      DOUBLE PRECISION R(4),CONC(5)
      DIMENSION FK(4),RK(4)
C
C       CALCULATE THE GLOBE REACTION RATE
C     OF FORTH REACTION, KGMOLE/(KG OF CAT-HR)
C

      R(4)=FK(4)*CONC(4)-RK(4)*CONC(5)

      RETURN
      END
C *************************************************************
C *    THIS SUBROUTINE SOLVE 3 EQUATIONS SIMULTANEOUSLY IN *
C *  ORDER TO FIND THE THERMODYNAMIC EQUILIBRIUM MOLE      *
C *  FRACTION OF N-HEXANE, 3-MP, 2-MP, 2,3-DMB.            *
C *************************************************************

      SUBROUTINE SLTRES(EK,YO,EXC)
      DOUBLE PRECISION A(3,3),B(3),EXC(3)
      DIMENSION EK(4),YO(10)

      INTEGER IPVT(3)

C*** NOTE THAT A,B,X,IPVT MUST BE DOUBLE PRECISIONED AND
DIMENSIONED BY
C
C---- NUMBER OF UNKNOWNS (REACTION COORDINATES) C
      N=3
C---------------------------

C  ZERO B(I) AND A(I,J)

      DO 1 I=1,N
      B(I)=0.0
      DO 1 J=1,N
    1 A(I,J)=0.0

C  SET THE NONZERO VALUES OF A(I,J) AND B(I)

      A(1,1)=EK(1)+1.
      A(1,2)=-1.
      A(2,1)=EK(2)
      A(2,2)=-EK(2)-1.
```

```
      A(2,3)=1.
      A(3,2)=EK(3)
      A(3,3)=-EK(3)-1.
      B(1)=YO(1)*EK(1)-YO(2)
      B(2)=YO(3)-YO(2)*EK(2)
      B(3)=YO(4)-EK(3)*YO(3)

C  SOLVE REACTION COORDINATES EXC(1),EXC(2),EXC(3)

C  CALL LINPAC
C
      CALL LINPAC(N,A,B,EXC,IPVT)

      YO(1)=YO(1)-EXC(1)
      YO(2)=YO(2)+EXC(1)-EXC(2)
      YO(3)=YO(3)+EXC(2)-EXC(3)
      YO(4)=YO(4)+EXC(3)
      YO(5)=YO(5)

      RETURN
      END
```

APPENDIX B

COMPUTER PROGRAM FOR HEXCR

```
$debug

C ************************ ABSTRACT ***********************
C *                                                       *
C *    This program calculates the performance of an      *
C *  CSTCR . Using a steady state mole balance for each   *
C *  species, a system of two linear equations containing *
C *  two unknown is generated.  This system of equations  *
C *  is solved using the " Newton's Method ".             *
C *                                                       *
C * ******************  NOMENCLATURE  *********************
C *
C *   W - weight of catalyst, kg
C *   Q - volumetric flow rate, m^3/hr
C *   N - no. of linear equations
C *   TM - average temperature, K
C *   NC - no. of components
C *   NR - no. of reactions
C *   ID - flag which determine reaction type
C *   CDO - initial concentration of 2,3-DMB, kgmole/m^3
C *   CEO - initial concentration of 2,2-DMB, kgmole/m^3
C *   FTO - total flow rate, kgmole/hr
C *   HH1 -  enthalpy of 2,3-DMB at temp t_2, kj/kgmole
C *   HH2 -  enthalpy of 2,2-DMB at temp t_2, kj/kgmole
C *   HG1 -  enthalpy of 2,3-DMB at temp t_1, kj/kgmole
C *   HG2 -  enthalpy of 2,2-DMB at temp t_1, kj/kgmole
C *   TIN - feed input temperature, K
C *   TOUT - product output temperature, K
C *   CONS - conversion
C *   FMP1 - feed mole percentage of n-hexane
C *   FMP2 - feed mole percentage of 3-MP
C *   FMP3 - feed mole percentage of 2-MP
C *   FMP4 - feed mole percentage of 2,3-DMB
C *   FMP5 - feed mole percentage of 2,2-DMB
C *   FMP6 - feed mole percentage of inert gas
C *   PMP1 - product mole percentage of n-hexane
C *   PMP2 - product mole percentage of 3-MP
C *   PMP3 - product mole percentage of 2-MP
C *   PMP4 - product mole percentage of 2,3-DMB
C *   PMP5 - product mole percentage of 2,2-DMB
C *   PMP6 - product mole percentage of inert gas
C *   YO(I) - mole fractions of hexane isomers, I=1,5
C *   YO(6) - mole fraction of inert gas
C *   FX(I) - value of linear equation
C *   RK(4) - reverse rate constant, m^3/(kg of cat-hr)
C *   FK(4) - forward rate constant, m^3/(kg of cat-hr)
C *   EK(I) - equilibrium constants, dimensionless
C *   CP(I) - heat capacity of the i-th component at
C *             temperature t, kj/(kgmole-K)
C *   EXC(I) - reaction coordinates, I=1,3
C *   GFERN(I) - gibbs free energy, kj/kgmole
C *   CPV(I,J) - a vector containing heat capacities of
C *                 component i at discrete value of
```

```
C *               temperature, kj/(kgmole-K)
C *   DHRXN(I) - the heat of reaction of the i-th reaction
C *               ,kj/kgmole
C ********************************************************
C
C                  INPUT DESCRIPTION
C
C    The initial guesses are specified in the main program
C  as well as the error criteria and the number of linear
C  equations.  The functions are specified in subroutine
C  FUNC AND FADI, the partial derivatives of the functions
C  with respect to the independent variables are specified
C  in subroutine DER and ADER.
C
C*********************************************************

$storage:2

      INTEGER RC
      DIMENSION X(2),FX(2)
      COMMON /DHRX/TIN,YO(6),yd(6)
      COMMON /ONE/ Q,CDO,CEO,HH1,HH2,HG1,HG2
      COMMON /DATA5/ NC,FTO,NR
      DIMENSION RK(4),FK(4)
      DOUBLE PRECISION CA(5),GFERN(4),DHRXN(4)

C
C      set up data for EZVU
C

      RC=0
      CALL ISPFFV(5,'AI F1',RC,AI,4)
      CALL ISPFFV(6,'TIN F5',RC,TIN,4)
      CALL ISPFFV(7,'TOUT F5',RC,TOUT,4)
      CALL ISPFFV(4,'Q F5',RC,Q,4)
      CALL ISPFFV(6,'FTO F5',RC,FTO,4)
      CALL ISPFFV(4,'W F5',RC,W,4)
      CALL ISPFFV(7,'FMP1 F6',RC,FMP1,4)
      CALL ISPFFV(7,'FMP2 F6',RC,FMP2,4)
      CALL ISPFFV(7,'FMP3 F6',RC,FMP3,4)
      CALL ISPFFV(7,'FMP4 F6',RC,FMP4,4)
      CALL ISPFFV(7,'FMP5 F6',RC,FMP5,4)
      CALL ISPFFV(7,'FMP6 F6',RC,FMP6,4)
      CALL ISPFFV(7,'PMP1 F6',RC,PMP1,4)
      CALL ISPFFV(7,'PMP2 F6',RC,PMP2,4)
      CALL ISPFFV(7,'PMP3 F6',RC,PMP3,4)
      CALL ISPFFV(7,'PMP4 F6',RC,PMP4,4)
      CALL ISPFFV(7,'PMP5 F6',RC,PMP5,4)
      CALL ISPFFV(7,'PMP6 F6',RC,PMP6,4)
C
C      set function keys
C
```

```
      ZF10='QUIT'
      ZCMD='    '
      ZATR='WRI'
      ZF01='CSR1'
      ZF02='CSR2'
C
C     set initial values of function keys
C

      CALL ISPFFV(6,'ZATR C',RC,ZATR,4)
      CALL ISPFFV(6,'ZF01 C',RC,ZF01,4)
      CALL ISPFFV(6,'ZF02 C',RC,ZF02,4)
      CALL ISPFFV(6,'ZF10 C',RC,ZF10,4)
      CALL ISPFFV(6,'ZCMD C',RC,ZCMD,4)
C
C          data for screens cs1,cs2
C      get default values from profile
C

      CALL ISPFF(10,'VGET TIN P',RC)
      CALL ISPFF(8,'VGET Q P',RC)
      CALL ISPFF(10,'VGET FTO P',RC)
      CALL ISPFF(8,'VGET W P',RC)
      CALL ISPFF(11,'VGET FMP1 P',RC)
      CALL ISPFF(11,'VGET FMP2 P',RC)
      CALL ISPFF(11,'VGET FMP3 P',RC)
      CALL ISPFF(11,'VGET FMP4 P',RC)
      CALL ISPFF(11,'VGET FMP5 P',RC)
      CALL ISPFF(11,'VGET FMP6 P',RC)
C
C          start screen inputs
C

 101  ZCMD='    '
      CALL ISPFF(13,'DISPLAY KEYC1',RC)
      CALL ISPFF(12,'DISPLAY CSR1',RC)
         IF(ZCMD.EQ.'QUIT') CALL EXIT
         IF(ZCMD.EQ.'CSR2') GOTO 202
         GOTO 303

 202  ZCMD='    '
      CALL ISPFF(13,'DISPLAY KEYC2',RC)
      CALL ISPFF(12,'DISPLAY CSR2',RC)
         IF(ZCMD.EQ.'QUIT') CALL EXIT
         IF(ZCMD.EQ.'CSR1') GOTO 101
         GOTO 303

 303  ZCMD='    '
C
C        id=1 for adiabatic condition
C        id=2 for isothermal condition
C
```

```
      ID=1
      IF(AI.GT.1.5) ID=2
C
C        assume isothermal case
C

      TOUT=TIN
C
C          input initial mole fraction
C          of n-hexane ------>  YO(1)
C             3-MP ---------->  YO(2)
C             2-MP ---------->  YO(3)
C             2,3-DMB ------->  YO(4)
C             2,2-DMB ------->  YO(5)
C

      YO(1)=FMP1/100.
      YO(2)=FMP2/100.
      YO(3)=FMP3/100.
      YO(4)=FMP4/100.
      YO(5)=FMP5/100.
      YO(6)=FMP6/100.
C
C         let yd(i) be yo(i)
C

      yd=yo
C
C         check initial condition
C

      IF((W.EQ.0.).AND.(ID.EQ.1)) GOTO 555
      IF((W.EQ.0.).AND.(ID.EQ.2)) GOTO 320
C
C         set up data for reaction model
C

      CALL DATAN
C
C        calculate heat capacities
C        and reaction heats
C

      CALL ARRAY
C
C        make initial guesses of Newton's method
C        x(1) = concentration of 2,3-DMB
C        x(2) = concentration of neo-hexane
C
C         unit : (kgmole/m³)
C

      X(1)=10.0
```

```
      X(2)=10.0
C
C      calculate the thermo equilibrium
C       mole fraction of hexane isomers
C

      TINN=TIN
      CALL THEQ(YD,FK,RK,TINN,ID)
C
C
C        convert mole fractions into concentrations,
C          (kgmole/m³)
C
C        cdo = new conc. of 2,3-DMB
C        ceo = new conc. of neo-hexane
C

      CDO=YD(4)*FTO/Q
      CEO=YD(5)*FTO/Q

      IF(ID.EQ.1) GOTO 139
C
C                 perform isothermal condition
C
C                     call Newton's method
C      calculate the output conc. of 2,3-DMB & neo-hexane
C

      CALL NEWTN(X,FX,W,FK,RK,ID,TINN,TOUT)
C
C         From Newton's method, we can find the final
C       conc.s of 2,3-DMB [x(1)] and neo-hexane [x(2)].
C       Then convert  them  into mole fraction, YD(4) and
C       YD(5).
C

      YD(5)=X(2)*Q/FTO
      YD(4)=X(1)*Q/FTO
      GOTO 224
C
C       adiabatic case (id=1)
C

  139 CONTINUE
C
C      assumed the final output temperature
C

      TOUT=TINN+100.
  145 CALL NEWTN(X,FX,W,FK,RK,ID,TINN,TOUT)
```

```
C
C     calculate the conversion the following
C     reaction for adiabatic case:
C
C       2,3-DMB <=======> neo-hexane
C
C
      CONS=W*(FK(4)*X(1)-RK(4)*X(2))/(YD(4)*FTO)
C
C     using average temperature to estimate the
C     heat capacities of 2,3-DMB and neo-hexane
C
      TM=(TINN+TOUT)/2.
      CALL PROP(TM,DHRXN,CA,GFERN)
C
C     check convergence
C
      USUM=CA(5)*TINN*CONS+CA(4)*TINN-CA(4)*TINN*CONS-
           H1*CONS
      DSUM=CA(5)*CONS+CA(4)-CA(4)*CONS
      TF2=USUM/DSUM
      TERML=ABS(TF2-TOUT)
      TOUT=TF2
      IF(TERML.LT.1.0) GOTO 542
      GOTO 145
C
C     end of adiabatic case
C
C
C          print out results of
C          isothermal condition
C
  224 CONTINUE
C
C     calculate the conversion of the following reaction
C        for isothermal case
C
C           2,3-DMB  <====>  neo-Hexane
C
      CONS=W*(FK(4)*X(1)-RK(4)*X(2))/(YD(4)*FTO)
C
C     ****   final outputs to EZVU  ****
C
  320 CONTINUE
```

```
C       ------------> Isothermal condition <------------
C
C         moles of hexane isomers at the end of the
C       reaction (convert into percentage form)
C
C          PMP1 ----> n-hexane
C          PMP2 ----> 3-MP
C          PMP3 ----> 2-MP
C          PMP4 ----> 2,3-DMB
C          PMP5 ----> 2,2-DMB
C          PMP6 ----> inert gas
C

        PMP1=YD(1)*100.
        PMP2=YD(2)*100.
        PMP3=YD(3)*100.
        PMP4=YD(4)*100.
        PMP5=YD(5)*100.
        PMP6=YD(6)*100.

        GOTO 101
C
C           adiabatic condition
C
C           final outputs to EZVU
C

 542    CONTINUE

        YD(5)=YD(5)+YD(4)*CONS
        YD(4)=YD(4)*(1.-CONS)
        CONS=CONS*100.

 555    CONTINUE
C       ------------> Adiabatic  condition <------------
C
C         moles of hexane isomers at the end of the
C       reaction (convert into percentage form)
C
C          PMP1 ----> n-hexane
C          PMP2 ----> 3-MP
C          PMP3 ----> 2-MP
C          PMP4 ----> 2,3-DMB
C          PMP5 ----> 2,2-DMB
C          PMP6 ----> inert gas
C

        PMP1=YD(1)*100.
        PMP2=YD(2)*100.
        PMP3=YD(3)*100.
        PMP4=YD(4)*100.
        PMP5=YD(5)*100.
        PMP6=YD(6)*100.
```

```
      GOTO 101
 666  STOP
      END
C
C         end of the main program !!!
C

C     *******************   ABSTRACT ************************
C     *                                                      *
C     *   THIS SUBROUTINE CALCULATES THE PARTIAL DERIVATIVES*
C     *  OF THE FUNCTIONS WITH RESPECT TO THE INDEPENDENT   *
C     *  VARIABLES. A(I,J) REPRESENTS THE PARTIAL OF THE ith*
C     *  FUNCTION WITH RESPECT TO THE JTH VARIABLE.         *
C     *             (ISOTHERMAL CASE)                       *
C     ******************************************************
C
      SUBROUTINE DER(N,A,FK,RK,W)
      DIMENSION A(2,2)
      COMMON /ONE/Q,CDO,CEO,HH1,HH2,HG1,HG2
      DIMENSION RK(4),FK(4)

      DO 1 I=1,N
      DO 1 J=1,N
    1 A(I,J)=0.0
      A(1,1)=-1.-W/Q*FK(4)
      A(1,2)=RK(4)*W/Q
      A(2,1)=W/Q*FK(4)
      A(2,2)=-1.-W/Q*RK(4)

      RETURN
      END
C     *******************   ABSTRACT ************************
C     *                                                      *
C     *   THIS SUBROUTINE CALCULATES THE PARTIAL DERIVATIVES*
C     *  OF THE FUNCTIONS WITH RESPECT TO THE INDEPENDENT   *
C     *  VARIABLES. A(I,J) REPRESENTS THE PARTIAL OF THE ith*
C     *  FUNCTION WITH RESPECT TO THE JTH VARIABLE.         *
C     *             (ADIABATIC  CASE)                       *
C     ******************************************************
C
      SUBROUTINE ADER(N,A,FK,RK,W)
      DIMENSION A(2,2),RK(4),FK(4)
      COMMON /ONE/ Q,CDO,CEO,HH1,HH2,HG1,HG2

      DO 1 I=1,N
      DO 1 J=1,N
    1 A(I,J)=0.0

      A(1,1)=-HH1-(HH1*W/Q)*FK(4)
      A(1,2)=(HH1*W/Q)*Rk(4)
      A(2,1)=(HH2*W/Q)*FK(4)
      A(2,2)=-HH2-(HH2*W/Q)*RK(4)
```

```
      RETURN
      END
C    * *****************************************************
C    *     THIS SUBROUTINE CALCULATES THE VALUES OF EACH   *
C    *   LINEAR EQUATION GIVEN THE VALUE OF X(I) AND N.    *
C    *  THESE VALUES ARE SUPPLIED TO THIS SUBROUTINE WHEN  *
C    *  IT IS CALLED BY NEWTN. (ISOTHERMAL CASE)           *
C    *******************************************************

      SUBROUTINE FUNC(X,FX,FK,RK,W)
      COMMON /ONE/Q,CDO,CEO,HH1,HH2,HG1,HG2
      DIMENSION RK(4),FK(4),X(2),FX(2)

      FX(1)=CDO-X(1)+W/Q*(RK(4)*X(2)-FK(4)*X(1))
      FX(2)=-X(2)+CEO+W/Q*(FK(4)*X(1)-RK(4)*X(2))

      RETURN
      END
C    * *****************************************************
C    *     THIS SUBROUTINE CALCULATES THE VALUES OF EACH   *
C    *  LINEAR EQUATION GIVEN THE VALUE OF X(I) AND N.     *
C    *  THESE VALUES ARE SUPPLIED TO THIS SUBROUTINE WHEN  *
C    *  IT IS CALLED BY NEWTN. (ADIABATIC CASE)            *
C    *******************************************************

      SUBROUTINE FADI(X,FX,FK,RK,W,T1,T2)
      COMMON /ONE/ Q,CDO,CEO,HH1,HH2,HG1,HG2
      DIMENSION RK(4),FK(4),X(2),FX(2)
      DOUBLE PRECISION CA(5),DHRXN(4),GFERN(4)

      CALL PROP(T1,DHRXN,CA,GFERN)
      CA3=CA(4)
      CA4=CA(5)
      H1=DHRXN(4)
      TM=(T1+T2)/2.
      CALL PROP(TM,DHRXN,CA,GFERN)
      CA1=CA(4)
      CA2=CA(5)
      HH1=-CA1*(T2-298.15)-176.80*1000.
      HH2=-CA2*(T2-298.15)-184.68*1000.
      HG1=-(T1-298.15)*CA3-176.8*1000.
      HG2=-(T1-298.15)*CA4-184.68*1000.
      FX(1)=-HH1*X(1)+CDO*HG1+(W/Q)*(RK(4)*X(2)*HH1-
     &       FK(4)*X(1)*HH1)
      FX(2)=-HH2*X(2)+CEO*HG2+(W/Q)*(FK(4)*X(1)*HH2-
     &       RK(4)*X(2)*HH2)

      RETURN
      END
C    ****************** ABSTRACT ***********************
C    *                                                  *
C    *      THIS SUBROUTINE EMPLOYES NEWTON'S METHOD IN *
C    *    ORDER TO SOLVE A SET OF N LINEAR EQUATIONS    *
C    *    CONTAINING N UNKNOWNS.  THIS SUBROUTINE IS    *
```

```
C    *    CALLED BY THE MAIN PROGRAM AND IS CCSUPPLIED     *
C    *    THE VALUES OF THE INITIAL GUESS FOR X(I)'S AS    *
C    *    WELL AS THE VALUE OF N.  THIS SUBROUTINE USES    *
C    *    THE VALUES OF THE FUNCTION FROM FUNC AND THE     *
C    *    VALUES OF THE PARTIAL DERIVATIVES OF THE         *
C    *    FUNCTION IN ORDER TO DETERMINE THE SOLUTION.     *
C    *    THIS C METHOD USES THE LIBRARY ROUTINE LINPAC    *
C    *    TO SOLVE THE C SYSTEM OF LINEAR EQUATION USED    *
C    *    BY NEWTON'S METHOD.                              *
C    ******************************************************
C
      SUBROUTINE NEWTN(X,FX,W,FK,RK,ID,T,T2)
      DIMENSION A(2,2),X(2),FX(2),B(2),RAT(2),FK(4),RK(4)

      DOUBLE PRECISION AA(2,2),BB(2),XX(2)
      INTEGER IPVT(2)

      N=2
      ERLIM=1.0E-3

    1 CONTINUE
      ITEST=0
C
C          MAKE FUNCTION EVALUATIONS
C

      IF (ID.EQ.1) GOTO 10
      CALL FUNC(X,FX,FK,RK,W)
      GOTO 4

   10 CALL FADI(X,FX,FK,RK,W,T,T2)
C
C           set up constant terms
C           in jacobian matrix
C

    4 DO 3 I=1,N
    3 B(I)=-FX(I)
C
C         evaluate JACOBIAN matrix
C

      IF(ID.EQ.1) GOTO 15
      CALL DER(N,A,FK,RK,W)
      GOTO 20

   15 CALL ADER(N,A,FK,RK,W)
C
C         establish coefficients
C         in jacobian matrix
C

   20 DO 32 I=1,N
```

```
      DO 32 J=1,N
   32 AA(I,J)=A(I,J)
      DO 35 I=1,N
   35 BB(I)=B(I)
C
C      Using linpac to solve jacobian matrix
C
C         CALL LINEAR EQUATION SOLVER
C

      CALL LINPAC(N,AA,BB,XX,IPVT)
C
C      make an improved value for x(i)
C

      DO 5 I=1,N
      RAT(I)=XX(I)/X(I)
    5 X(I)=X(I)+XX(I)
C
C       CHECK FOR CONVERGENCE
C

      DO 125 I=1,N
  125 IF(ABS(RAT(I)).GT.ERLIM)ITEST=ITEST+1
      IF(ITEST.NE.0)GO TO 1
      RETURN
      END
C
C         This subroutine supplied the majority of the
C      data for the CSCTR reactor model. Feed conditions,
C      stoichiometric coefficients of reaction model.
C

      SUBROUTINE DATAN
      COMMON /DHRX/ TIN,YO(6),YD(6)
      COMMON /DATA5/ NC,FTO,NR
      COMMON /DATA6/ GAM(5,4)

C
C      The number of reactions
C

      NR=4
C
C      THE NUMBER OF COMPONENTS,
C      (except  the inert gas because it
C      dosen't react with other reactants)
C

      NC=5
```

```
C
C      The stoichiometric coefficients
C        **  INITIALIZE GAM(I,J) **
C
      DO 1 I=1,NC
      DO 1 J=1,NR
    1 GAM(I,J)=0.0
C
C      (1) n-HEXANE <———> (1) 3-methylpantane
C       |                  |
C       └———>GAM(1,1)      └———>GAM(2,1)
C
      GAM(1,1)=-1.0
      GAM(2,1)=1.0
C
C     (1) 3-methylpantane <———> (1) 2-methylpantane
C      |                         |
C      └———>GAM(2,2)             └———>GAM(3,2)
C
      GAM(2,2)=-1.0
      GAM(3,2)=1.0
C
C     (1) 2-methylpantane <———> (1) 2,3-dimethylbutane
C      |                         |
C      └———>GAM(3,3)             └———>GAM(4,3)
C
      GAM(3,3)=-1.0
      GAM(4,3)=1.0
C
C     (1) 2,3-dimethylbutane <———> (1) 2,2-dimethylbutane
C      |                            |
C      └———>GAM(4,4)                └———>GAM(5,4)
C
      GAM(4,4)=-1.0
      GAM(5,4)=1.0

      RETURN
      END
C     *******************************************************
C     *     THIS SUBROUTINE CALCULATES THE HEAT CAPACITIES  *
C     *   OF EACH SPECIES AND THE HEATS OF REACTION AT T    *
C     *   (K).                                              *
C     *******************************************************

      SUBROUTINE ARRAY
      COMMON /DATA5/ NC,FTO,NR
      COMMON /DATA6/ GAM(5,4)
      COMMON /DHRX/ TIN,YO(6),YD(6)
```

```
      COMMON /VECTR/ DHRXV(4,150),CPV(5,150),GFERV(4,150)
      DOUBLE PRECISION SUM,SUM1
C
C        decide the integration interval
C       (temp range from 298.15  to 1000 K)
C
      TI=298.15
      DT=(1000.-TI)/90.
C
C      REACTION HEAT (KJ/KGMOLE)  AT 298.15 K
C
C        n-HEXANE <-------> 3-METHYLPANTANE (3-MP)
C
      DHRXV(1,1)=-5.050*1000.
C
C        REACTION HEAT (KJ/KGMOLE) AT 298.15 K
C
C        3-METHYLPANTANE <-------> 2-METHYLPANTANE
C
      DHRXV(2,1)=-2.580*1000.
C
C        REACTION HEAT (KJ/KGMOLE) AT 298.15 K
C
C       2-METHYLPANTANE <-------> 2,3-DIMETHYLBUTANE
C
      DHRXV(3,1)=-2.250*1000.
C
C        REACTION HEAT (KJ/KGMOLE) AT 298.15 K
C
C      2,3-DIMETHYLBUTANE <-------> 2,2-DIMETHYLBUTANE
C
      DHRXV(4,1)=-7.880*1000.
C++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
C   CALCULATE REACTION HEAT AT EVERY T+DT, (KJ/KGMOLE)
C---------     From T=298.15 K TO 1000 K   ------
C  For example: 1st reaction
C        n-Hexane -----> 3-Methylpantane
C
C
C               ⌠T2
C               | (Cp'-Cp)dT = heat of reaction
C               ⌡T1
C
C       where  Cp'= heat capacity of 3-MP
C              Cp = heat capacity of n-Hexane
C
C
```

```
C  p.s. 1st reaction: I=1
C                     TI=298.15 K (referance temp)
C                     sum=0.0
C                     K=2
C     we want to evaluate reaction heat at 305.98 K (TI+DT)
C        sum=0.0+DT*GAM(1,1)*Cp(1,305.98)=-DT*Cp(1,305.98)
C        sum=sum+DT*GAM(2,1)*Cp(2,305.98)=-DT*Cp(1,305.98)
C                +DT*1*Cp(2,305.98)
C        sum=sum+DT*GAM(3,1)*Cp(3,305.98)=-DT*Cp(1,305.98)
C               +DT*Cp(2,305.98)+DT*0.0*Cp(3,305.98)
C           =-DT*Cp(1,305.98)+DT*Cp(2,305.98)
C        sum=sum+DT*GAM(4,1)*Cp(4,305.98)
C           =-DT*Cp(1,305.98)+DT*Cp(2,305.98)
C        sum=sum+DT*GAM(5,1)*Cp(5,305.98)
C           =-DT*Cp(1,305.98)+DT*Cp(2,305.98)
C
C      Therefore, heat of reaction with respect to reference
C temp is  delta H= DT*( Cp(2,305.98)-Cp(1,305.98))
C
C+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++

      DO 4 I=1,NR
      TI=298.15
      SUM=0.0D0
      DO 5 K=2,91
      TI=TI+DT
      DO 6 J=1,NC
      SUM=SUM+DT*GAM(J,I)*CP(J,TI)
  6   CONTINUE

      IF (TI.GT.1000.) GOTO 4
C
C         new value of reaction heat
C         at (t+dt) with respect to 298.15 K
C

      DHRXV(I,K)=DHRXV(I,K-1)+sum

  5   SUM=0.0D0

  4   CONTINUE
C
C       CALCULATE THE GIBBS ENERGY OF FORMATION
C                OF EACH REACTION
C                 GFERV(I,J), (KJ/KGMOLE)
C
C      For example: 1st reaction
C               reference temp=298.15 K
C               DT=7.8 K
C               new temp to evaluate : 305.9 K
C               suml=0.0
C
C               n-Hexane <-----> 3-methylpantane
```

```
C       Show steps:
C          suml=GAM(1,1)*GF(1,305.9)+suml
C              =-1*GF(1,305.9)+0.0
C
C          suml=GAM(2,1)*GF(2,305.9)+suml
C              = 1*GF(2,305.9)-GF(1,305.9)
C          suml=GAM(3,1)*GF(3,305.9)+suml
C              =GF(2,305.9)-GF(1,305.9)
C          suml=GAM(4,1)*GF(4,305.9)+suml
C              =GF(2,305.9)-GF(1,305.9)
C          suml=GAM(5,1)*GF(5,305.9)+suml
C              =GF(2,305.9)-GF(1,305.9)
C
C           Therefore, Gibbs energy of formation
C       of 1st reaction at t+dt
C             GFERV(1,305.9)=suml
C
C

      DO 34 I=1,NR
      TI=298.15
      SUM1=0.0
      DO 35 K=2,91
      TI=TI+DT
      DO 36 J=1,NC
      SUM1=GAM(J,I)*GF(J,TI)+SUM1
  36  CONTINUE
      IF (TI.GT.1000.) GO TO 34
      GFERV(I,K)=SUM1
  35  SUM1=0.0

  34  CONTINUE
C
C          SET UP CPV(I,J) ——>> convert every value of
C        Cp(I,TI) into vector in order to use linear
C       interpolation
C
      DO 10 I=1,NC
      TI=298.15

      DO 11 J=1,90
      CPV(I,J)=CP(I,TI)
  11  TI=TI+DT
  10  CONTINUE
      RETURN
      END
C
C         This function subroutine calculates the heat
C       capacity of each species from 200 - 1000 (K)
C       (KJ/KGMOLE-K)
C

      FUNCTION CP(I,T)
```

```
      IF (I.EQ.1) GOTO 1
      IF (I.EQ.2) GOTO 2
      IF (I.EQ.3) GOTO 3
      IF (I.EQ.4) GOTO 4
      IF (I.EQ.5) GOTO 5

    1 CP=(-1.0540+1.39E-1*T-7.449E-5*T²+1.551E-8*T³)*4.184
      RETURN
    2 CP=(-0.570+1.359E-1*T-6.854E-5*T²+1.202E-8*T³)*4.184
      RETURN
    3 CP=(-2.5240+1.477E-1*T-8.533E-5*T²+1.931E-8*T³)*4.184
      RETURN
    4 CP=(-3.489+1.469E-1*T-8.063E-5*T²+1.629E-8*T³)*4.184
      RETURN
    5 CP=(-3.973+1.503E-1*T-8.314E-5*T²+1.636E-8*T³)*4.184
      RETURN
      END
C
C        This function calculates the gibbs free
C        energy of formation of hexane isomers
C        from 200-1000°K, KJ/KGMOLE
C

      FUNCTION GF(I,T)
      IF (I.EQ.1) GOTO 1
      IF (I.EQ.2) GOTO 2
      IF (I.EQ.3) GOTO 3
      IF (I.EQ.4) GOTO 4
      IF (I.EQ.5) GOTO 5

    1 GF=-0.000087*T³+0.219336*T²+453.119366*T-151738.80896
      RETURN
    3 GF=-0.000092*T³+0.225563*T²+458.412884*T-158998.25354
      RETURN
    2 GF=-0.000085*T³+0.216435*T²+460.331617*T-156934.60254
      RETURN
    5 GF=-0.000092*T³+0.224945*T²+481.313618*T-169166.74548
      RETURN
    4 GF=-0.000091*T³+0.22493*T²+473.536175*T-161194.52295
      RETURN
      END

C
C        This subroutine calculates the rate constants,
C      heat capacitites and also the output temperature of
C      reaction n-hexane ———> 2,3-DMB
C

      SUBROUTINE THEQ(YO,FK,RK,T,ID)
      COMMON /DATA5/ NC,FTO,NR
      COMMON /DATA6/ GAM(5,4)
      DIMENSION EK(4),FK(4),RK(4),YO(6)
      DOUBLE PRECISION CA(5),DHRXN(4),GFERN(4)
```

```
      DOUBLE PRECISION EXC(3)
C
C         Calculate the heats of reactions, heat
C       capacities and gibbs energies at any temp
C       between (298 -1000 K)
C           Using linear interpolation
C
      CALL PROP(T,DHRXN,CA,GFERN)
C
C         Calculate the equilibrium constants,
C       forward and reverse rate constants
C
     CALL EQCON(EK,FK,RK,GFERN,T)
C
C         calculate the equilibrium mole fractions
C                of hexane isomers
C       Using 'LINPAC' To Solve Reaction Coordinates
C
      CALL SLTRES(EK,YO,EXC)
      IF(ID.EQ.2) GOTO 100
C
C         do energy balance
C
      CALL ENGBALS(YO,EXC,DHRXN,T)

 100  RETURN
      END

C
      SUBROUTINE ENGBALS(YO,EXC,DHRXN,T)
      COMMON /DATA5/ NC,FTO,NR
      DOUBLE PRECISION EXC(3),DHRXN(4),CA(5),GFERN(4)
      DIMENSION YO(6),EK(4),FK(4),RK(4)

C
C         input term =0
C

C
C        disappearance term
C

      SDIS=0.0
      DO 20 I=1,3
 20   SDIS=EXC(I)*FTO*DHRXN(I)+SDIS

C
C        input=output+acc+disapp
C
```

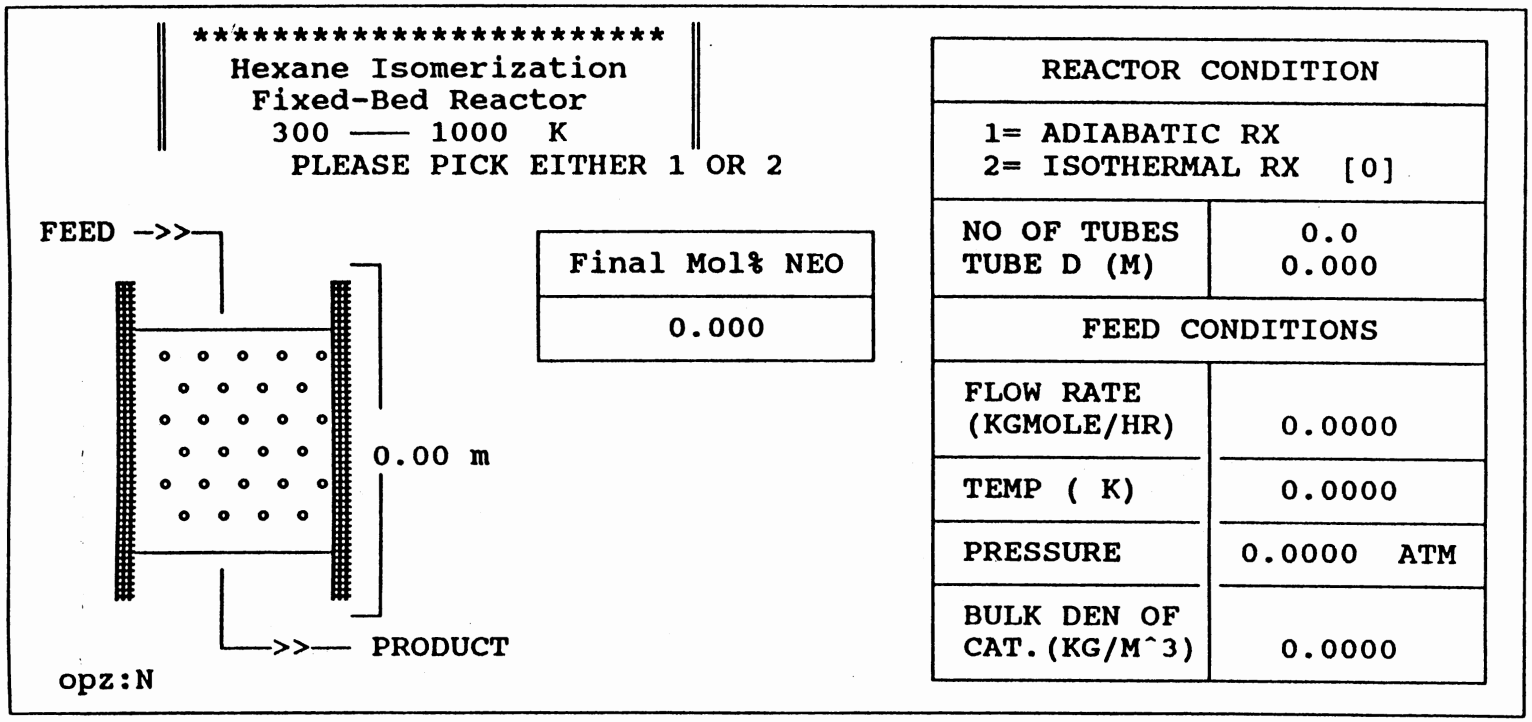
```
      DIF=-SDIS
C     ┌───────────────┐
C     │  output term  │
C     └───────────────┘

      TM=T
      TE=T
      INX=1
 50   CALL PROP(TM,DHRXN,CA,GFERN)
      SOUT=0.0
      DO 25 I=1,4
 25   SOUT=SOUT+(TE-T)*CA(I)*YO(I)*FTO
      ERM1=ABS(DIF-SOUT)
      IF(INX.EQ.1) GOTO 77
      ERM=ERM2-ERM1
      IF(ERM.LT.0.) GOTO 100
 77   ERM2=ERM1
      TE=TE+0.2
      INX=INX+1
      CALL PROP(TE,DHRXN,CA,GFERN)
      CALL EQCON(EK,FK,RK,GFERN,TE)
      CALL SLTRES(EK,YO,EXC)
      TM=(TE+T)/2.
      GOTO 50
100   T=TE

110   RETURN
      END

C ***********************************************************
C *     THIS SUBROUTINE CALCULATES THE HEAT CAPACITY AND   *
C *   THE HEATS OF REACTIONS FOR A GIVEN TEMPERATURE BY    *
C *   LINEARLY INTERPOLATING BETWEEN VALUES OF CPV(I,J) AND*
C *   DHRXV(I,J), RESPECTIVELY.                            *
C ***********************************************************

      SUBROUTINE PROP(T,DHRXN,CA,GFERN)
      DOUBLE PRECISION DHRXN(4),CA(5),GFERN(4)
      COMMON /VECTR/ DHRXV(4,150),CPV(5,150),GFERV(4,150)
      COMMON /DATA5/ NC,FTO,NR

      DT=(1000.-298.15)/90.
      I=IFIX((T-298.15)/DT)+1
      PRO=(T-298.15-DT*FLOAT(I-1))/DT
C   ┌─────────────────────────────────┐
C   │  CALCULATE THE HEATS OF REACTIONS│
C   │  AT SPECIFIED TEMP, KJ/KGMOLE    │
C   └─────────────────────────────────┘

      DO 1 J=1,NR
  1   DHRXN(J)=DHRXV(J,I)+PRO*(DHRXV(J,I+1)-DHRXV(J,I))
```

```
C
C   CALCULATE THE HEAT CAPACITIES OF
C   ISOMERS AT SPECIFIED TEMP, KJ/KGMOLE-K
C
      DO 2 J=1,NC
    2 CA(J)=CPV(J,I)+PRO*(CPV(J,I+1)-CPV(J,I))
C
C     CALCULATE THE GIBBS ENERGIES
C     AT SPECIFIED TEMP, (KJ/KGMOLE)
C
      DO 3 J=1,NR
    3 GFERN(J)=GFERV(J,I)+PRO*(GFERV(J,I+1)-GFERV(J,I))

      RETURN
      END
C **********************************************************
C *     THIS SUBROUTINE CALCULATES THE EQUILIBRIUM          *
C *  CONSTANTS OF EACH REACTION AND THE FORWARD AND REVERSE*
C *  REACTION RATE CONSTANTS.                               *
C **********************************************************

      SUBROUTINE EQCON(EK,FK,RK,GFERN,T)
      DIMENSION EK(4),FK(4),RK(4)
      DOUBLE PRECISION GFERN(4)
C
C   CALCULATE EQUILIBRIUM CONSTANT OF NORMAL
C   HEXANE TO IT'S ISOMERS
C      delta G=-RT*lnK
C

      DO 5 I=1,4
    5 EK(I)=EXP(-GFERN(I)/(8.314*T))
C
C   CALCULATE REVERSE REACTION RATE CONSTANTS,
C   (FT³/LB of CAT-HR)
C             kr=k*exp(-E/RT)
C

      TR=9./5.*(T-273.15)+32.+459.67
      RK(4)=5.24*1000.* EXP(-9.55*1000./1.987/TR)
C
C    CALCULATE FORWARD REACTION
C    RATE CONSTANTS, (FT³/LB-HR)
C        K=kf/kr ———> kf=K*kr
C

      FK(4)=RK(4)*EK(4)
C
C   CONVERT FORWARD AND REVERSE
C   RATE CONSTANTS TO, M³/KG-HR)
C
      FK(4)=FK(4)*0.06243
      RK(4)=RK(4)*0.06243
```

```
      RETURN
      END
C **********************************************************
C *    THIS SUBROUTINE SOLVE 3 EQUATIONS SIMULTANEOUSLY IN *
C *  ORDER TO FIND THE THERMODYNAMIC EQUILIBRIUM MOLE      *
C *  FRACTION OF N-HEXANE, 3-MP, 2-MP, 2,3-DMB.            *
C **********************************************************

      SUBROUTINE SLTRES(EK,YO,EXC)
      DOUBLE PRECISION A(3,3),B(3),EXC(3)

      DIMENSION EK(4),YO(10)
      INTEGER IPVT(3)

C*** NOTE THAT A,B,X,IPVT MUST BE DOUBLE PRECISIONED AND
DIMENSIONED BY
C
C---- NUMBER OF UNKNOWNS (REACTION COORDINATES) C
      N=3
C---------------------------

C  ZERO B(I) AND A(I,J)

      DO 1 I=1,N
      B(I)=0.0
      DO 1 J=1,N
    1 A(I,J)=0.0

C  SET THE NONZERO VALUES OF A(I,J) AND B(I)

      A(1,1)=EK(1)+1.
      A(1,2)=-1.
      A(2,1)=EK(2)
      A(2,2)=-EK(2)-1.
      A(2,3)=1.
      A(3,2)=EK(3)
      A(3,3)=-EK(3)-1.
      B(1)=YO(1)*EK(1)-YO(2)
      B(2)=YO(3)-YO(2)*EK(2)
      B(3)=YO(4)-EK(3)*YO(3)
C  SOLVE REACTION COORDINATES EXC(1),EXC(2),EXC(3)

      CALL LINPAC(N,A,B,EXC,IPVT)
      YO(1)=YO(1)-EXC(1)
      YO(2)=YO(2)+EXC(1)-EXC(2)
      YO(3)=YO(3)+EXC(2)-EXC(3)
      YO(4)=YO(4)+EXC(3)
      YO(5)=YO(5)

      RETURN
      END
```

APPENDIX C

LISTING OF CONTROL PANELS



```
*************************
Hexane Isomerization
Fixed-Bed Reactor
300 —— 1000  K
PLEASE PICK EITHER 1 OR 2
```

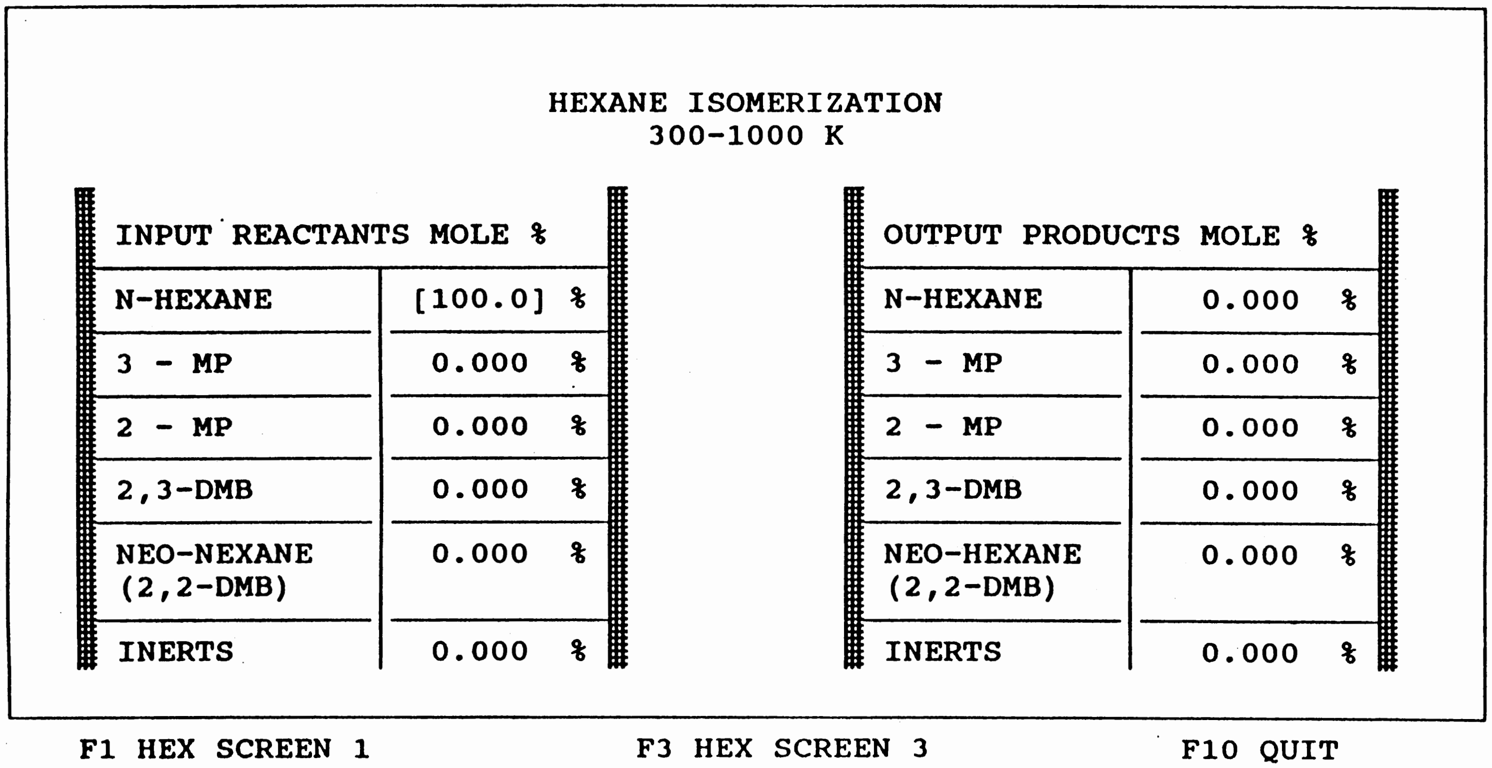
Final Mol% NEO
0.000

REACTOR CONDITION	
1= ADIABATIC RX 2= ISOTHERMAL RX [0]	
NO OF TUBES TUBE D (M)	0.0 0.000
FEED CONDITIONS	
FLOW RATE (KGMOLE/HR)	0.0000
TEMP (K)	0.0000
PRESSURE	0.0000 ATM
BULK DEN OF CAT.(KG/M^3)	0.0000

opz:N

F2 HEX SCREEN 2   F3 HEX SCREEN 3   F10 QUIT

Figure 18. Control Panel 1 for Fixed-Bed Reactor Initial Parameter Settings



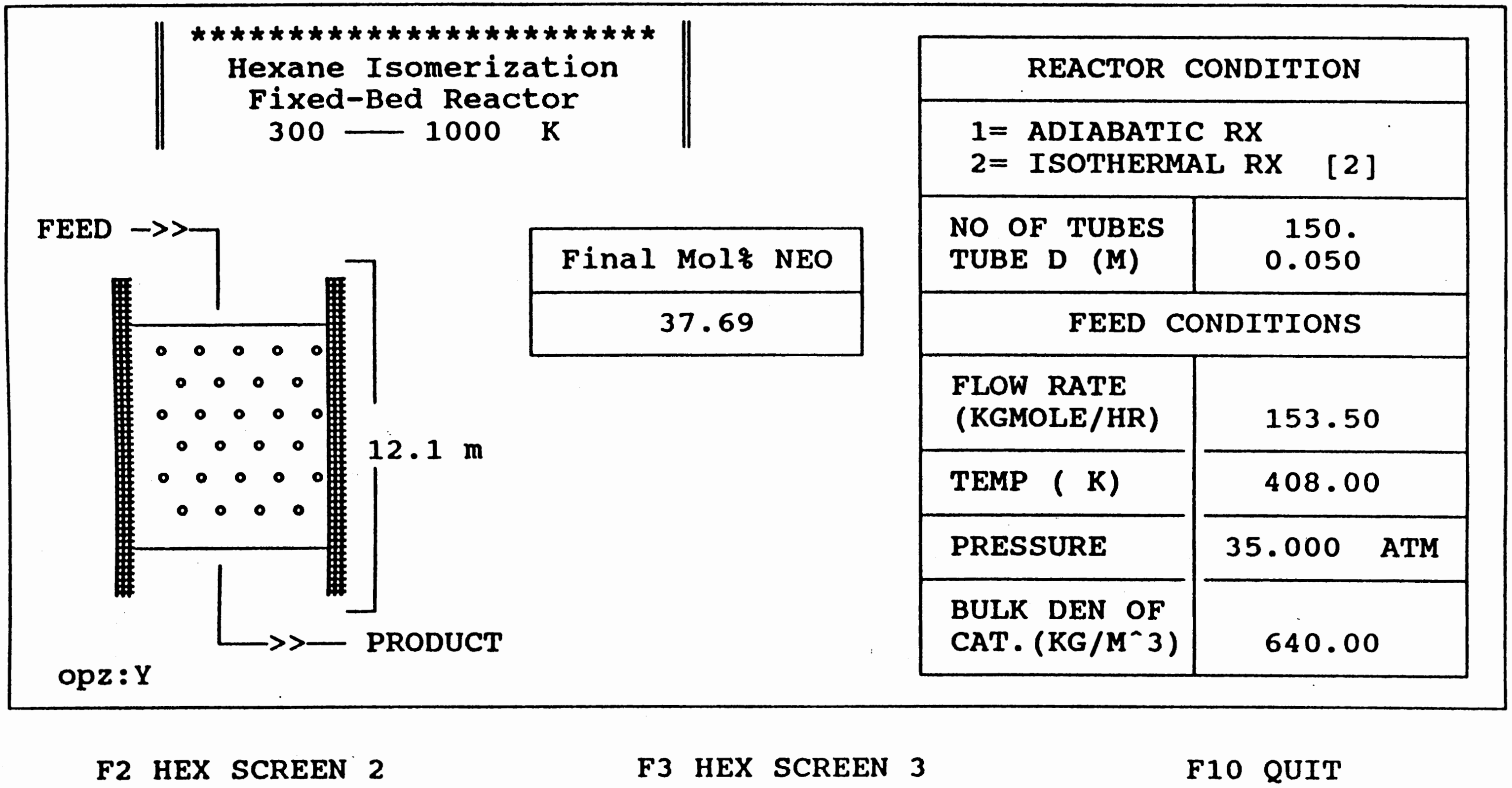
HEXANE ISOMERIZATION
300-1000 K

INPUT REACTANTS MOLE %	
N-HEXANE	[100.0] %
3 - MP	0.000 %
2 - MP	0.000 %
2,3-DMB	0.000 %
NEO-NEXANE (2,2-DMB)	0.000 %
INERTS	0.000 %

OUTPUT PRODUCTS MOLE %	
N-HEXANE	0.000 %
3 - MP	0.000 %
2 - MP	0.000 %
2,3-DMB	0.000 %
NEO-HEXANE (2,2-DMB)	0.000 %
INERTS	0.000 %

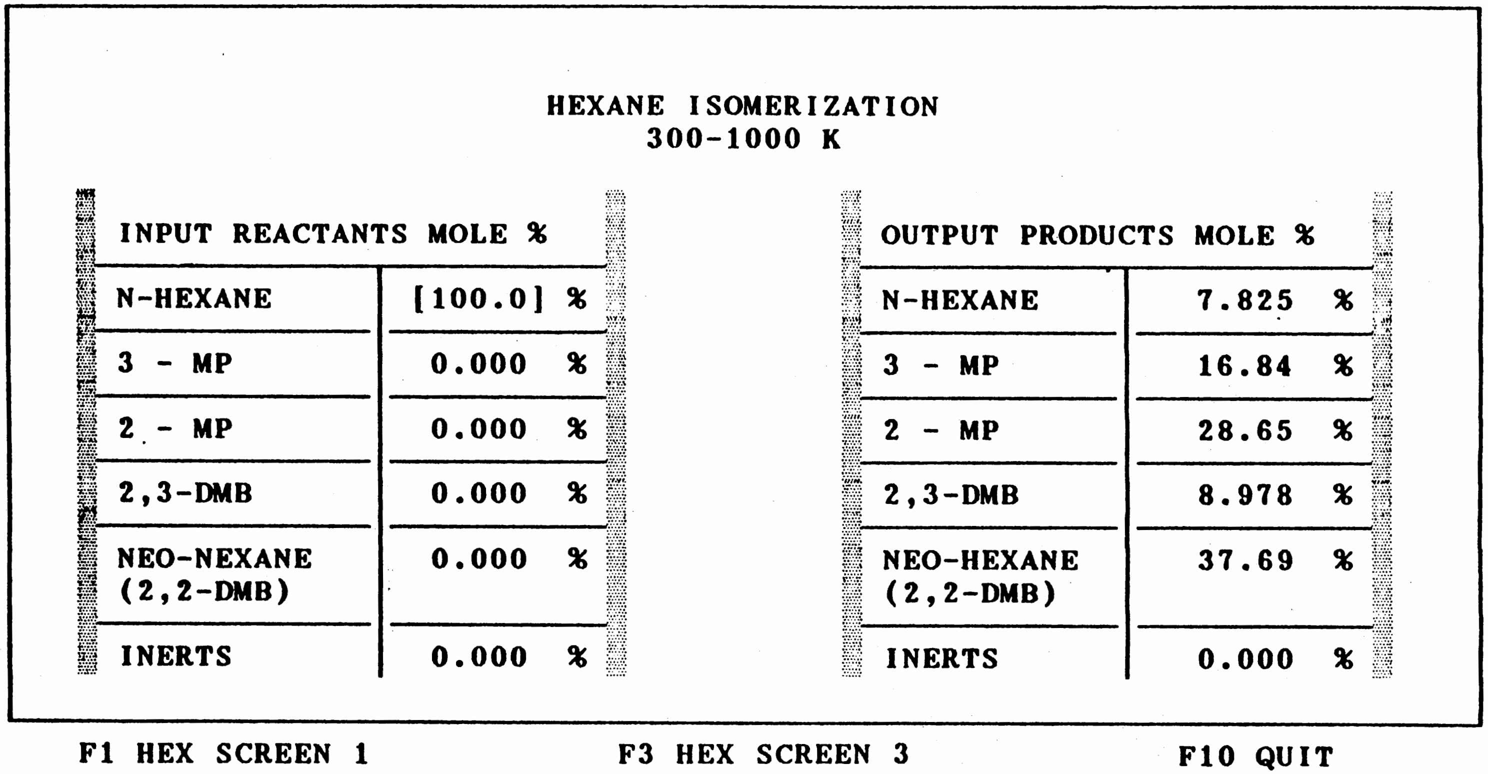
F1 HEX SCREEN 1 F3 HEX SCREEN 3 F10 QUIT

Figure 19. Control Panel 2 for Fixed-Bed Reactor
Initial Parameter Settings



```
*************************
Hexane Isomerization
Fixed-Bed Reactor
300 —— 1000  K

Final Mol% NEO
37.69

opz:Y

REACTOR CONDITION
1= ADIABATIC RX
2= ISOTHERMAL RX   [2]

NO OF TUBES             150.
TUBE D (M)              0.050

FEED CONDITIONS
FLOW RATE
(KGMOLE/HR)             153.50
TEMP ( K)               408.00
PRESSURE                35.000  ATM
BULK DEN OF
CAT.(KG/M^3)            640.00

F2 HEX SCREEN 2          F3 HEX SCREEN 3          F10 QUIT
```

Figure 20. Control Panel 1 for Fixed-Bed Reactor Optimized Model, Isothermal Reaction

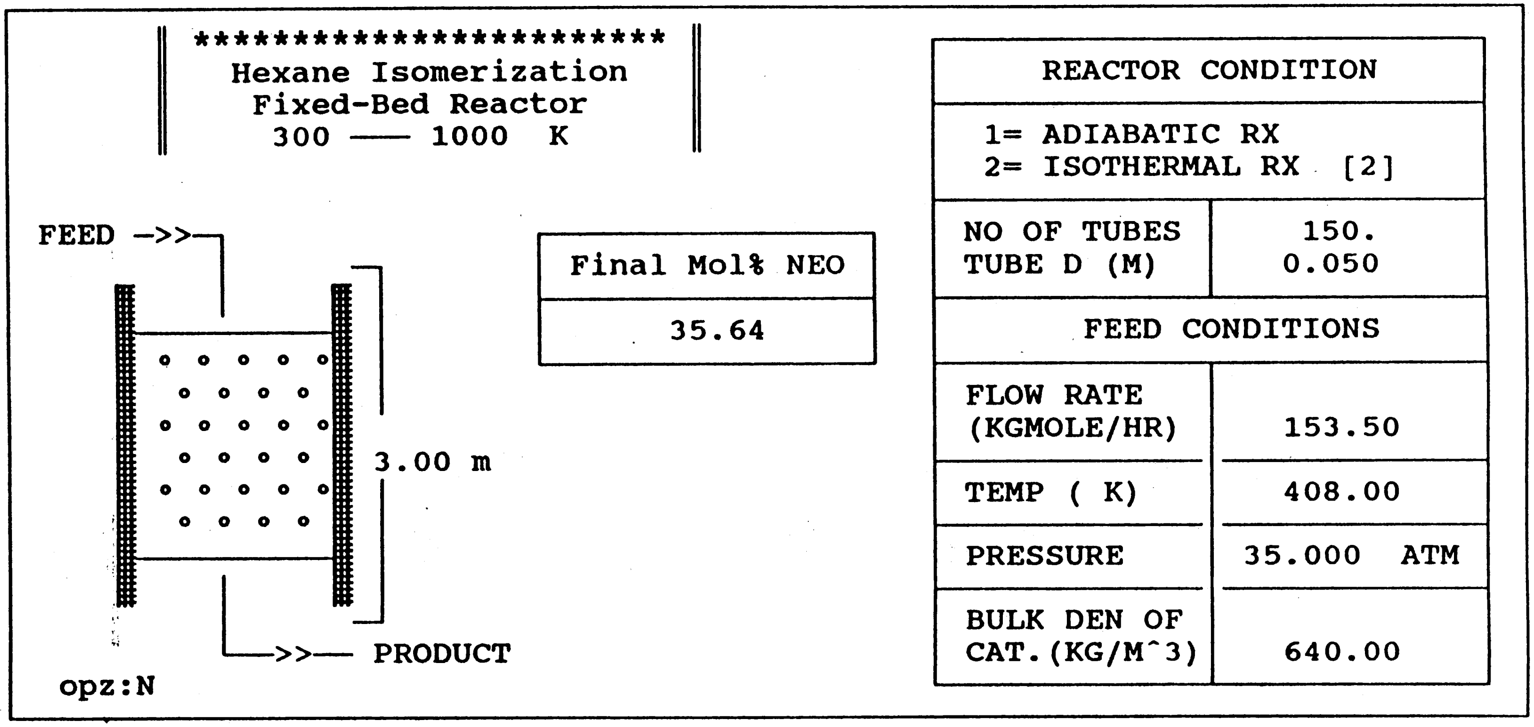


HEXANE ISOMERIZATION
300-1000 K

INPUT REACTANTS MOLE %	
N-HEXANE	[100.0] %
3 - MP	0.000 %
2 - MP	0.000 %
2,3-DMB	0.000 %
NEO-NEXANE (2,2-DMB)	0.000 %
INERTS	0.000 %

OUTPUT PRODUCTS MOLE %	
N-HEXANE	7.825 %
3 - MP	16.84 %
2 - MP	28.65 %
2,3-DMB	8.978 %
NEO-HEXANE (2,2-DMB)	37.69 %
INERTS	0.000 %

Figure 21. Control Panel 2 for Fixed-Bed Reactor Optimized Model, Isothermal Reaction



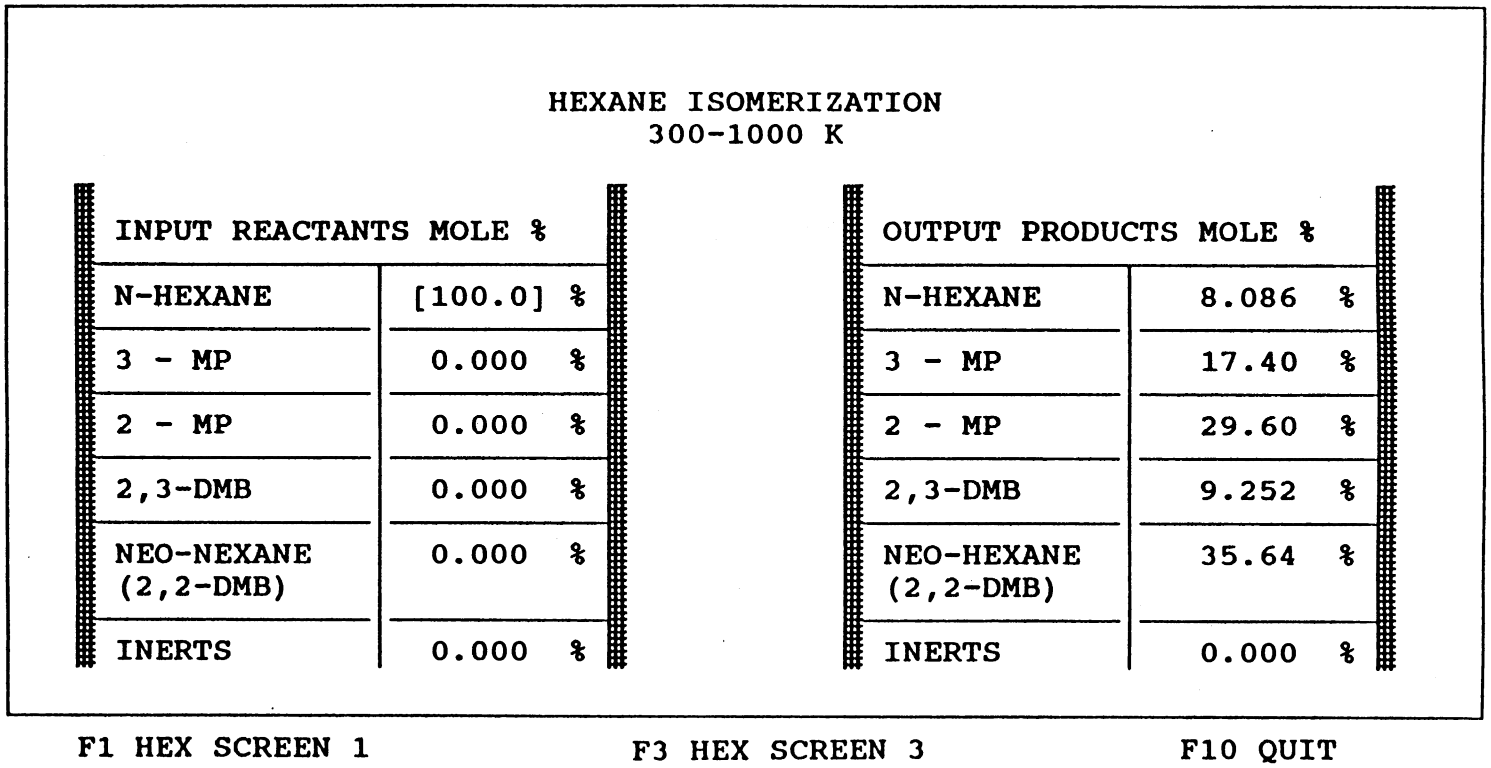
****
Hexane Isomerization
Fixed-Bed Reactor
300 —— 1000 K

Final Mol% NEO
35.64

REACTOR CONDITION	
1= ADIABATIC RX 2= ISOTHERMAL RX [2]	
NO OF TUBES TUBE D (M)	150. 0.050
FEED CONDITIONS	
FLOW RATE (KGMOLE/HR)	153.50
TEMP (K)	408.00
PRESSURE	35.000 ATM
BULK DEN OF CAT.(KG/M^3)	640.00

F2 HEX SCREEN 2 F3 HEX SCREEN 3 F10 QUIT

Figure 22. Control Panel 1 for Fixed-Bed Reactor
Fixed-Length Model, Isothermal Reaction



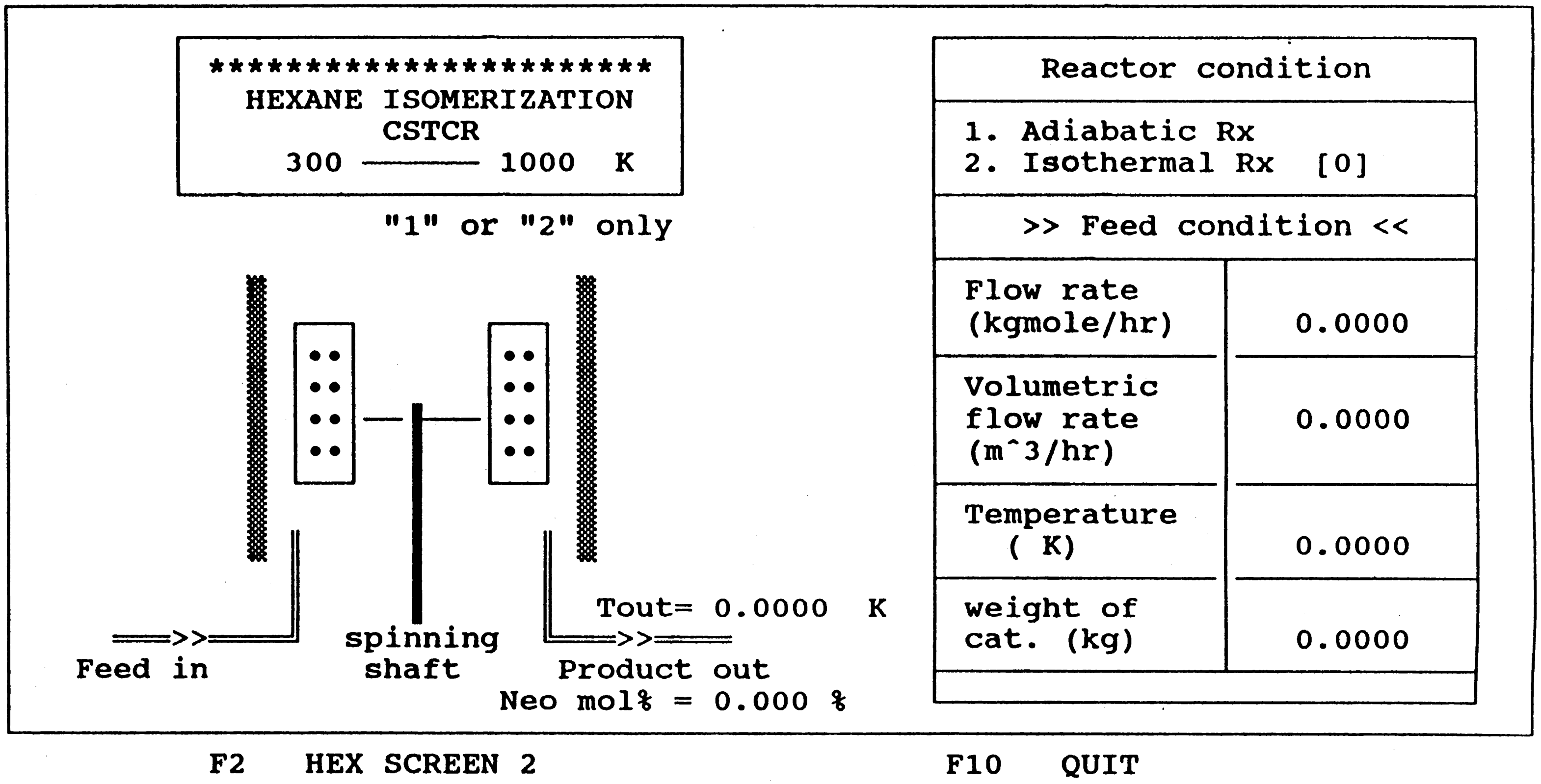
HEXANE ISOMERIZATION
300-1000 K

INPUT REACTANTS MOLE %	
N-HEXANE	[100.0] %
3 - MP	0.000 %
2 - MP	0.000 %
2,3-DMB	0.000 %
NEO-NEXANE (2,2-DMB)	0.000 %
INERTS	0.000 %

OUTPUT PRODUCTS MOLE %	
N-HEXANE	8.086 %
3 - MP	17.40 %
2 - MP	29.60 %
2,3-DMB	9.252 %
NEO-HEXANE (2,2-DMB)	35.64 %
INERTS	0.000 %

F1 HEX SCREEN 1 F3 HEX SCREEN 3 F10 QUIT

Figure 23. Control Panel 2 for Fixed-Bed Reactor
Fixed-Length Model, Isothermal Reaction

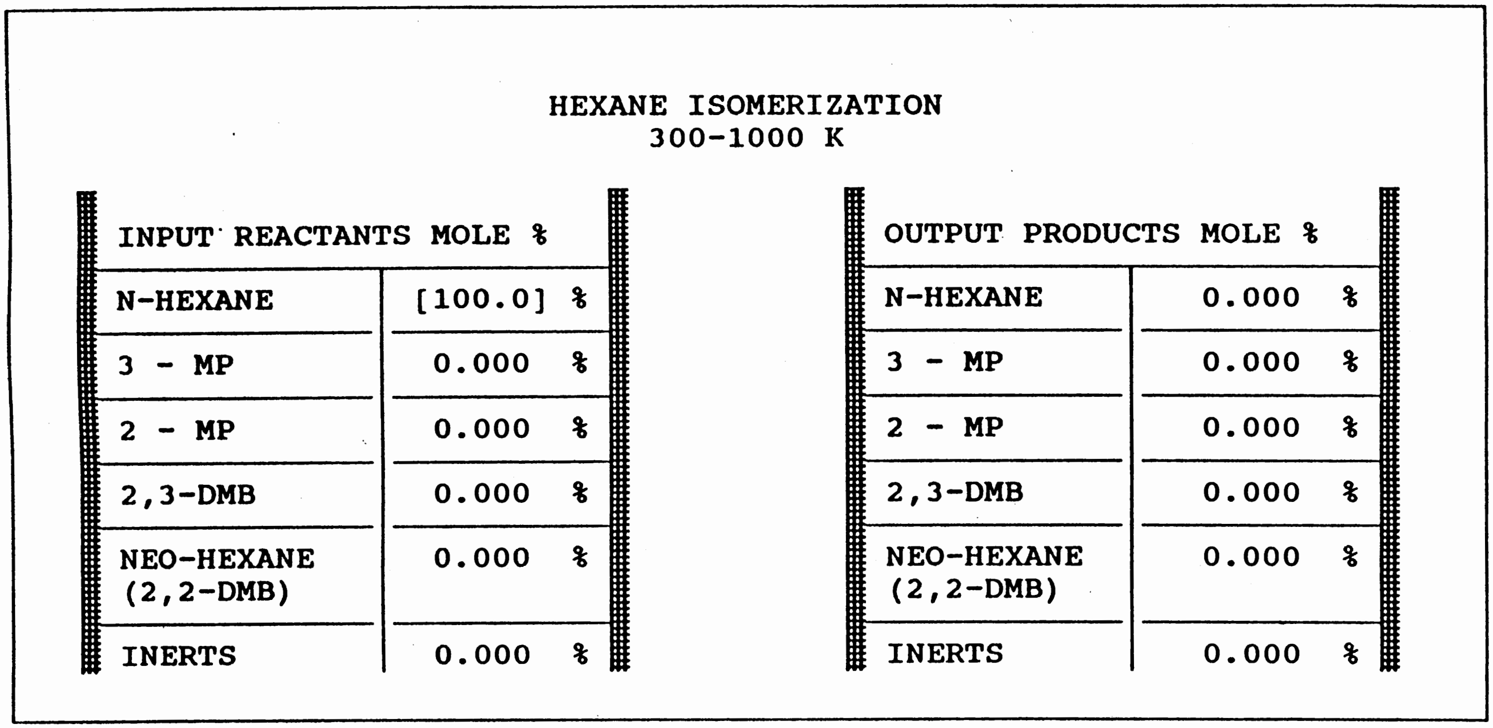


Tout= 0.0000 K

Neo mol% = 0.000 %

Reactor condition	
1. Adiabatic Rx 2. Isothermal Rx [0]	
>> Feed condition <<	
Flow rate (kgmole/hr)	0.0000
Volumetric flow rate (m^3/hr)	0.0000
Temperature (K)	0.0000
weight of cat. (kg)	0.0000

Figure 24. Control Panel 1 for CSTCR
Initial Parameter Settings



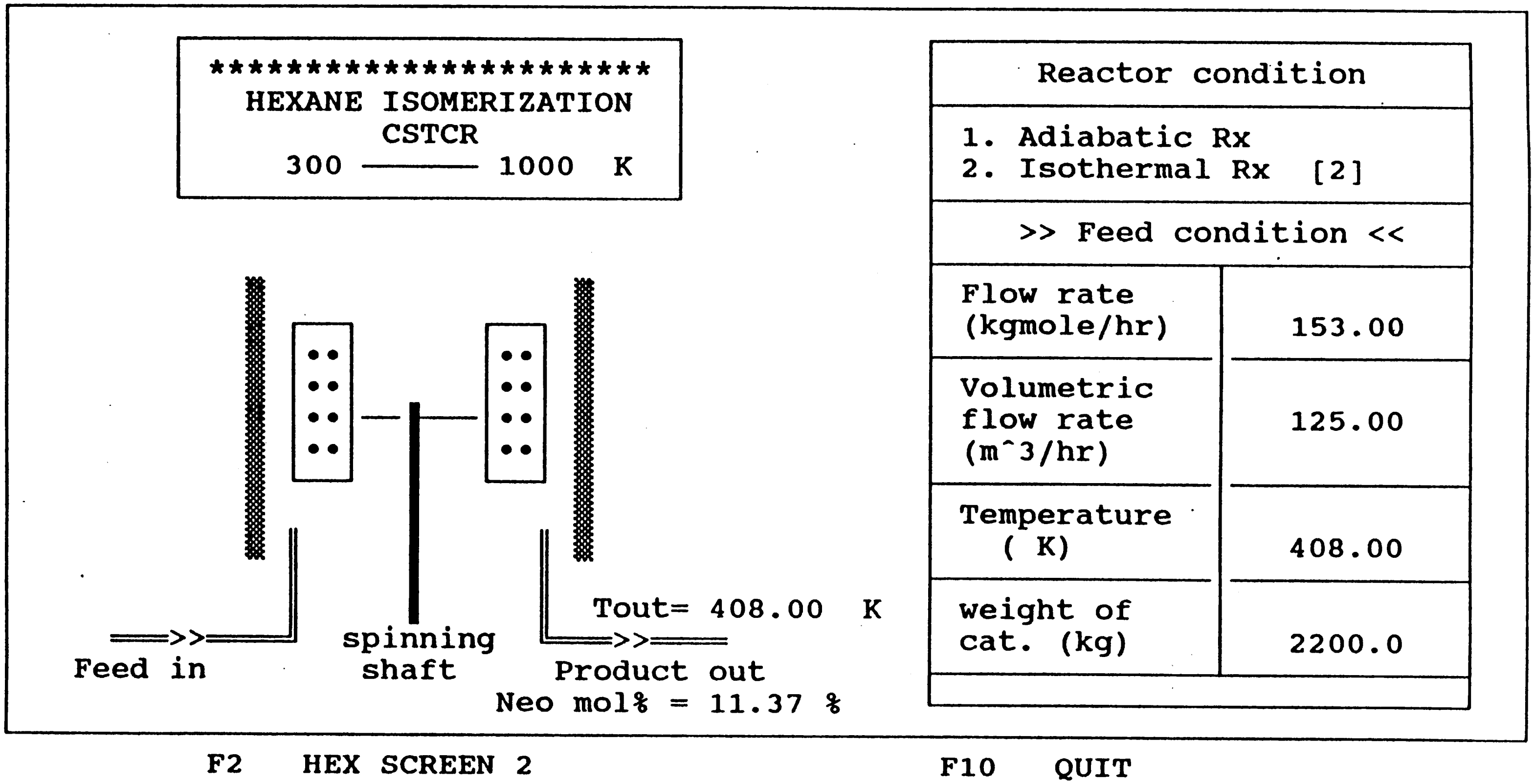
HEXANE ISOMERIZATION
300-1000 K

INPUT REACTANTS MOLE %	
N-HEXANE	[100.0] %
3 - MP	0.000 %
2 - MP	0.000 %
2,3-DMB	0.000 %
NEO-HEXANE (2,2-DMB)	0.000 %
INERTS	0.000 %

OUTPUT PRODUCTS MOLE %	
N-HEXANE	0.000 %
3 - MP	0.000 %
2 - MP	0.000 %
2,3-DMB	0.000 %
NEO-HEXANE (2,2-DMB)	0.000 %
INERTS	0.000 %

F1 HEX SCREEN 1 F10 QUIT

Figure 25. Control Panel 2 for CSTCR
Initial Parameter Settings



****
HEXANE ISOMERIZATION
CSTCR
300 ——— 1000 K

Tout= 408.00 K

Neo mol% = 11.37 %

Reactor condition

1. Adiabatic Rx
2. Isothermal Rx [2]

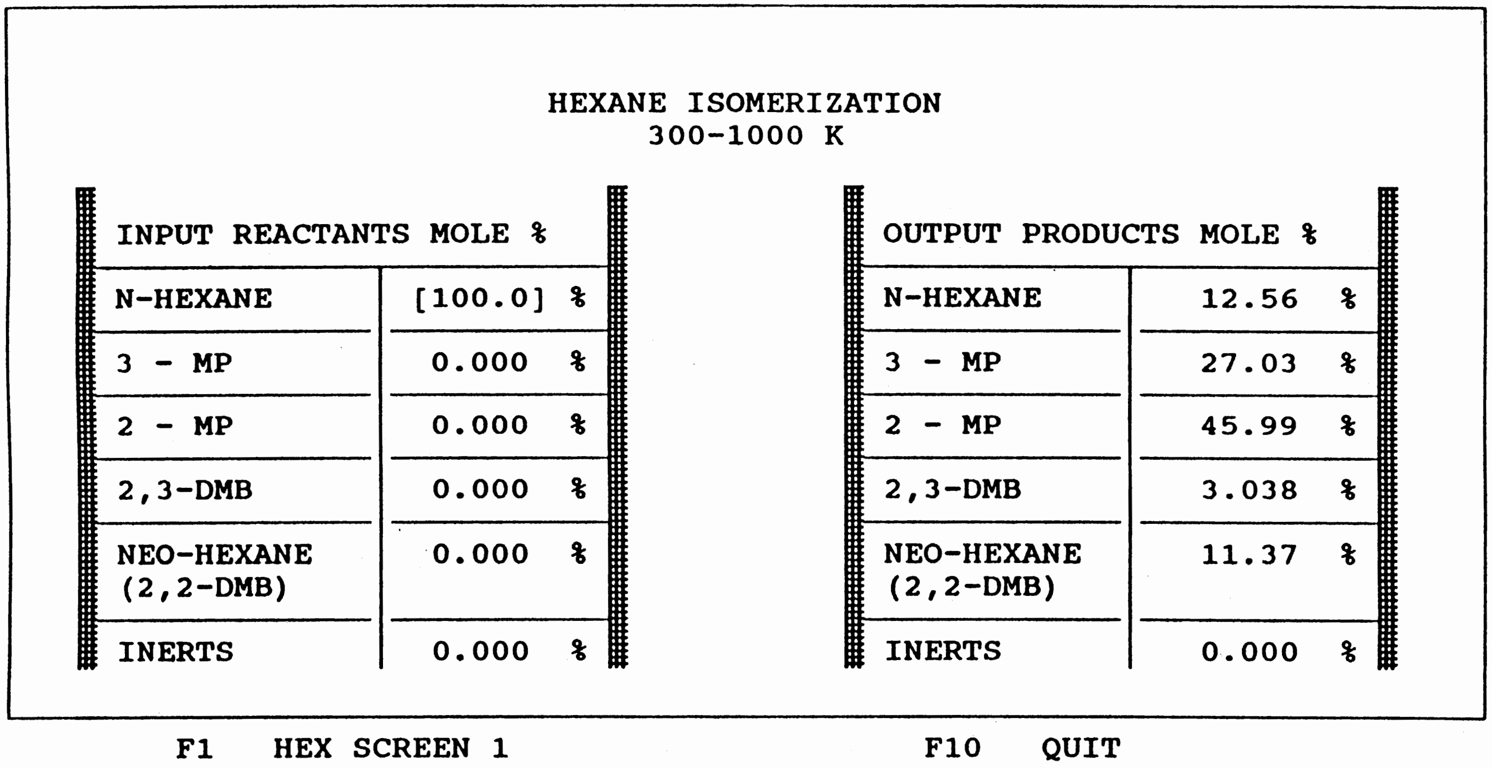
\>> Feed condition <<

Flow rate (kgmole/hr)	153.00
Volumetric flow rate (m^3/hr)	125.00
Temperature (K)	408.00
weight of cat. (kg)	2200.0

F2 HEX SCREEN 2

F10 QUIT

Figure 26. Control Panel 1 for CSTCR Isothermal Reaction



HEXANE ISOMERIZATION
300-1000 K

INPUT REACTANTS MOLE %	
N-HEXANE	[100.0] %
3 - MP	0.000 %
2 - MP	0.000 %
2,3-DMB	0.000 %
NEO-HEXANE (2,2-DMB)	0.000 %
INERTS	0.000 %

OUTPUT PRODUCTS MOLE %	
N-HEXANE	12.56 %
3 - MP	27.03 %
2 - MP	45.99 %
2,3-DMB	3.038 %
NEO-HEXANE (2,2-DMB)	11.37 %
INERTS	0.000 %

F1 HEX SCREEN 1

F10 QUIT

Figure 27. Control Panel 2 for CSTCR Isothermal Reaction

APPENDIX D

EFFECT OF PRESSURE UPON THE EQUILIBRIUM CONSTANT

This appendix explains that the effect of pressure on the equilibrium constant.

As mentioned earlier, ΔG° is based upon a fixed initial and final state and is not influenced by the conditions at any intermediate point. In fact, pressure does affect equilibrium yield for a gas phase reaction. This effect of pressure can be accounted for in the relationship between Ky, K. The detailed steps are shown below.

For reaction $aA + bB \longrightarrow cC + dD$

$$f_{iv} = \phi_{iv}\, y_i\, P$$

where

f_{iv} = the fugacity of components

ϕ_{iv} = mixture fugacity coefficients

y_i = mole fraction in the gaseous mixture

P = Total pressure

Using this expression for the fugacity, K becomes

$$K = \frac{[\phi P]_C^{c}\ [\phi P]_D^{d}}{[\phi P]_A^{a}\ [\phi P]_B^{b}}\ \frac{y_C^{c}\ y_D^{d}}{y_A^{a}\ y_B^{b}} \qquad \text{(D-1)}$$

where K_y = equilibrium constant in terms of mole fractions.

Assuming the mixture fugacity coefficients are equal to unity is equivalent to assuming that the gas phase behaves as an ideal solution. With this simplification, equation (D-1) becomes

$$K = [P^{(c+d)-(a+b)}]\ K_y; \quad (\because c+d-a-b = 0)$$
$$= K_y$$

Therefore, pressure does not affect the equilibrium yield if ideal gas behavior is assumed.

VITA

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