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SIMULATION OF ETHYLBENZENE DEHYDROGENATION IN MICROPOROUS CATALYTIC MEMBRANE REACTORS

Topical Report

April 1989

Work Performed Under Contract No. FC07-88ID12778

For
U.S. Department of Energy
Office of Industrial Technologies
Washington, D.C.

By
Alcoa
Warrendale, Pennsylvania

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Prepared for the
U.S. Department of Energy
Under DOE Idaho Field Office
Sponsored by the Office of the Assistant Secretary
for Conservation and Renewable Energy
Office of Industrial Technologies
Washington, D.C.

Prepared by
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1. ABSTRACT OF PROGRAM

Current state-of-the-art inorganic oxide membranes offer the potential of being modified to yield catalytic properties. The resulting modules may be configured to simultaneously induce catalytic reactions with product concentration and separation in a single processing step. Processes utilizing such catalytically active membrane reactors have the potential for dramatically increasing yield of reactions which are currently limited by either thermodynamic equilibria, product inhibition, or kinetic selectivity. Examples of systems of commercial interest include hydrogenation, dehydrogenation, partial and selective oxidation, hydrations, hydrocarbon cracking, olefin metathesis, hydroformylation, and olefin polymerization. A large portion of the most significant reactions fall into the category of high temperature, gas phase chemical and petrochemical processes. Microporous oxide membranes are well suited for these applications.

A program is proposed to investigate selected model reactions of commercial interest (i.e., dehydrogenation of ethylbenzene to styrene and dehydrogenation of butane to butadiene) using a high temperature catalytic membrane reactor. Membranes will be developed, reaction dynamics characterized, and production processes developed, culminating in laboratory-scale demonstration of technical and economic feasibility.

As a result of the anticipated increased yield per reactor pass, large economic incentives are envisioned. First, a large decrease in the temperature required to obtain high yield should be possible because of the reduced driving force requirement. Significantly higher conversion per pass implies a reduced recycle ratio, as well as reduced reactor size. Both factors result in reduced capital costs, as well as savings in cost of reactants and energy. Moreover, the controlled, defined reaction zone (the membrane interface), will facilitate the reactor design process and permit greater control of reactor dynamics, including mass and heat transfer (both of which will now be convective, rather than conductive) should result in more efficient reactor control and design. Lower reactor temperatures also imply possibly less stringent catalyst requirements, as well as the potential to carry out reactions directly that were previously multi-step. Because of the unnumerable reactions of commercial interest in the chemical process industries fall into these categories, commercial impact could be enormous.

2. TECHNICAL HIGHLIGHTS

A mathematical model describing dehydrogenation of ethylbenzene to styrene with membrane reactors has been developed. The model has been established by incorporating thermodynamic equilibrium of the reaction with gas permeation through microporous ceramic membranes. This model has been used to simulate the conversion ratio of the dehydrogenation for a wide range of temperature and pressure.

The use of membrane reactors can achieve a >90% conversion which is substantially higher than the theoretical equilibrium ratio of 66% at a typical operating condition (i.e., 900°K and 1.5 atm containing 20% of ethylbenzene in the feed). This degree of enhanced conversion would reduce significant energy requirement in the down stream product separations. Additional advantages in hardware and catalyst materials can be achieved and were identified in the previous quarterly report.

The effect of operating conditions, such as temperature, pressure, and diluent ratio in a membrane reactor, has been studied. The favorable condition for the traditional reactor, i.e., high temperature and low pressure, is applicable for the use of membrane reactors. An experimental plan will be developed for verification with a laboratory reactor, which will be the focus of the study in the third quarter.

Once the experimental data becomes available, the mathematical model developed here will be modified to take into account the non-ideal situations, such as side reactions, and incomplete local thermodynamic equilibrium. The model will then be used for process development and optimization, which will be conducted in the second and third year.

3. INTRODUCTION

A mathematical model has been developed to simulate the dehydrogenation of ethylbenzene to styrene with microporous ceramic membrane reactors. The simulation outcome will (1) demonstrate the degree of conversion improvement, and (2) provide directions on our experimental program. After comparing with the experimental results, this simulation program will be modified in order to precisely describe the catalytic conversion process with microporous ceramic membranes. The ultimate goal of this work is to provide the basis for process development and optimization in the second and third year of this research program.

4. MATHEMATICAL MODEL

The mathematical model is developed by incorporating gas permeation through microporous ceramic membranes with catalytic reactions. Gas permeation has been discussed in detail in the first quarterly report, which includes Knudsen diffusion, and Poiseuille flow. Assumptions made for developing the mathematical model are listed as follows:

- Gas permeation through surface diffusion is negligible. The catalytic reaction we are pursuing is operated at a low pressure and high temperature environment.
- Ideal gas law is used to describe the gas behavior of single components and gas mixtures. The suitable operating condition for ethylbenzene dehydrogenation is in the moderate high temperature (400 to 650°C) and low pressure (0 - 2 atms). Ideal gas law appears adequate according to the compressibility factor determined for each component listed in Table 1.
- An isothermal condition is assumed through the entire calculation. Dehydrogenation of ethylbenzene is endothermic, which requires to supply the heat to maintain the isothermal condition.
- A simple dehydrogenation of ethylbenzene to styrene and hydrogen is studied in this model. No side reactions are considered.

4.1 Material Balance

The tubular membrane reactor is separated into a "n" number of continuous stirred tank reactors as shown in Figure 1. Material balance is imposed upon each reactor as illustrated in Figure 2.

For a given reactor, j,

Reject, j, = Feed, j, - Permeate, j, + Chemical Reaction, j,

$$R_j = F_j - P_j + \Delta x_j \tag{1}$$

and ,

$$P,_j = (Q_k + Q_p) \bullet \Delta P \bullet A \tag{2}$$

where		
	Q_k	permeability contributed by Knudsen diffusion
	Q_p	permeability contributed by Poiseuille flow
	ΔP	pressure drop across transmembrane
	A	effective surface area for permeation

Estimation of Q_k, Q_p, and Δx is discussed individually in the following sections.

4.2 Chemical Reaction

$$Kp = \frac{P_{H2} \bullet P_{ST}}{P_{EB}} \tag{3}$$

$$\begin{array}{lccccccccc} & EB & + & N_2 & \rightarrow & H_2 & + & ST & + & N_2 \\ \text{Initial} & x & & n & & y & & z & & n \\ \text{equilibrium} & x-\Delta x & & n & & y+\Delta x & & z+\Delta x & & n \end{array} \tag{4}$$

$$\text{Total moles} = x + y + z + \Delta x + n$$

Assuming ideal gas, Pt: total pressure

$$P_{EB} = \left(\frac{x - \Delta x}{x + y + z + \Delta x + n}\right) Pt \tag{5}$$

$$P_{ST} = \left(\frac{z + \Delta x}{x + y + z + \Delta x + n}\right) Pt \tag{6}$$

$$P_{H2} = \left(\frac{y + \Delta x}{x + y + z + \Delta x + n}\right) Pt \tag{7}$$

$$P_{N2} = \left(\frac{n}{x + y + z + \Delta x + n}\right) Pt \tag{8}$$

$$Kp = \frac{\left(\frac{y+\Delta x}{x+y+z+\Delta x+n}\right) Pt \left(\frac{z+\Delta x}{x+y+z+\Delta x+n}\right) Pt}{\left(\frac{x-\Delta x}{x+y+z+\Delta x+n}\right) Pt} \tag{9}$$

$$\left(1 + \frac{Kp}{Pt}\right) \bullet \Delta x^2 + \left(\frac{Kp}{Pt} \bullet (y+z+n) + (y+z)\right) \bullet \Delta x -$$

$$\left(\frac{Kp}{Pt}\right) \bullet x \bullet (x+y+z+n) + yz = 0 \tag{10}$$

The styrene and hydrogen production (Δx) can be calculated by solving the equation 10. The chemical equilibrium constants can be found in the literature [1].

4.3 Knudsen Diffusion [2]

$$D_k = \frac{2}{3} r \bullet \sqrt{\left(8000 \bullet R \bullet \frac{T}{(\tau \bullet M)}\right)} \tag{11}$$

$$Q_k = \frac{\varepsilon_p \bullet D_k}{\tau \bullet R \bullet T \bullet L} \tag{12}$$

where:

r	pore radius, M
T	temperature, K
R	gas constant, 8.313 (Pa-M^3) (1/g-mole) (1/K)
M	molecular weight, g/mole
D_k	Knudsen effective diffusivity, M^2/s
Q_k	Knudsen permeability, g-mole/(Pa-M^2-s)
εp	porosity of membrane layer
τ	tortuosity
L	permselective layer thickness, M

In the Knudsen regime, each species diffuses independently so that the diffusivity does not depend on either composition or total gas concentration.

4.4 Poiseuille Flow [2]

$$Qp = \frac{10 \bullet \varepsilon_p \bullet P \bullet r^2}{8 \bullet \mu \bullet \tau \bullet R \bullet T \bullet L} \tag{13}$$

where: P pressure, Pa
μ viscosity, Pa-s, or, poise/10

Gas viscosity is required for the estimation of Poiseuille flow. It is the function of temperature and pressure. Viscosity at low pressure is estimated by using the theoretical Hirschfelder method which was further modified by Bomley and Wilke [3].

$$\mu^o = \frac{33.3 \bullet (MTc)^{0.5}}{Vc^{0.333}} (f(1.33Tr)) \tag{14}$$

$$f(1.33Tr) = 1.058 \bullet Tr^{0.645} - \frac{0.261}{(1.9 \bullet Tr)^{0.9 \bullet \log(1.9 \bullet Tr)}} \tag{15}$$

where: μ^o viscosity at low pressure, micropoise
Tc critical temperature, K
Tr reduced temperature
Vc critical volume, ml/g-mole

5. COMPUTER ALGORITHM

Figure 3 presents the flow chart of the computer program. The input data are divided into four groups: (a) gas component, molecular weight, and its dipole moment; (b) critical temperature, critical pressure, critical density, and reaction equilibrium constant; (c) membrane porosity, tortuosity, pore radius, thickness, reactor number in calculation, total surface area; and (d) total flow rate, operation temperature and pressure, and feed composition.

The surface area of each reactor is calculated by dividing the total surface area with the input number of reactors, NS. The computation is then carried out reactor by reactor. Figure 4 shows the calculation diagram. For a given reactor, reaction conversion is first calculated, and then, product separation is estimated from Knudsen diffusion and Poiseuille flow. The composition of permeate and reject is computed by mass balance. The flow rate and composition of reject are assigned as the feed to the next subsequential reactor. The computer program and a typical input data are listed in the appendix.

Two operating conditions are identified in the permeate side (Figure 4). One condition is operated without vacuum in the permeate side. The permeate species are accumulated in the permeate side. The repeated calculation continues till the last reactor is encountered. The other is operated with vacuum to the permeate side. Thus, a significant pressure drop across the membrane is maintained in every reactor. Finally, the species of permeate in each reactor are added together as the total permeate output. It is anticipated that the field operation would approximate the latter condition.

6. RESULTS

Tables 2 and 3 give the flow rate and composition of permeate and reject for the two conditions. Nitrogen is used as inert diluent. The volume flow rate (0.03 M^3/s) is measured at the simulation temperature. The feed composition is kept at 20% ethylbenzene balanced with nitrogen which is in the proximity of the feed partial pressure in the commercial operation. The conversion is calculated by the following equation:

$$\text{Conversion (\%)} = \frac{\text{styrene in permeate} + \text{styrene in reject}}{\text{ethylbenzene in feed}} \bullet 100\% \qquad (16)$$

Figure 5 shows that the reaction conversion is enhanced by using membranes under a typical operating condition, e.g., 900°K, 0.03 M^3/s of feed with 20% ethylbenzene in nitrogen. About 12.5% above the equilibrium conversion can be achieved at the mid-point of the membrane tube, i.e., at 0.6 M^2, for the condition without vacuum. Membrane >0.6 M^2 does not provide any additional enhancement. The conversion is even higher, i.e., >90%, when vacuum is performed in the permeate side. The temperature effect is shown in Figure 6. Since ethylbenzene dehydrogenation is endothermic, a high temperature condition is favorable for this reaction. At 700°K, 5%~10% above the equilibrium conversion is achieved with membrane reactors. While 12%~22% is achieved at 900°K. Figure 7 illustrates the influence of total pressure on this reaction. The lower the total pressure, the higher the conversion. The effect of nitrogen diluent, or partial pressure of ethylbenzene, is shown in Figure 8. It has the similar effect as that of total pressure. Figures 5, 6, and 7 conclude that the condition favorable for the traditional reactor, i.e., high temperature and low pressure, is applicable for the operation with membrane reactors.

7. NUMERICAL METHOD

The tubular membrane reactor is approximated by reactors in series. The number of reactors required to achieve an acceptable accuracy can be determined with a convergence test. Generally, the more number of reactors are selected, the more accurate the simulated results will be. For a typical operating condition, 2 to 20 reactors are selected here to test the convergence of numerical calculation. Figure 8 shows that about 8 reactors are required to give a converged conversion ratio for both conditions with and without vacuum in the permeate side. In this study, 10 reactors are selected for most of the calculation to insure the accuracy of the simulated results.

8. DISCUSSIONS

The advantage of using membranes is that hydrogen can be removed in situ during dehydrogenation. Hence the yield of styrene can be higher than that of the thermodynamic equilibrium (Figures 6-8). With the help of permeate side vacuum, an even higher conversion can be achieved because hydrogen in reject is removed more efficiently than those without permeate side vacuum.

Figure 5 shows that conversion reaches a maximum at the surface area of 0.6 M^2 for the condition without vacuum at the permeate side. At this point, the partial pressure of hydrogen is equal on the permeate and the reject side, no more hydrogen can be removed to the permeate to enhance the dehydrogenation. One should note that the conversion decreases slightly with surface area greater than 0.6 M^2.

When vacuum is applied to the permeate side, it is expected that the reaction should reach 100% conversion. Ethylbenzene, like hydrogen, permeates from the reject although at a much slower rate. Some reactants will permeate through the membrane before dehydrogenation takes place. Therefore, the conversion is improved further by vacuum; but it can not reach 100%.

9. LIMITATIONS OF MODEL

9.1 Side Reactions

As discussed in the assumption, only simple dehydrogenation without any side reactions is considered in this study. The selectivity of styrene in the industrial operation ranges from 60% to 95%, depending on temperature, pressure of the operating condition, and conversion ratio [5]. Major side reaction products includes xylene, toluene, benzene, etc. The side reaction is ignored to simplify the simulation. Since the selectivity can be as high as 95%, an assumption like this is realistic for the preliminary analysis. Once the experimental data are collected, the model will be modified to include the side reaction for the purpose of process optimization and development.

9.2 Isothermal Condition

Because of the endothermic nature of dehydrogenation, the reaction can be operated under either adiabatic or isothermal depending upon any heat input or not. Both processes have been practiced commercially. The membrane reactor can be designed to be suitable for both operations. In the lab operation, an isothermal condition will be performed. Thus, an isothermal condition is selected in this simulation for directing the design of our experimental study. In the future the model will be modified to include the energy balance for both isothermal and adiabatic conditions since energy consumption will be one of the key considerations in this study.

9.3 Validity of Knudsen Diffusion

Knudsen equation used in this study is valid under the condition that Knudsen diffusion dominates. The rule of thumb is that the ratio of mean free path to pore diameter is larger than 10 [5]. Table 4 shows the mean free path of major components involved: hydrogen, ethylbenzene, styrene, and nitrogen. For a 40Å membrane, the transport mechanism is within the valid range of Knudsen equation. Further, our experimental results on gas separations are consistent with the prediction based on Knudsen diffusion [6]. However, the program does not discriminate this constraint. Since mean free path is a function of molecular weight, pressure, and temperature, false result may occur if the ratio of mean free path to pore diameter is not carefully examined before using this program.

9.4 Local Equilibrium Conversion

The tubular membrane reactor is approximated by completely stirred tank reactors in series. Thus, a local equilibrium is assumed throughout the entire tubular reactor. Since the reactor is likely to be operated at the tubulent flow region, the gas component in the tubular reactor could be well mixed. A local equilibrium assumption is valid if the reaction rate is sufficiently fast and the catalytic surface area is sufficient. The former is dependent upon the operating temperature and concentration for a given catalyst, while the latter is determined by the surface area to volume ratio in a membrane reactor. An effectiveness factor can be determined once the experimental data are available. The factor can be incorporated into the model easily to account for the discrepancy of the assumption. The effectiveness factor will be useful information in the design of of the membrane reactor configuration, which will be studied in the second and third year.

10. REFERENCES

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11. Tables & Figures

TABLE 1

Critical Properties and Operation Conditions

	H_2	Ethylbenzene	Styrene	N_2
Tc (K)	33.2	617.2	647.0	126.2
Pc (atm)	12.8	35.5	39.4	33.5
T (K)	773-923	773-923	773-923	773-923
P (atm)	0.0-0.5	0.5-0.0	0.0-0.5	0.8-2.0
Tr	23.3-27.8	1.3-1.5	1.2-1.4	6.1-7.3
Pr	0.0-0.04	0.02-0.0	0.0-0.01	0.02-0.06
Z	1-1	0.99-1	1-0.99	1-1

Total pressure: 1-2.5 atm, 20% EB, 80% N_2

Z = PV/RT, compressibility factor

TABLE 2

Composition of Membrane Separation

	Permeate					Reject					Conversion (%)
	Flow (Mole/s)	EB (%)	ST (%)	H2 (%)	N2 (%)	Flow (Mole/s)	EB (%)	ST (%)	H2 (%)	N2 (%)	
700 K	0.49	13	2	4	80	0.32	21	5	1	73	15.6
800 K	0.36	8	6	13	72	0.39	11	12	3	74	47.8
900 K	0.35	3	10	25	63	0.36	3	19	4	74	83.1

Feed composition: 20% EB, 80% N_2

Feed rate:
700 K, 0.783 mole/s (0.03 M^3/s)
800 K, 0.685 mole/s (0.03 M^3/s)
900 K, 0.609 mole/s (0.03 M^3/s)

TABLE 3

Composition of Membrane Separation with Permeate Vacuum

	Permeate					Reject					Conversion (%)
	Flow (Mole/s)	EB	ST	H2	N2	Flow (Mole/s)	EB	ST	H2	N2	
		(%)					(%)				
700 K	0.66	12	3	5	81	0.15	30	10	0	60	20.6
800 K	0.63	6	7	13	74	0.14	12	26	0	61	59.1
900 K	0.58	2	10	19	69	0.14	1	36	0	63	90.3

Feed composition: 20% EB, 80% N_2

Feed rate:
700 K, 0.783 mole/s (0.03 M^3/s)
800 K, 0.685 mole/s (0.03 M^3/s)
900 K, 0.609 mole/s (0.03 M^3/s)

TABLE 4

Mean Free Path at 1 atm

	298 K	673 K	923 K
H_2	1018	2595	3727
EB	126	429	666
ST	126	430	670
N_2	639	1733	2467

unit: Å

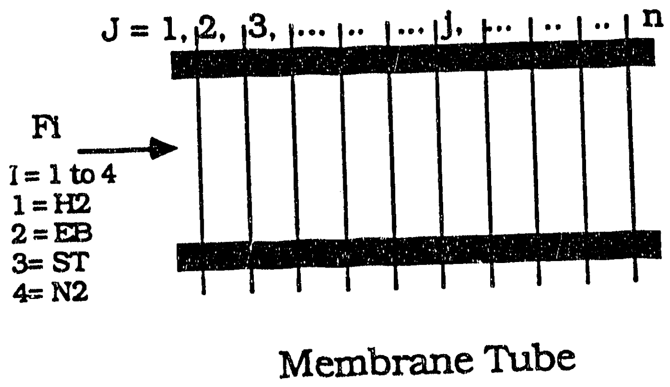


Figure 1 Separation of Membrane Reactor into "n" Number of Stages

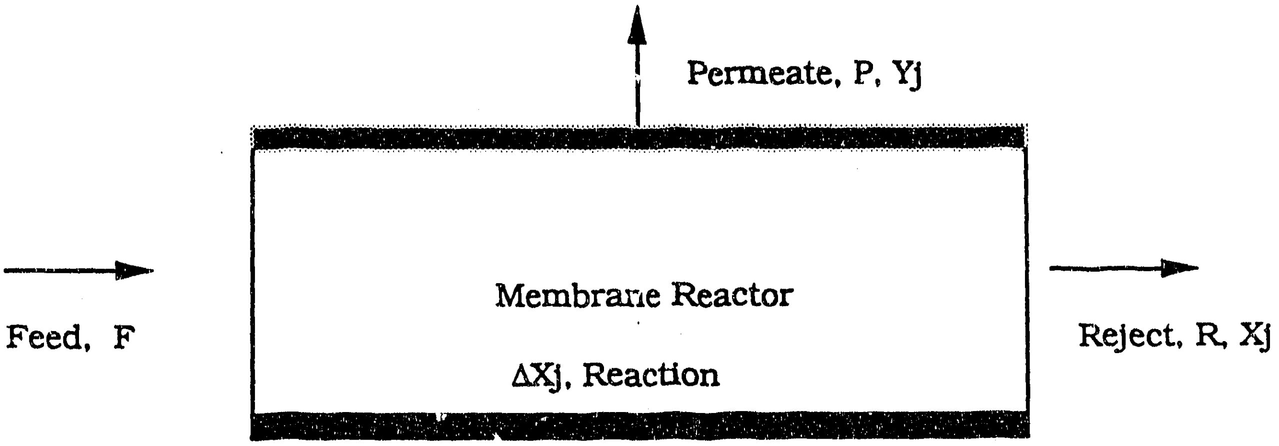


Figure 2 Material Balance of Given Stage, j

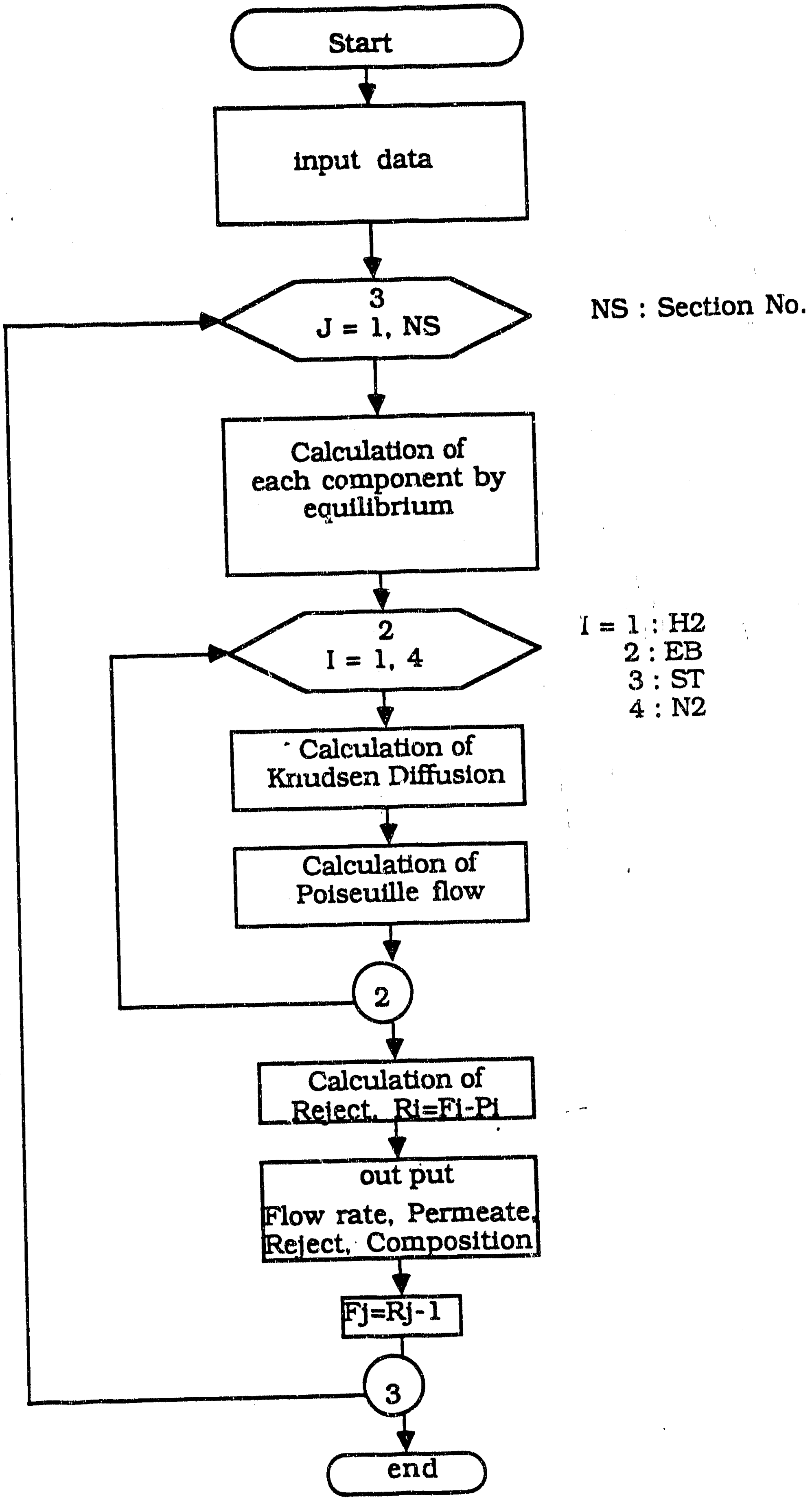
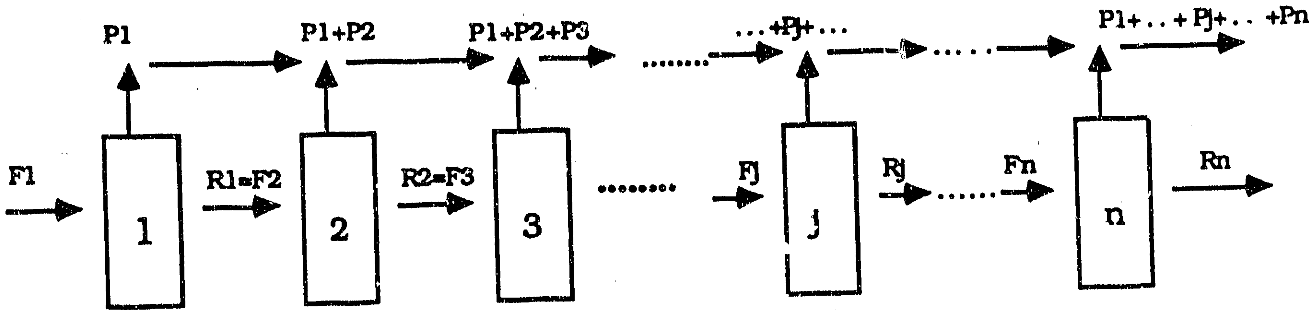
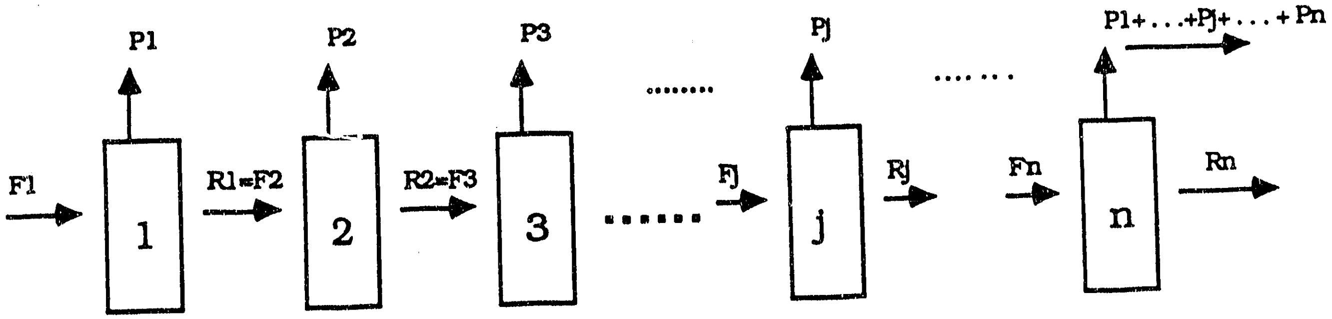


Figure 3 Flow Chart of Computer Program



Option a : No Vacuum at Permeate Side



Option b : Vacuum at Permeate Site

Figure 4 Sectional Calculation Diagram

FIGURE 5

The Effect of Surface Area on Ethylbenzene Dehydrogenation
40 A Membrane, T=900K, P=1.5 atm, V=0.03 M3/s, EB=20%

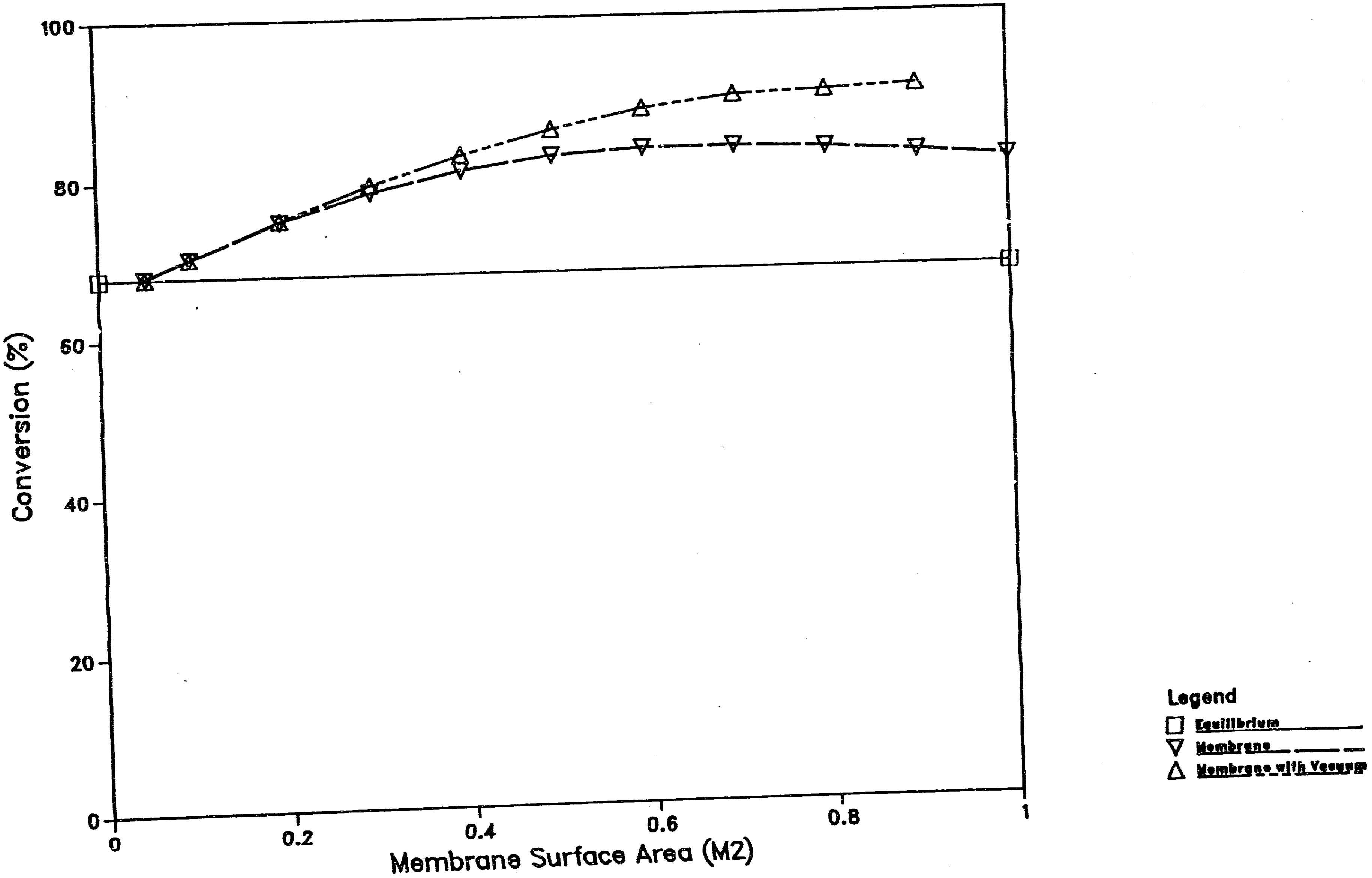


FIGURE 6

Temperature Effect on Ethylbenzene Dehydrogenation
40 A Membrane, P=1.5 atm, V=0.03 M3/s, EB=20%

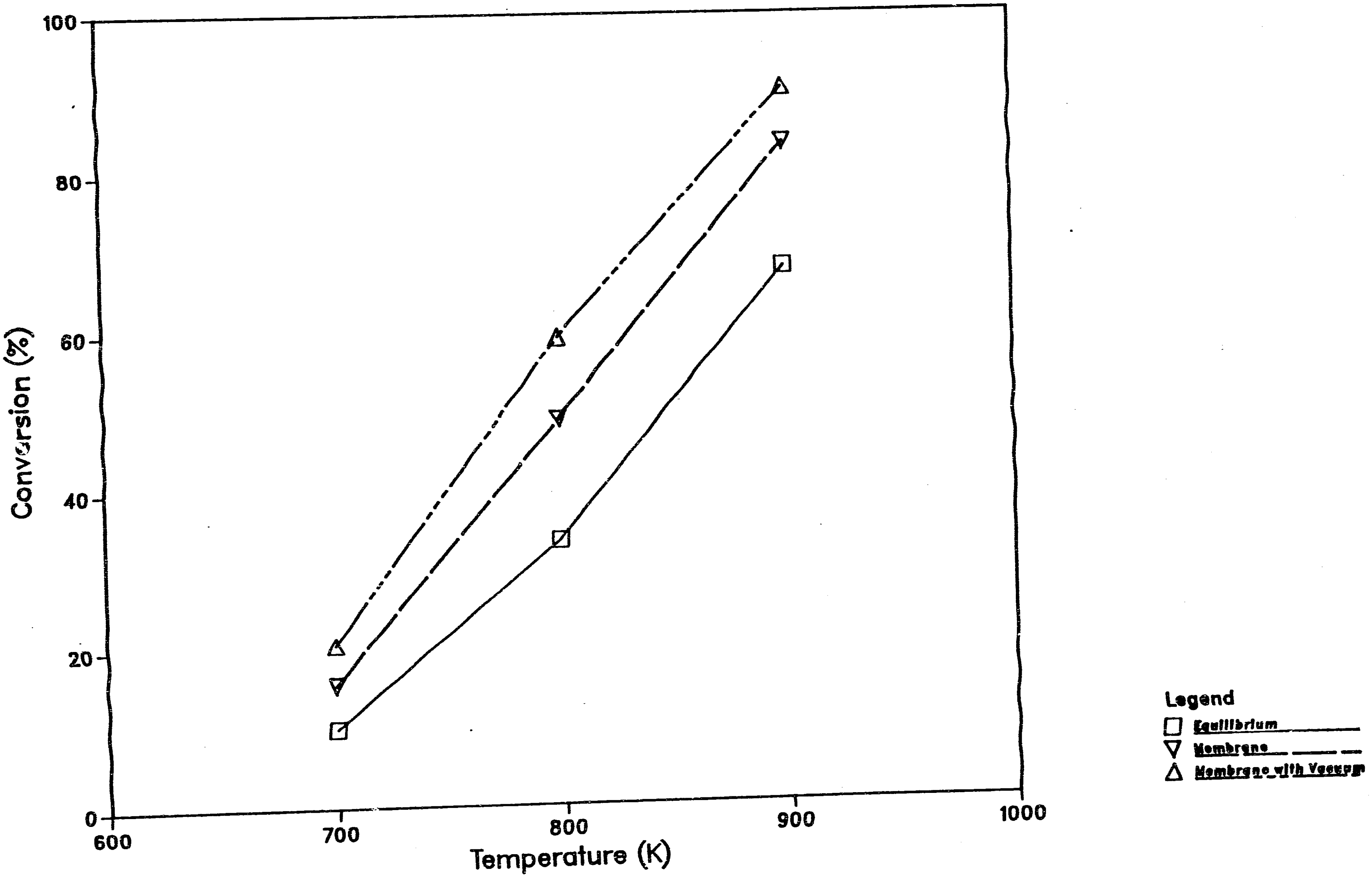


FIGURE 7

Pressure Effect on Ethylbenzene Dehydrogenation
40 A Membrane, T=900K, V=0.03 M3/s, EB=20%

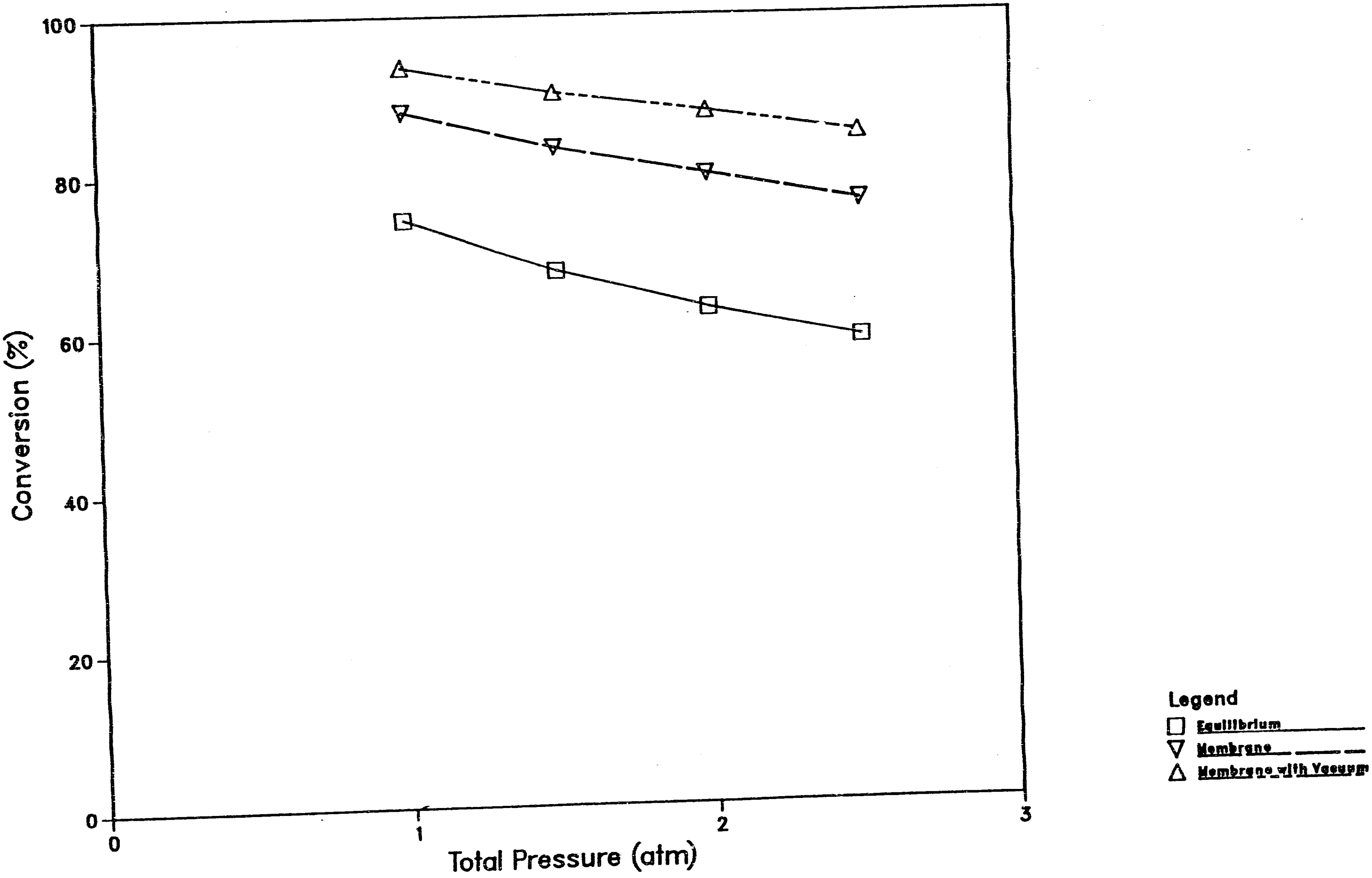


FIGURE 8
N2 Diluent Effect on Ethylbenzene Dehydrogenation
40 A Membrane, T=900K, P=1.5 atm, V=0.03 M3/s

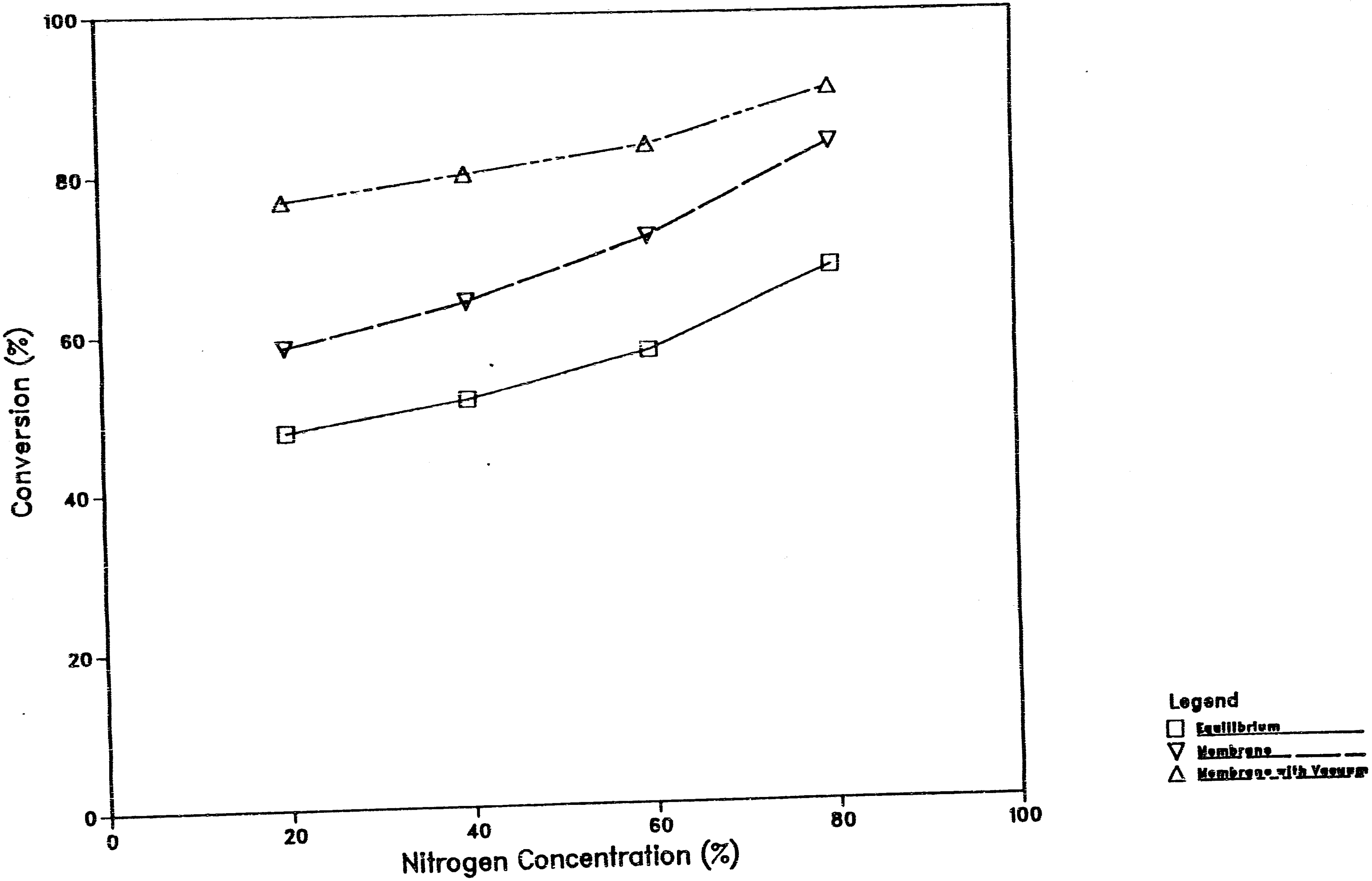
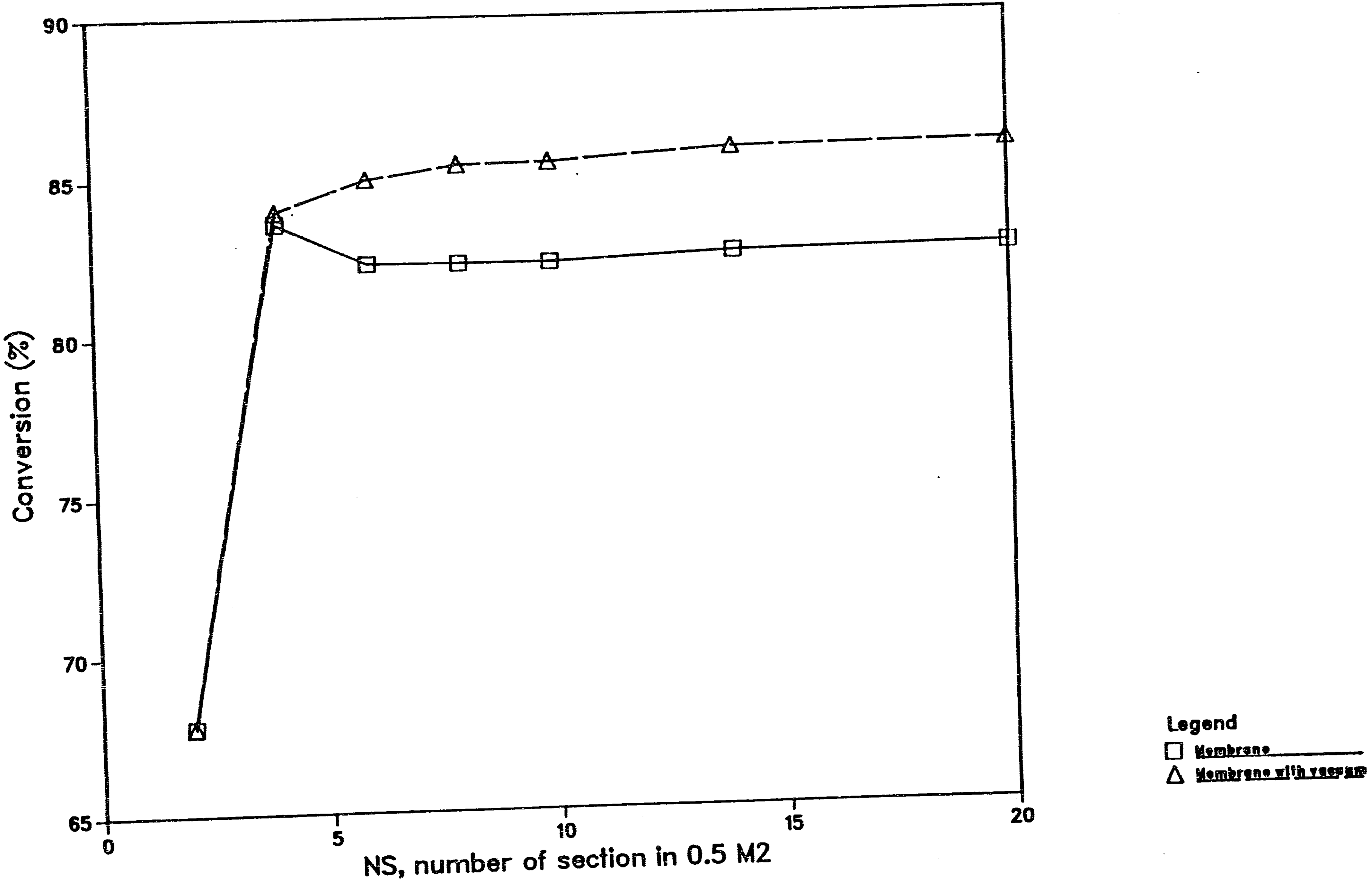


FIGURE 9
Convergence Test of Simulation
T=900K, P=1.5 atm, V=0.03 M3/s, EB=20%, A=0.5 M2



12. Appendix

```
      IMPLICIT real*8(A-h,o-z)
      CHARACTER*5 XNAME(4)
      dimension Xm(4),tc(4),pc(4),rhoc(4),vc(4), DIP(4)
      DIMENSION COMP(4),PSC(4),FK(4),FL(4),FS(4),FF(4)
      DIMENSION QK(4),QL(4),DS(4),DQDP(4),RF(4),PF(4),PPC(4)
      DIMENSION QS(4),SLOPE(4),RC(4),COM(4),SUMP(4,100),PERMEA(4)
      NAMELIST /DATA1/ XM,DIP,XNAME,
     @         /DATA2/ TC,PC,RHOC,XKP
     @         /DATA3/ EP,UK,R,TL,NS,AREA
     @         /DATA4/ FRATE,T,TP,COMP
     @         /DATA5/ PSC
     @         /DATA6/ SLOPE
      COMMON EP,UK,R,TL,RG
      OPEN(UNIT=5,FILE='INPUT',STATUS='OLD')
      OPEN(UNIT=6,FILE='REACT2.DAT',STATUS='NEW')

         DATA1 INCLUDES M, DIP
         M, MOLECULAR WEIGHT, IN G/GMOLE
         DIP, DIPOLE MOMENT, IN DEBYE

         DATA2 INCLUDES TC,PC,RHOC
         TC, CRITICAL TEMPERATURE, IN KELVIN
         PC, CRITICAL PRESSURE, IN ATMOSPHERE
         RHOC, CRITICAL DENSITY, IN G/CC
         XKP, EQUILIBRIUM CONSTANT, ATM

         DATA3 INCLUDES EP,UK,R,TL
         EP, POROSITY OF MEMBRANE, -
         UK, SHAPE FACTOR OF POROSITY, 1/TORTUOSITY, -
         R, PORE RADIUS OF MEMBRANE, M
         TL, THICKNESS OF THE MEMBRANE LAYER, M
         NS, SECTION NUMBER IN SIMULATION, -
         AREA, MEMBRANE SURFACE AREA, M2

         DATA4 INCLUDES FRATE,T,TP,COMP
         FRATE, FEED RATE M3/SEC,
         T, TEMPERATURE  KELVIN
         TP, TOTAL PRESSURE    ATM
         COMP, PERCENT COMPOSITION

         DATA5  SATURATED VAPOR PRESSURE AT CRITICAL
         TEMPERATURE, ATM

         DATA6  SLPOE OF ISOTHERMS VS P/PS, MOLE/G

    READ IN DATA

       READ(5,DATA2)
       READ(5,DATA1)
       READ(5,DATA3)
       READ(5,DATA4)
       READ(5,DATA5)
       READ(5,DATA6)
       RG=8.306
       RHO=2.9E6

    WRITE THE TITLE

       WRITE(6,10) R*2.E10,AREA
 10    FORMAT(///,7X,F6.1,' A PORE SIZE MEMBRANE WITH CATALYTIC
```

```
   @RXN',//,25X,'SURFACE AREA = ',F10.4,' M2')
 INITIALIZE THE VARIABLES

      TPF=0.0
      TRF=0.0
      SSA=0
      DO 4 I=1,4
        COM(I)=COMP(I)/100.0
        PPC(I)=0.0
        DO 5 J=1,100
5         SUMP(I,J)=0.0
4     CONTINUE

 START CALCULATION

      TN=TP*FRATE/(82.06E-6*T)
      TNN=TN
      SA=AREA/NS
      DO 3 J=1,NS
        SSA=SSA+SA
        CALL REACTION(XKP,COM,TP,NS,TNN)
        DO 2 I=1,4
          PM=TP*(COM(I)*TNN-PPC(I)*TPF)/(TNN+TPF)
          QK(I)=X_KNUDSEN(XM(I),T)
          QL(I)=X_LAMINAR(XM(I),RHOC(I),TC(I),PC(I),DIP(I),T,PM)
          QS(I)=SURFACE(PSC(I),TC(I),SLOPE(I),RHO,T)
          PERMEA(I)=QK(I)+QL(I)+QS(I)
          FK(I)=QK(I)*PM*1.013E05*SA
          FL(I)=QL(I)*PM*1.013E05*SA
          FS(I)=QS(I)*PM*1.013E5*SA
          FF(I)=TNN*COM(I)
          PF(I)=FK(I)+FL(I)+FS(I)
          SUMP(I,J+1)=SUMP(I,J)+SUMP(I,J+1)+PF(I)
          TPF=TPF+SUMP(I,J+1)
          RF(I)=FF(I)-PF(I)
          TRF=TRF+RF(I)
2       CONTINUE
        WRITE(6,30) T,TP
30      FORMAT(///,15X,'TEMP=',F6.1,' K',10X,'PRESS=',F7.2,' ATM')
        DO 300 I=1,4
          PPC(I)=SUMP(I,J+1)/TPF
          RC(I)=RF(I)/TRF
300     CONTINUE
        WRITE(6,70) SSA
70      FORMAT(/,25X,'SECTION AREA = ',F10.4,' M2')
        WRITE(6,60) FRATE,TN,TPF,TRF
60      FORMAT(//,5X,'FEED VOLUME RATE=',F7.3,' M3/S',2X,'FEED=',F9.3,
     @' MOLE/S',//,5X,'PERMEAT=',F9.3,' MOLE/S',5X,'REJECT=',F9.3,
     @' MOLE/S')
        WRITE(6,45)
45      FORMAT(//,18X,'FEED(%)',6X,'PERMEABILITY',6X,'PERMEATE(%)',
     @6X,'REJECT(%)')
        DO 400 I=1,4
400       WRITE(6,50) XNAME(I),COM(I)*100,PERMEA(I),PPC(I)*100,
     @RC(I)*100
50        FORMAT(7X,A5,4X,F6.2,9X,E9.2,9X,F6.2,10X,F6.2)
        DO 7 I=1,4
7         COM(I)=RC(I)
        TNN=TRF
```

```
       TRF=0.0
       TPF=0.0
3     CONTINUE
      CLOSE(UNIT=5,STATUS='SAVE')
      STOP
      END

*********************************************
  KNUDSEN PERMEABILITY

      FUNCTION X_KNUDSEN(XM,T)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON EP,UK,R,TL,RG
      V=SQRT((8.*RG*T)/(3.142*XM)*1000.)
      X_KNUDSEN=(2.*EP*UK*R*V)/(3.*RG*TL*T)
      RETURN
      END

*********************************************
  LAMINAR PERMEABILITY

      FUNCTION X_LAMINAR(XM,RHOC,TC,PC,DIP,T,PM)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON EP,UK,R,TL,RG
      VC=XM/RHOC
      TR=T/TC
      FTR=1.058*(TR**0.645)-0.261/((1.9*TR)**(0.9*LOG10(1.9*TR)))
      AMU=33.3*SQRT(XM*TC)*FTR/(VC**0.667)*1.0E-6
      PR=PM/PC
      CALL AMUCAL(TR,DIP,TC,PC,AMU,AMUP)
      PMPA=PM*1.0E5
      X_LAMINAR=EP*UK*R*R*PMPA/(8.0*AMUP*RG*T*TL)*10
      RETURN
      END

*********************************************
  SURFACE DIFFUSION PERMEABILITY

      FUNCTION SURFACE(PSC,TC,SLOPE,RHO,T)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON EP,UK,R,TL,RG
      DS=1.345E-6*EXP(-3142.177/T)
      PS=PSC*(T/TC)**2
      DQDP=SLOPE/(PS*1.013E5)
      SURFACE=UK*RHO*(1-EP)*DS*DQDP/TL
      RETURN
      END

*************************************************

      SUBROUTINE AMUCAL(TR,DIP,TC,PC,AMU,AMUP)
      IMPLICIT REAL*8(A-H,O-Z)
      A=1.9824E-03/TR*EXP(5.2683*TR**(-0.5767))
      B=A*(1.6552*TR-1.2760)
      C=0.1319/TR*EXP(3.7035*TR**(-79.8678))
      D=2.9496/TR*EXP(2.9190*TR**(-16.6169))
      DIPR=52.46*DIP*DIP*PC/(TC*TC)
      Q=1.-5.655*DIPR
      AMUP=B*PR+1./(1.+C*PR**D)
      AMUP=Q*A*PR**1.5/AMUP
```

```
      AMUP=AMU*(1.+AMUP)
      RETURN
      END
*****************************************************
 THERMAL REACTION

      SUBROUTINE REACTION(XKP,COM,TP,NS,TNN)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION COM(4)
      XEB=COM(1)*TNN/NS
      XSTY=COM(2)*TNN/NS
      XH2=COM(3)*TNN/NS
      XN2=COM(4)*TNN/NS
      D=XKP/TP
      A=1+D
      B=XH2+XSTY+D*(XH2+XSTY+XN2)
      C=-XH2*XSTY+D*XEB*(XEB+XH2+XSTY+XN2)
      DELTA_X=(-B+SQRT(B*B+4*A*C))/(2*A)
      TNN=(XEB+XSTY+XH2+DELTA_X+XN2)*NS
      COM(1)=(XEB-DELTA_X)*NS/TNN
      COM(2)=(XSTY+DELTA_X)*NS/TNN
      COM(3)=(XH2+DELTA_X)*NS/TNN
      COM(4)=(XN2)*NS/TNN
      RETURN
      END
```

```
$DATA2 TC=617.2,647.0,33.2,126.0
       PC=35.54,39.39,12.83,33.5
       RHOC=0.2839,0.2888,0.031,0.3110
       XKP=0.375$END

$DATA1 XNAME='EB    ','STY   ','H2    ','N2    ',
       XM=106.168,104.152,2.016,28.02
       DIP=0.4,0.1,0.0,0.0$END

$DATA3 EP=0.5, UK=0.339,R=20.E-10,TL=5.0E-06,NS=20,AREA=1.0$END

$DATA4 FRATE=0.03, T=900.0, TP=1.5,
       COMP=20.0,0.0,0.0,80.0$END

$DATA5 PSC=35.54,39.39,12.83,33.46$END

$DATA6 SLOPE=0.0,0.0,0.0,0.0$END
```

END

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9/01/92