Petroleum & Coal
ISSN 1337-7027

Available online at www.vurup.sk/pc

Petroleum & Coal 46 (1), 55-63, 2004

Modelling and Simulation Of Benzene Alkylation Process Reactors For Production Of Ethylbenzene

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Received 16 August 2004;received in revised form 18 October 2004; accepted 28 October 2004

Abstract

The goal of this paper is to develop a simulation software for the ethyl benzene production unit in a Petrochemical Complex of Iran. Ethyl benzene whose consumption has rapidly increased in recent years, is the feed for production of styrene monomer. This material is produced from alkylation of benzene with ethylene. A process simulator can play a very important role in the development of this process. In this research, alkylation of benzene for production of ethylbenzene has been simulated. First the mass, energy and momentum balance equations have been developed for the axial flow reactor. Optimization techniques have then been applied to modify the kinetic equations presented in literature to somehow satisfy the unit conditions. Finally the model predicted values such as pressure, reactor temperature, reactant conversion and products compositions have been compared with those of experimental ones adopted from the industrial unit. The comparison reveals that the model predicted values are adequately in compliance with the experimental data and hence can be used, with sufficient accuracy, to design pilot plants and other new units.

Key words: simulation, ethylene, benzene, alkylation , kinetic

Introduction

In 1958, UOP developed a new process for alkylation of benzene with ethylene at presence of aluminium chloride catalyst. This resulted in production of ethyl benzene which is the feed for production of styrene monomer. Ethyl benzene is a colorless liquid with a smell similar to that of gasoline and a quantity of less than 2 pmm in air. Ethyl benzene exists in crude oil with a small quantity and in addition to styrene, it is used in the production of acetone, diethyl benzene, cellelouse acetate, etc. The need to ethyl benzene has a growth of 4.3% per year. Requisition for this material reached 25 million tons in 2003.

Generally benzene alkylation process, for the production of ethyl benzene, consists of the following three steps:

1- Alkylation step, in which benzene reacts with ethylene
2- Trans alkylation step, in which poly ethyl benzenes (generally Diethyl benzene and three ethyl benzene) at presence of benzene are converted to ethyl benzene on a reverse alkylation process.
3- Separation step, in which un-reacted benzene, poly ethyl-benzenes and other components are separated from each other and high purity ethyl benzene is produced.

The applied catalyst in this process (aluminium chloride) is highly corrosive, and

hence expensive equipment which are resistant against acid are required. In recent years, lots of research activities have been carried out on different catalysts and their efficiencies among which special notice has been paid to zeolite[1,2].
To develop this process, a simulating software can be of great importance. Using such a software, it will be possible to investigate the system behaviour against process variables which can be used in the design of new pilots and units. Of course this process has been formerly simulated by some researchers but their simulation can not be applied to all industrial units because of the type of kinetics and catalyst they've used. So a dedicated software had to be developed for the existing ethyl benzene unit in an Iranian Petrochemical Complex which is unique in production of ethyl benzene in Iran. This software has been developed for this unit and is now under operation.

Process Description

In this process benzene feed from storage tank is mixed with recycled benzene from separation unit, and after heating and mixing with ethylene, enters the first reactor (R-101). Ethylene is completely converted in the reactor. Outlet from the first reactor warms up the feed of the second reactor while cooling down and after mixing with ethylene enters the second reactor (R-102). The outlet from the second reactor is then sent to benzene tower in separation unit. The reaction between poly ethyl benzene with ethyl benzene (trans-alkylation) will be carried out in trans-alkylation reactor (R-103). The feed to this reactor is a mixture of benzene stream taken from benzene tower and recycled poly ethyl benzene stream. This feed is first heated by reactor outlet stream and furnace before entering the reactor. The outlet stream of transalkylator reactor is then sent to benzene tower in separation unit.

Reactors

As already mentioned, the reactor unit is comprised of alkylation and transalkyaltion sections. The alkylation reactors are in series and have got two catalytic beds. The transalkylator reactor is larger than each alkylator and has got three catalytic beds. Stream direction in reactors is from bottom to top. Figure 1 illustrates a simple schematic diagram of the reactors. The specifications of these reactors are given in table 1.

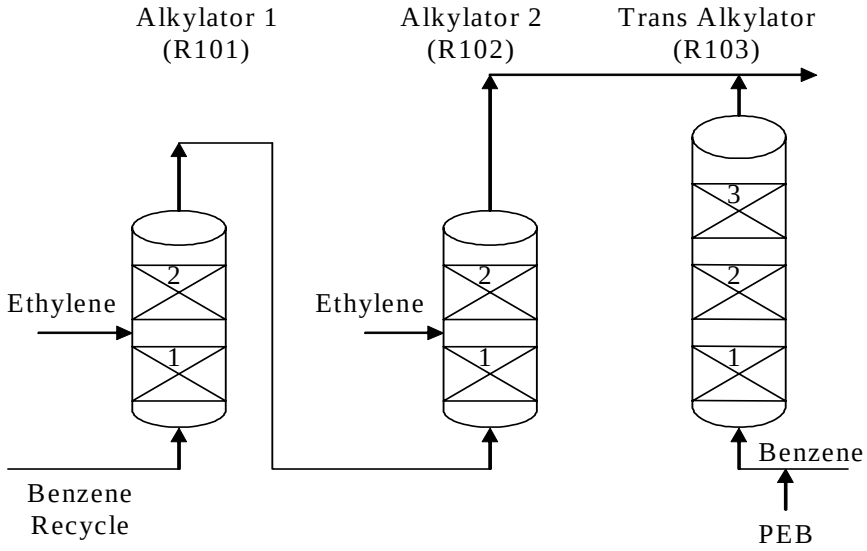

Fig.1- Simple Schematic of Ethyl Benzene Reactors

Table 1 Reactor Identification in Ethyl Benzene Unit

Reactor	R-101	R-102	R-103
Number of Beds	2	2	3
Bed Height (m)	5.15	5.15	5.58
Internal Diameter (m)	1.1	1.1	1.5
Beds Distance (m)	0.51	0.51	0.71
Weight of Catalyst in each Bed (kg)	4370	4370	6042

Modelling of Alkylation Section (Reactors R-101, R-102)

Model Development

The pseudo-homogeneous model has been used to simulate the reactors. Considering the mass balance equation on a differential cross section of a bed with length dz we can write:

$$-u\frac{dc_i}{dz} = r_i\ \rho_b \qquad (1)$$

in which

ri : reaction rate for component i u: Velocity

c_i: Concentration ρ_b : bulk density

The main reactions in alkylation reactors are as follow:

$Et + BZ \rightarrow EB$ Reaction No.1

$Et + EB \rightarrow DEB$ Reaction No.2

$Et + DEB \rightarrow TEB$ Reaction No.3

Where Et, BZ, EB, DEB, TEB stand for ethylene, benzene, ethyl benzene, diethyl benzene and three ethyl benzene respectively.

Equation (1) can also be written in the following forms:

$$-\frac{dF_i}{dz} = r_i\rho_b \qquad (2)$$

$$\frac{dX_{Etj}}{dz} = \frac{\rho_b.A.r_j}{F^{\circ}_{Et}} \qquad (3)$$

In these equations r_j represents the rate of the jth reaction and X_{Etj} shows the amount of its conversion and:

A: Bed cross sectional area F: Molar flow F^0: Initial molar flow

Considering the above relations, the molar flow of each component at different elevations of the bed can be obtained using the following relations:

$$F_{Et} = F_{Et}^{\circ} - F_{Et}^{\circ} X_{Et} \quad (4)$$

$$F_{BZ} = F_{BZ}^{\circ} - F_{BZ}^{\circ} X_{BZ} = F_{BZ}^{\circ} - F_{ET}^{\circ} X_{Et} \quad (5)$$

$$F_{EB} = F_{EB}^{\circ} + F_{EB}^{\circ} \left(X_{Et_1} - X_{Et_2} \right) \quad (6)$$

$$F_{DEB} = F_{DEB}^{\circ} + F_{Et}^{\circ} \left(X_{Et_2} - X_{Et3} \right) \quad (7)$$

$$F_{TEB} = F_{TEB}^{\circ} + F_{ET}^{\circ} X_{ET3} \quad (8)$$

Where : $X_{Et} = X_{Et1} + X_{Et2} + X_{Et3}$

The of momentum and energy balance equations in each bed will be as follow:

$$\frac{dT}{dz} = \frac{\sum_{j=1}^{n} (-\Delta \mathrm{H} j) r_j \, \rho_b \, A}{\sum_{i=1}^{m} F_i \, C_{p_i}} \quad (9)$$

$$\frac{dp}{dz} = -\frac{2 f G^2}{D_t \rho_m} \quad (10)$$

Where:

f : Friction factor — G: Mass flux

D_t: Internal Diameter — ρ_m : Mixture density

Simultaneously solving of equations (3), (9) and (10), will yield temperature, pressure and component concentration profiles in each bed. To solve the differential equations, Rung-Kutta method has been applied. In each position of reactor, C_P and ΔH must be calculated by means of measuring the temperature. The following relations have been used to calculate C_P and ΔH :

$$C_p = A + BT + CT^2 + DT^3 \quad (11)$$

$$\Delta \mathrm{H}_R(T) = \Delta \mathrm{H}_R(T_R) + \int_{TR}^{T} CpdT \quad (12)$$

in which ΔH (T_R) is the heat of reaction in standard temperature T_R which is calculated by means of (ΔH_f). As an example for reaction $aA + bB \rightarrow cC + dD$ we will have:

$$\Delta \mathrm{H}_R(T_R) = c\Delta \mathrm{H}_{f,C}(T_R) + d\Delta \mathrm{H}_{f,D}(T_R) - a\Delta \mathrm{H}_{f,A}(T_R) - b\Delta \mathrm{H}_{f,B}(T_R) \quad (13)$$

Table (2) shows the heat of formation (ΔH_f) of the dedicated materials of this process at standard temperature of 298^{o}K. These quantities are for gas phase reactions. They must be recalculated for liquid phase as the reaction is taken place in liquid phase. To convert ΔH_f from gas to liquid state, the following equation can be applied:

$$\Delta \mathrm{H}_f(l) = \Delta \mathrm{H}_f(g) - \Delta \mathrm{H}_v \quad (14)$$

in which:

ΔH_f (L) : Formation Heat in Liquid Phase

ΔH_f (g) : Formation Heat in Gas Phase

ΔH_f (V) : Heat of Vaporization

heat of vaporization at 298K for different materials of this process are given in table (2). Table (3) shows the constant values of equation Cp adopted from literature[3].

Table2 Heat of formation in gas phase and heat of vaporization values at 298K [4]

Component	ΔH_f (J/mol-^{o}K)	ΔH_v (J/mol-^{o}K)
Et	52287	-5743
BZ	80190	34480
EB	29229	41800
DEB	-18500	466500
TEB	-72510	41000

Table 3 Constant Values of Cp Equation

Component	A	B	C	D
Et	70.92	0.804	-0.0021	0.00005
BZ	-31.66	1.30	0.0036	0.00004
EB	183.37	0.169	0.0005	-
DEB	140.766	0.722	-0.0019	0.00003
TEB	-25.27	1.0	-0.006	-

Kinetics of Reactions

The most important factor in simulation of the reactor is to have proper kinetics for the reactions. As none of the existing kinetics in literature could exactly match the conditions of ethyl benzene unit in considered Petrochemical Complex, we had to modify the existing reaction rate equations [4] using the optimization techniques. For nonlinear parameter optimization, a random search method has been applied. To do so, a target function was defined as the difference between the weight percentage of the outlet quantities resulted from the model and those of experimental data(50 working days of plant) as follow:

$$OBJ = (wt\%BZ^{\,model} - wt\%BZ^{\,unit})^2 + (wt\%EB^{\,model} - wt\%EB^{\,unit})^2 + (wt\%PEB^{\,model} - wt\%PEB^{\,unit})^2 \quad (15)$$

Then a MATLAB based code was developed to minimize the target function as the parameters of the reactions rate equations are varied. This resulted in equations for reactions (1) and (2). Equation (3) was ignored due to low amount of TEB.

$$r_1 = \frac{k_r . C_{Et}}{1 + K_{EB} C_{EB}} \quad , \frac{kmol\ Bz}{kg.cat.hr} \quad (16)$$

$$k_r = 0.69 \times 10^6 \exp\left(\frac{-6.344 \times 10^4}{RT}\right), k_{EB} = -1.5202 \times 10^{-2} \exp\left(\frac{-3.933 \times 10^3}{RT}\right)$$

$$r_2 = 2.80 \times 10^2 \exp\left(\frac{-4.7030 \times 10^4}{RT}\right) C_{EB} . C_{Et} \quad , \left(\frac{kmol\ EB}{kg\ cat.hr}\right) \quad (17)$$

Modelling of transalkylation section (reactor R-103)

The main reactions of transalkylation reactor are as follow:

$DEB + BZ \rightarrow 2EB$ Reaction 4

$TEB + 2BZ \rightarrow 3EB$ Reaction 5

To obtain the profiles of temperature, pressure and concentration for this reactor, as before relations (3), (9) and (10) have been used with this difference that in equation (3) ethylene has been replaced with benzene. Using optimization techniques, the proper kinetics was obtained. The target function for this simulation was defined as:

$$OBJ = (wt\%BZ^{mod\,el} - wt\%BZ^{unit})^2 + (wt\%EB^{mod\,el} - wt\%EB^{unit})^2 + (wt\%PEB^{mod\,el} - wt\%PEB^{unit})^2 + (X_{PEB}^{mod\,el} - X_{PEB}^{unit})^2 \quad (18)$$

where X_{PEB} shows the percentage of poly ethyl benzene conversion:

The following reaction rate equations were obtained for reactions 4 and 5 in terms of $\left(\frac{kmol\ BZ}{kg\ \cot.hr}\right)$;

$$r_4 = 2.378\times10^2 \exp\left(\frac{-6.128\times10^4}{RT}\right) C_{DEB}\ C_{BZ}^{1.0218} \Big/ \left(1+3\times10^{-6} C_{BZ}\right) \quad (19)$$

$$r_5 = 2.434\times10^2 \exp\left(\frac{-5.5077\times10^4}{RT}\right) C_{TEB} C_{BZ}^{-1.0503} \Big/ \left(1+1.76\times10^{-5} C_{BZ}\right) \quad (20)$$

Results and Conclusion

After obtaining the model equations and required parameters, a Fortran based computer program was developed to solve the model which could yield the output variables of the reactors such as temperature, components percentage and pressure. These values could then be compared with those of experimental ones.

Simulation Results

To investigate the operation of the developed simulating software, the unit was under test for five days. Table (4) illustrates the input values of R-101 and R-102 and table(5) shoes input values of R-103. Tables (6) , (7) and (8) show the output values of reactors R-101 , R-102 and R-103 respectively resulted from model and physical unit. It is observed that these data are in good compliance with each other and this shows that the software operates properly.

Table 4 Inlet data of R-101 & R-102

Day	Inlet P (bar)	R101 in T$\left(^{\circ}c\right)$	R102 in T$\left(^{\circ}c\right)$	BZ to R101$\left(kg/hr\right)$	Et to R101$\left(kg/hr\right)$	Et to R102$\left(kg/hr\right)$
1	38	212.81	217.10	63742.53	1781.50	1782.88
2	38	212.37	216.90	66221.17	2059.70	2053.20
3	38	212.64	217.43	62241.14	1804.50	1804.50
4	38	212.21	217.35	65557.37	1949.72	1950
5	38	212.54	216.72	64630.51	1899.86	1899.97

Table 5 Inlet data for reactor R-103

Day	Inlet Flow (kg/hr)	Inlet T (^{o}C)	Inlet P (bar)	BZ mass%	EB mass%	PEB mass%
1	39777	218.05	38	94.6	0.38	4.15
2	43103	217.27	38	94.6	0.38	4.15
3	38712	217.93	38	94.6	0.38	4.15
4	38100	216.93	38	94.6	0.38	4.15
5	40422	217.10	38	94.6	0.38	4.15

Table 6 Comparison of outlet data of reactor (R-101) resulted from model and physical unit

Day		T(^{o}C)	Wt% BZ	Wt% EB	Wt % PEB
1	Unit	252.31	89.17	9.86	0.51
	Model	254.72	87.20	10.05	0.49
2	Unit	252.90	89.17	9.68	0.51
	Model	254.88	87.02	10.16	0.49
3	Unit	252.34	89.17	9.89	0.51
	Model	254.30	87.30	9.92	0.48
4	Unit	252.03	89.17	9.89	0.51
	Model	254.18	87.10	9.85	0.48
5	Unit	253.10	89.17	9.95	0.51
	Model	254.98	86.30	10.22	0.47

Table 7 Comparison of outlet data of reactor (R-102) resulted from model and physical unit

Day		T(^{o}C)	P(bar)	Wt% BZ	Wt% EB	Wt % PEB
1	Unit	255.73	36	79.79	18.21	1.33
	Model	256.70	36.09	77.70	18.34	1.60
2	Unit	256.91	36	79.79	18.21	1.33
	Model	257.63	36.04	77.48	18.35	1.63
3	Unit	256.41	36	79.79	18.21	1.33
	Model	256.83	36.24	77.95	18.13	1.65
4	Unit	256.91	36	77.79	18.21	1.33
	Model	257.23	36.15	77.92	18.08	1.41
5	Unit	256.10	36	77.79	18.21	1.33
	Model	256.23	36.65	77.65	18.20	1.34

Table 8 Comparison of outlet data of reactor (R-103) resulted from model and physical unit

Day		P(bar)	Wt% BZ	Wt% EB	Wt % PEB	X_{PEB}
1	Unit	35	93.69	3.46	1.98	84.17
	Model	34.82	93.42	3.60	2.11	84.90
2	Unit	35	93.69	3.48	1.98	84.17
	Model	34.27	93.45	3.50	2.17	82.34
3	Unit	35	93.69	3.48	1.98	84.17
	Model	34.99	93.41	3.62	2.10	85.48
4	Unit	35	93.69	3.48	1.98	84.17
	Model	34.75	93.51	3.52	2.03	84.41
5	Unit	35	93.69	3.48	1.98	84.17
	Model	34.62	93.55	3.68	2.17	85.01

6-2- Reactor profiles

By this software we can find temperature and flow profiles in reactors. Reactors temperature profiles are plotted in fig. (2). Due to exothermic nature of alkylation reactions, the temperature is risen in these reactors. Transalkylation reactions are endothermic and therefore temperature is coming down smoothly. These figures show that the reaction at the inlet of alkylator beds is rapid because of larger values of ethylene. At the entering of second bed of two alkylator reactors the temperature comes down because of entering cold ethylene.

Figs. (3) and (4) show mass flow profile of species in alkylation reactors. These Figures show that Benzene and Ethylene are consumed and other species are produced in the reactors. Mass flow profiles of transalkylation reactor is plotted in fig. (5). According to this figure reaction of benzene with poly ethyl benzenes (reactions 4 & 5) produces ethyl benzene in the reactor R-103.

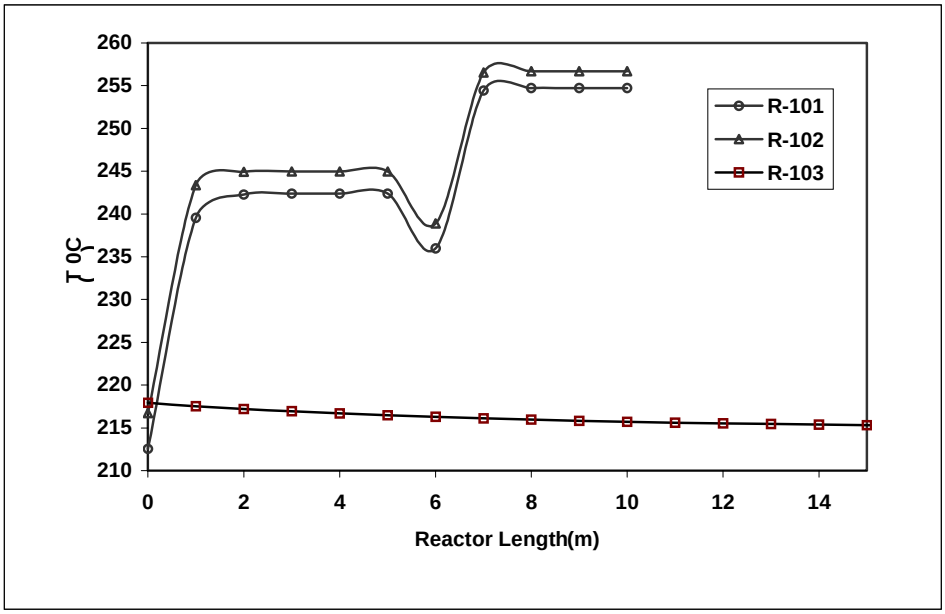

Fig. 2- Temperature profile in reactors

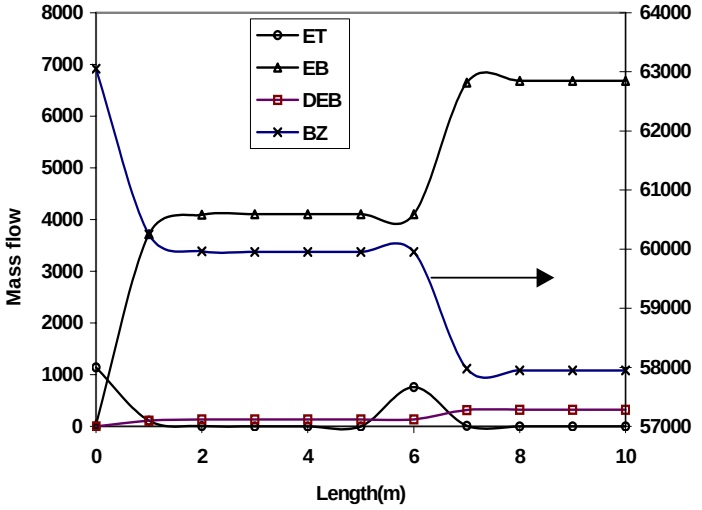

Fig. 3- Mass flow profile in R-101(kg / hr

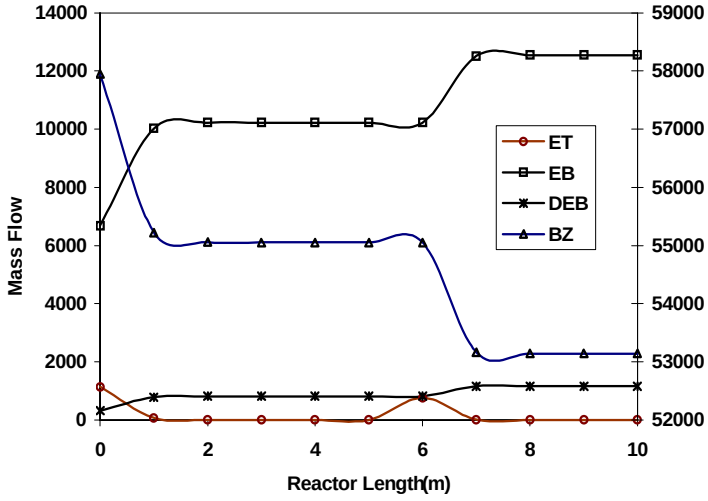

Fig. 4- Mass flow profile in R-102(kg / hr)

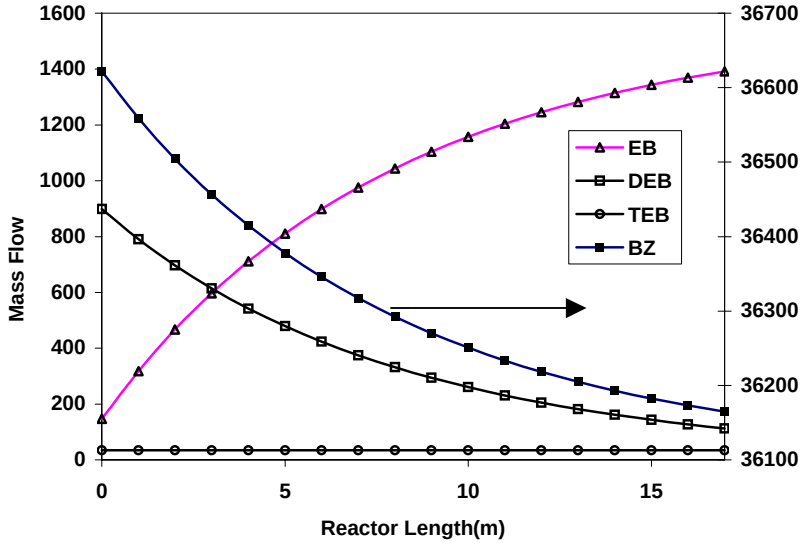

Fig. 5- Mass flow profile in R-103(kg / hr)

Symbols

A	Bed cross section area (m^2)	r	Reaction rate $\left(\frac{kmol}{kg\ cat.hr}\right)$
C	Concentration $\left(kmol/m^3\right)$	T	Reaction temperature($^\circ c$ or $^\circ k$)
C_P	Specific heat $\left(Kj/kmol^o k\right)$	T_R	Reference temperature $(^\circ K)$
D_t	Tube internal diameter(m)	u	Velocity $\left(m/hr\right)$
f	Tube friction factor(-)	X	Percent conversion
F	Mole flow $\left(kmol/hr\right)$	X_{PEB}	Poly ethylbenzene conversion
F^0	Initial mole flow $\left(kmol/hr\right)$	ρ_b	Bulk density($\frac{kg\ cat}{m^3 bed}$)
G	Mass flux ($kg/m^2.hr$)	ρ_m	Mixture density(kg / m^3)
m	Number of species	ΔH	Heat of reaction $\left(kj/kmol\right)$
n	Number of reactions		

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