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# Modeling and Simulation a Catalytic Fixed Bed Reactor to Produce Ethyl Benzene from Ethanol

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## Abstract

Ethyl benzene used increasingly each year is the raw material of producing styrene monomer. This substance is produced from benzene alkylation with ethylene or ethanol, depending on the availability and cost of raw materials. In this study benzene alkylation in the presence of ethanol in a catalytic fixed bed reactor in three states of isotherm, adiabatic and non-isotherm-non-adiabatic is mathematically modeled with one-dimensional pseudo-homogeneous model; and then has been programmed with math lab software. The reaction kinetics model is used in this study which comes from the experimental equations found by Mr. U.S Ridevi et al. in a zeolite catalyst impregnated with  $AlCl_3$  obtained in isotherm mode. The results of this simulation in isotherm state are comparable with experimental data. The adiabatic and non-isotherm-non-adiabatic states also show acceptable results. Furthermore, in this study the effect of various factors such as the feed flow rate, substrate temperature, substrate density, fixed and variable heat capacity and viscosity of fluid has been investigated.

**Keywords:** Fixed Bed Reactor, Ethyl Benzene, Modeling, Simulation, Ethanol, Catalyst

## 1. Introduction

In 1985 the American Company of UOP developed a new process for benzene alkylation with ethylene gas in the presence of aluminum chloride whose main product was ethyl benzene which is the raw material of styrene monomer [1]. However, in countries which have no access to gas resources, benzene alkylation is used with ethanol. Ethylbenzene is a colorless liquid that has a gasoline-like odor and the air odor threshold concentration is 2.3 parts per million (ppm) parts of air. The amount of ethyl benzene in the crude oil is very low and it is used in other construction such as building stephen, diethyl

benzene, cellulose acetate and etc in addition to the styrene production [2,3].

Benzene alkylation process with ethylene on the catalyst by Friedel - Crafts is a commercial way for creating more than ninety percents of ethyl benzene. However using this catalyst has many problems including loading them inside the reactor, safety, waste and corrosion. A recently great effort was developed for using environmentally friendly catalytic processes [4 and 5]. Zeolite-based catalyst types are used for this purpose. Currently benzene alkylation in vapor phase with ethanol on ZSM-5 catalyst is carried out which is the well-known process of Mobil – Badger. This process is used in the commercial scale for production of ethyl benzene. There are many advantages of direct

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use of ethanol instead of ethylene and benzene alkylation. One advantage is the catalyst long activity when alcohol was used instead of Olefin and the other one is that using ethanol instead of ethylene is more economical for countries in which ethanol is produced through biological processes.

Many surveys have been carried out to compare alkylation reactions of zeolite ZSM and zeolite X. Many researchers have performed aromatic alkylation reactions based on the X type of Zeolites. Benzene alkylation reaction with 1-decen and trans alkylation of dialkyl benzene with  $AlCl_3$  catalyst have been done, according to reports the alkylation reaction with this method is twice faster than trans alkylation reaction.

Catalyst activity has been increased in benzene alkylation reaction with propylene by using Cumen- $AlCl_3$  catalyst with alumina silicate [6]. Benzene alkylation and ethanol with zeolite impregnated with  $AlCl_3$  has been implemented by U.S. Ridvai et al. Modeling was performed to obtain a mathematical relationship that can almost exactly predict the function of process in different conditions. In this study, kinetic model obtained from experiments by U. S. Ridvi et al. for benzene alkylation with ethanol was used with the one-dimensional quasi-homogeneous model of a fixed bed reactor [7]. Then the equations obtained are solved with [10] numerical methods.

## 2. Reaction kinetics equation

The reaction of ethyl benzene alkylation with ethanol is performed according to the following relationship:



The catalytic reaction experiment to obtain kinetics model has been carried out in a fixed bed reactor and a stainless steel cylinder with 2.5 cm of inner diameter and 33 cm in length. It was experimentally observed that ethyl benzene is the only important product.  $Y_E$ ,  $Y_B$  and  $Y_{EB}$  are respectively ethanol, benzene and ethyl benzene. 1 mol of the product will contain  $Y_B$  moles of benzene,  $Y_E$  moles of

ethanol and  $Y_{EB}$  moles of ethyl benzene. Hence the amount of benzene converted by alkylation is  $Y_{EB}$  moles.

Hence, the amount of benzene conversion by alkylation process is equal to:

$$X_B = \frac{\text{moles of benzene converted}}{\text{moles of benzene fed}} = \left[ \frac{Y_{EB}}{Y_B + Y_{EB}} \right] \quad (2)$$

In examining any rate equation, internal and external resistance should be at least to develop an intrinsic rate equation. To estimate the impact of external influence two series of experiments were performed by different amounts of catalyst. For testing the effect of internal diffusion also two experiments were done by two different catalyst sizes of 1.58 and 1.36 mm. The results of these experiments have shown that the internal and external diffusion are ineffective. In the absence of internal diffusion resistance, mechanisms include chemical absorption and surface reactions and catalytic reaction controller. In the present study the chemical absorption, in the stage of rate controlling, has not been applied and it has been only carried out in surface reaction controller cases.

Then U.S. Ridvi et al. on the base of their experiments proposed the following model for rate of this reaction:

$$r_B = \frac{kK_E K_B p_E p_B}{(1 + K_B p_B + K_E p_E + K_{EB} p_{EB})^2} \quad (3)$$

partial pressures in the above equation are in relation with the conversion percent and total pressures as they are illustrated in the following equations:

$$p_E = \frac{(0.33 - X_B)P}{5.78 - X_B} \quad p_{EB} = \frac{X_B P}{5.78 - X_B} \quad p_B = \frac{(1 - X_B)P}{5.78 - X_B} \quad (4)$$

Putting partial pressures in the overall rate equation we will see the overall equation:

$$r_B = \frac{kK_B K_E (1 - X_B)(0.33 - X_B)P^2 / (5.78 - X_B)^2}{[1 + \{K_B(1 - X_B) + K_E(0.33 - X_B) + K_{EB}X_B\} \{P / (5.78 - X_B)\}]^2} \quad (5)$$

Four unknown parameters in the equation (5), obtained by experiments in three different temperatures, are calculated by regression in the following way:

$$\begin{aligned} \ln k &= 11.296473 - 7179.695\left(\frac{1}{T}\right) \\ \ln K_B &= -3.1544819 + 1776.81699\left(\frac{1}{T}\right) \\ \ln K_E &= -4.1913 + 1498.799\left(\frac{1}{T}\right) \\ \ln K_{EB} &= 3.32854 + 290.61918\left(\frac{1}{T}\right) \end{aligned} \quad (6)$$

### 3. Mass transfer equation

In all three modes isotherm, adiabatic and non-isotherm – non adiabatic, mass transfer equation is as the following, the adiabatic mode non-isotherm – non adiabatic mass transfer relationship also find temperature dependence.

$$r_B = \frac{kK_B K_E (1-X_B)(0.33-X_B)P^2 / (5.78-X_B)^2}{[1 + \{K_B(1-X_B) + K_E(0.33-X_B) + K_{EB}X_B\} \{P / (5.78-X_B)\}]^2} \quad (7)$$

### 4. Isotherm Equations

In this case there is no equation of temperature distribution in the reactor and all have the same temperature.

### 5. Adiabatic energy balance equation

In this case the energy balance equation are obtained as follows:

$$\frac{\partial T}{\partial z} = \frac{\rho_B(-\Delta H)}{GC_{pmix}} \frac{kK_B K_E (1-X_B)(0.33-X_B)P^2 / (5.78-X_B)^2}{[1 + \{K_B(1-X_B) + K_E(0.33-X_B) + K_{EB}X_B\} \{P / (5.78-X_B)\}]^2} \quad (8)$$

### 6. Non-isotherm – Non adiabatic energy balance equation

In this case the energy balance equation is obtained by the following way :

$$G \frac{\partial}{\partial z} (C_p T) + \frac{4}{D_T} h_w (T - T_w) = r_m \rho_B (-\Delta H) \quad (9)$$

Wall heat transfer term has been entered in this equation. Heat transfer coefficient which exists in this equation can be written as:

$$\frac{h_w D_p}{K_g} = 3.6 \left( \frac{D_p G}{\mu \varepsilon_B} \right)^{0.365} \quad (10)$$

Also this equation includes viscosity which is a function of temperature and is obtained from the following relationship:

$$\mu = 0.75 * 10^{\left( \frac{472.82}{T} - \frac{1}{264.22} \right)} + 0.25 * 10^{\left( \frac{686.64}{T} - \frac{1}{300.88} \right)} \quad (11)$$

$\Delta H_{rxn}$  can be calculated as:

$$\Delta H_{rxn} = \int_{T_1}^{298} C_{pmix}(feed) dT + \Delta H_f^{298} + \int_{298}^{T_2} C_{pmix}(product) \quad (12)$$

## 7. The results of mathematical modeling and equations

### 7.1. Isotherm mode

According to results of the study, the conversion percentage of benzene into ethyl benzene decreases by increasing the amount of feed flow as they are illustrated in fig. 1 and 2.

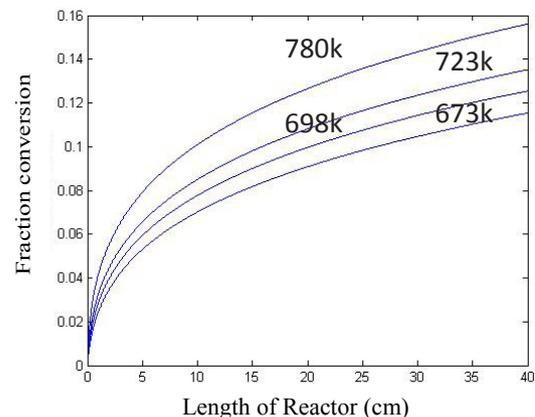
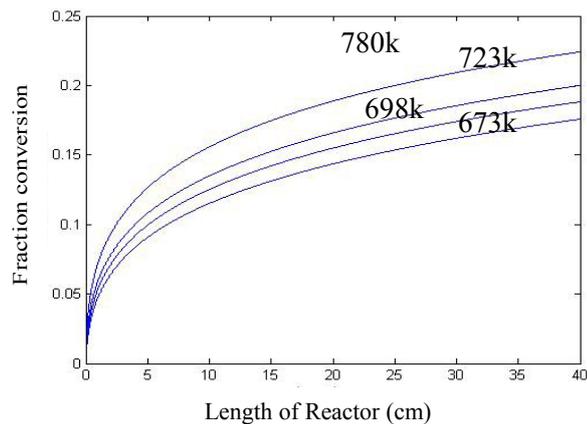
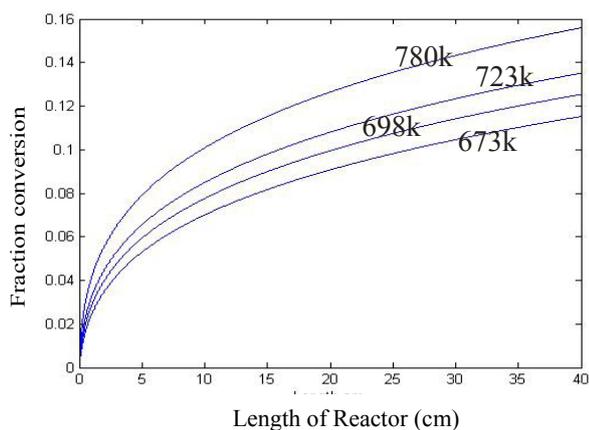


Fig.1. fraction conversion in 0.28 feed flows

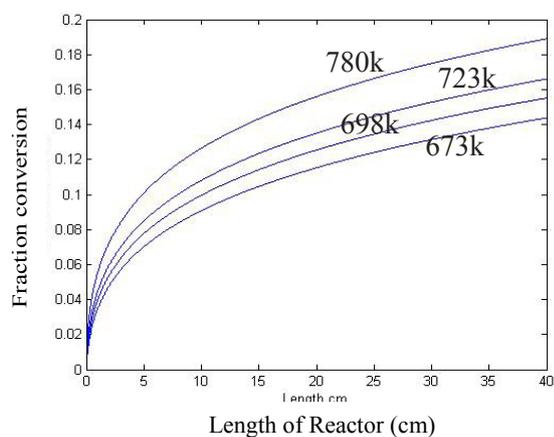


**Fig.2.** fraction conversion in 0.14 feed flows

According to results of this study, for a specific isotherm, the bed density increase leads to an increase in the conversion percentage of benzene to ethyl benzene. Isotherms are illustrated in fig. 3 and 4.

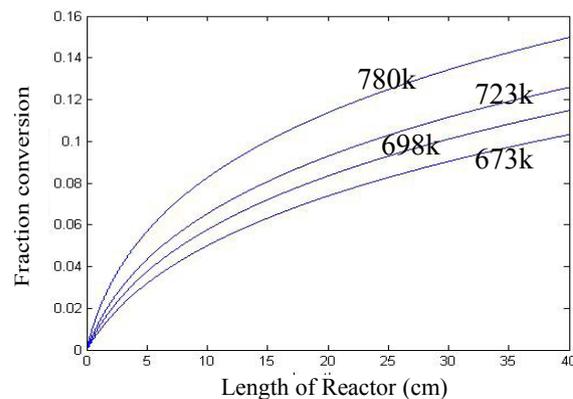


**Fig. 3.** fraction conversion in 0.3 Density of bed

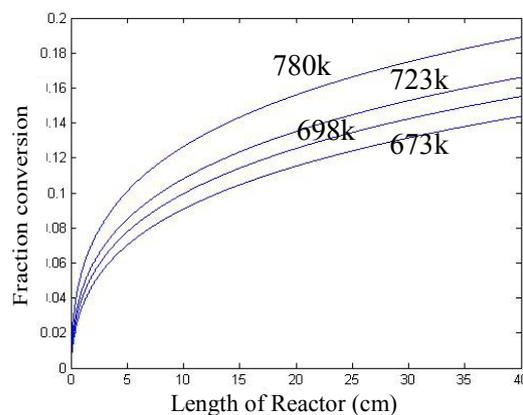


**Fig. 4.** fraction conversion in 0.6 Density of bed

According to the results, the increase of the total bed pressure for each specific isotherm increases exchange percentage ( see fig. 5 and 6).



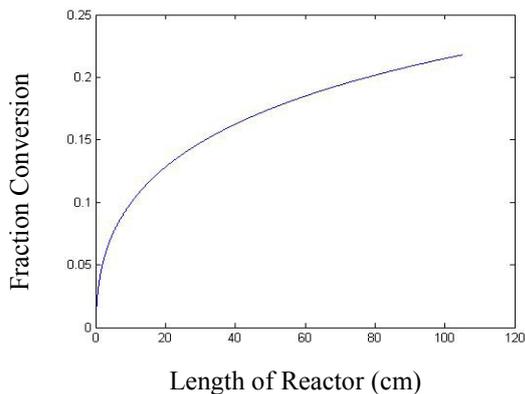
**Fig. 5.** fraction conversion in 2 atm total pressure



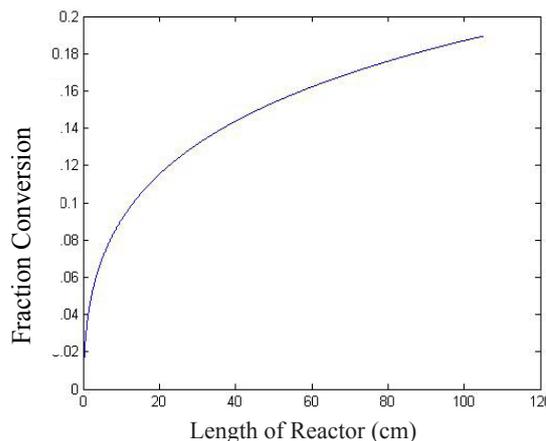
**Fig. 6.** fraction conversion in 22 atm total pressure

## 7.2. Adiabatic mode

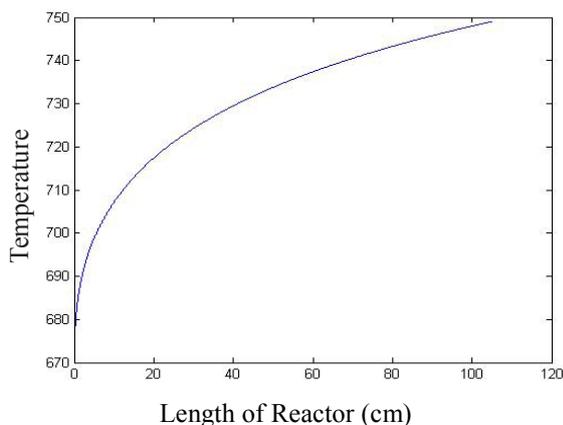
According to the results of this study, the bed density decrease and increase in the adiabatic mode and the constant heat capacity does not effect on the amount of conversion of benzene to ethyl benzene. However the conversion percentage is higher than the isotherm mode. Furthermore, the bed density changes do not affect on the bed temperature profile within the reactor. These results are shown in fig. 7 and 8.



**Fig. 7.** fraction conversion versus length of reactor in 0.6 bed density



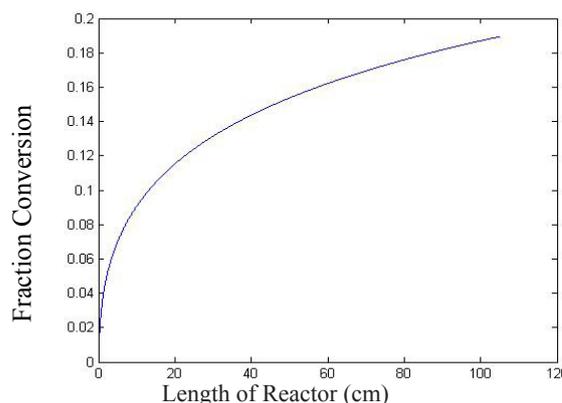
**Fig.10.** conversion percentage versus length of reactor in 700 Kelvin temperature feed flow



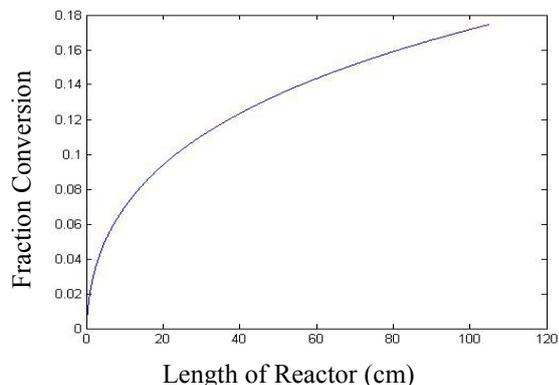
**Fig. 8.** Temperature versus length of reactor in 0.6 bed density

According to the results of this study, the feed temperature increase leads to a rise in the conversion percentage. Also results of the search show that the pressure increase and decrease do not affect on the conversion percentage and the temperature profile in a constant and variable heat capacity state (see fig. 9 and 10).

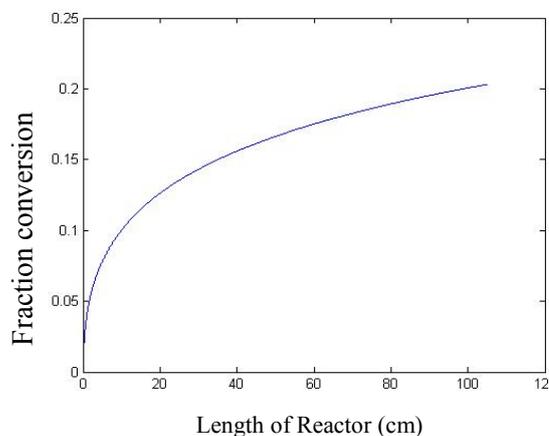
Also, the results indicated in fig. 11 and 12 show that the amount of conversion percentage of ethyl benzene in the variable heat capacity mode increases by temperature raising that is less than constant heat capacity state.



**Fig. 11.** fraction conversion versus length of reactor in 673 Kelvin temperature

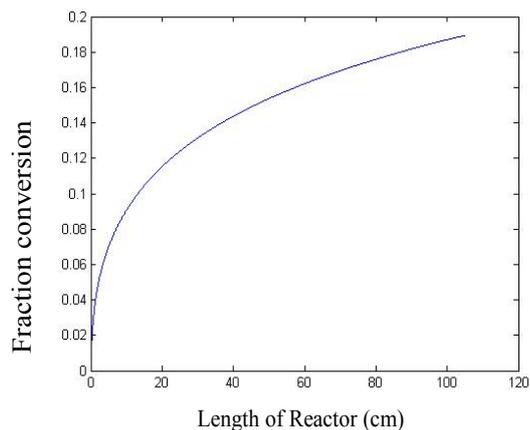


**Fig. 9.** fraction conversion versus length of reactor in 673 Kelvin temperature feed flow

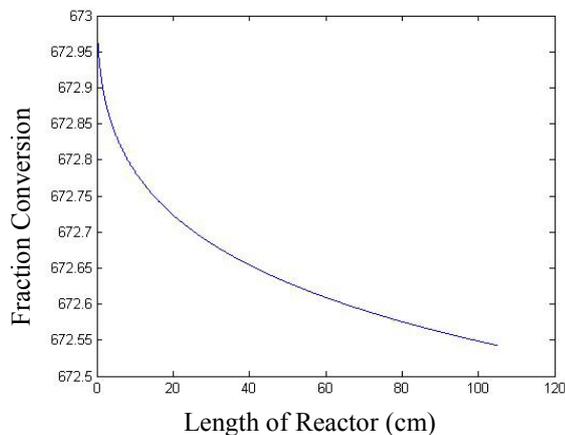


**Fig. 12.** fraction conversion versus length of reactor in 700 Kelvin temperature

According to the results, the input discharge changes do not have any effect on the conversion percentage in both fixed and variable heat capacity, and temperature profiles are the same with discharge changes. On the other hand the bed density affects on the conversion percentage and temperature profiles in variable heat capacity mode.



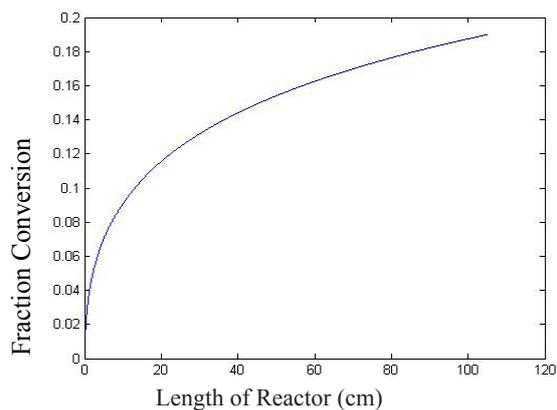
**Fig. 13.** fraction conversion versus length of reactor in 700 Kelvin temperature



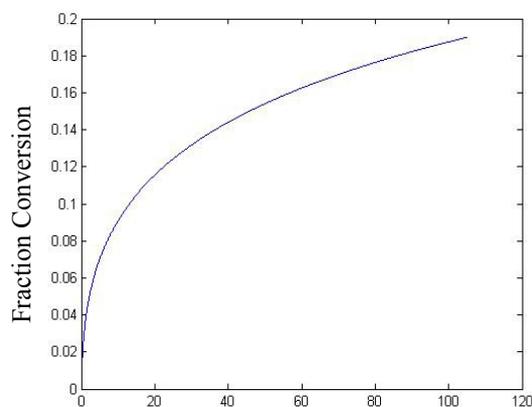
**Fig. 14.** fraction conversion versus length of reactor in 700 Kelvin temperature

### 7.3. Non-isotherm - non-adiabatic

According to this research, bed density changes in the fixed and variable heat capacities are similar and no changes have been observed in them (see fig 15, 16). Also changes in the amount of feed charge have no effect on ethyl benzene conversion percentage but this amount is more in fixed heat capacity than the variable heat capacity.

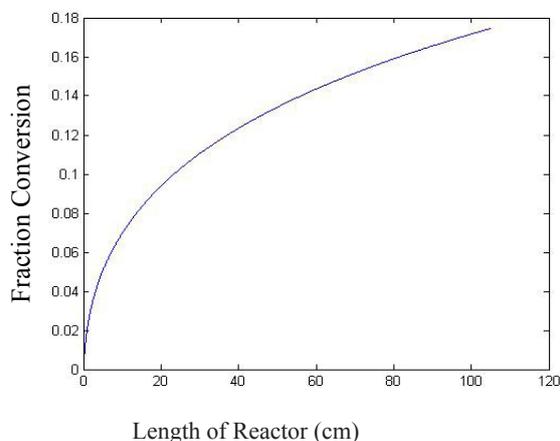


**Fig. 15.** fraction conversion versus length of reactor in variable fixed bed density and fixed heat capacity

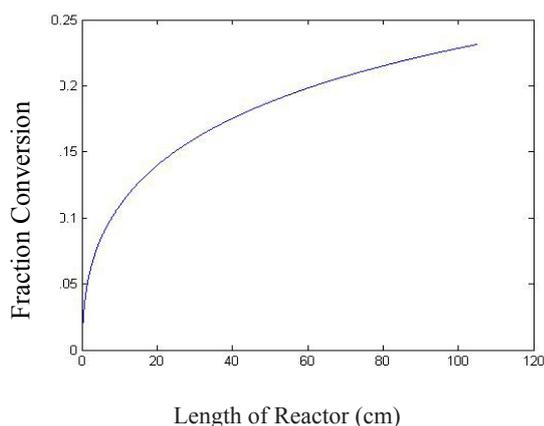


**Fig. 16.** fraction conversion versus length of reactor in variable fixed bed density and variable heat capacity

Fig. 17 and 18 demonstrate that the conversion percentage of ethyl benzene in a fixed heat capacity and variable heat capacity increases by increasing feed temperature.



**Fig. 17.** fraction conversion versus length of reactor in 600 Kelvin temperature



**Fig. 18.** fraction conversion versus length of reactor in 700 Kelvin temperature

## 8. Conclusion

With the results obtained in this study it can be observed that in the isotherm mode, by increasing temperature of isotherm, conversion percentage increases, and this result is similar to the experimental results of [7] observed. Also by increasing bed density and pressure, the conversion percentage of ethyl benzene increases in isotherm mode, and the conversion percentage decrease by rising flow rate. In the adiabatic mode, for the same bed density in a constant heat capacity, the degree of increase of conversion percentage is more than variable heat capacity. Also changes in temperature profiles along the reactor in a state of constant heat capacity and adiabatic are much higher than variable heat capacity, the temperature profiles increase in the constant heat capacity but they decrease in the variable heat capacity state along the reactor. Conversion percent profiles are alike in the non isotherm-non adiabatic mode for both fixed and variable heat capacities in the same flow rate. The temperature profile changes are very small however their slopes of changes are opposite.

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## Signs and symbols with their units

Particle diameter [cm]	$D_p$
Viscosity [centipoises]	$\mu$
Fluid thermal conductivity [w/mk]	$k_g$
Adsorption constant of benzene [1/atm]	$K_B$
Adsorption constant of Ethanol [1/atm]	$K_E$
Adsorption constant of ethyl benzene benzene [1/atm]	$K_{EB}$
Adsorption constant of water [1/atm]	$K_w$
Adsorption constant of hydrogen [1/atm]	$K_H$
Kinetic constant [kgmole/ (kg catalyst.hr)]	$k$
Density of bed [gr/cubic centimeter]	$\rho_B$
Partial pressure [atm]	$p$
Total pressure [atm]	$p$
Rate of reaction of benzene [kgmole/ (kg cat.h)]	$r_B$
Porosity of bed	$\varepsilon$
Heat transfer coefficient [w/mk]	$h_w$
Length of reactor [cm]	$z$
Fractional benzene conversion [dimensionless]	$X_B$
Enthalpy of formation [kcal/grmole]	$\Delta H_{298}^f$
Enthalpy of reaction [cal/grmole]	$\Delta H_{rxn}$
Heat capacity [cal/grmole K]	$C_p$
Mass velocity [gr/s.cm <sup>2</sup> ]	$G$
Ambient temperature [K]	$T_w$

