Partial oxidation of ethane in a fluidized bed reactor

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Partial oxidation of ethane in fluidized bed is studied. A simple model based on two-phase theory of fluidization is developed for the fluidized bed. The proposed configuration of the bed is composed of immersed cooling tubes that remove the heat generated from the exothermic reaction by liquid coolant flow in these tubes. Simulation of the model for a fluidized bed with inlet feed temperature of 520 k, pressure of 20 atm. and ethane mole fraction of 0.82 resulted in ethane conversion of 18.2 %, ethylene selectivity of 54.9 % and acetic acid selectivity of 42 %. Under similar operating conditions, reactions carried out using three consecutive fixed bed reactors resulted in ethane conversion of 16.5%, ethylene selectivity of 55.4% and acetic acid selectivity of 37.2 %. Preliminary economic analysis indicated that the estimated price of catalyst for both cases offset any profitability of the process. This may require further catalyst development, changing reaction conditions and reactor design optimization in order to reduce costs.

يتضمن البحث دارسة الأكسدة الجزئية للايثان في مفاعل ذو مهد مميع . وقد اختير نموذج الطورين المبسط لوصف المهد المميـــع الذي يتكون من مهد مغمور به أنابيب تبريد لامتصاص الحرارة الناتجة من التفاعل الطارد للحرارة باستخدام سائل تبريد. وقد تـم محاكاة النموذج باستخدام درجة حرارة ٥٢٠ كلفن وضغط ٢٠ جوي وكسرمولي لغاز الايثان ٨٢,و. نتج عنه تحـــول للايثـان مقداره ١٨,٢% وانتقائية لمنتج الايثلين وحمض الخليك مقدارهما ٥٤,٩% و٤٢% على التوالي. تحت نفـس ظـروف التشـغيل وباستخدام ثلا ث مفاعلا ت متتاليه تعمل بالمهد الثابته.كان التحول في الايثان مقداره ١٦,٥% وانتقائية الايثلين وحمض الخليـــك مقدارهما ٥٥,٤% و ٣٧,٢ %على التوالي. واشارت التحليلات الاقتصادية المبدئية على أن سعر المحفز المستخدم لكلا الحـــالتين يلغي الربحية لكل منهما . هذا يوضح أنه لازالت هناك حاجه إلى تطوير المحفزات المستخدمه للتفاعل وكذلك تغير طرق التشغيل والاتجاه إلى تحديد التصميم الأمثل للمفاعل لتقليل التكلفة.

Keywords: Ethane, Ethylene, Acetic acid, Fluidized bed, Modeling

1. Introduction

The oxidation reaction of hydrocarbons is usually exothermic. To avoid running the reaction inside the range of flammability, the reaction mixture should have either a high hydrocarbon to oxygen ratio or high oxygen to hydrocarbon ratio. In a previous study [1], the partial oxidation of ethane in a fixed bed reactor was investigated. At high oxygen to hydrocarbon ratio, complete combustion products are favored. Thus high hydrocarbon to oxygen ratio has to be used. To avoid working in the flammability range, control thermal runaway and to reduce the amounts of CO and CO_2 in product, the mole fraction of oxygen is limited to about 0.06. This means that in order to obtain a reasonable ethane conversion and to avoid recycling a large amount of ethane, many reactors (that could reach ten reactors) with fresh oxygen

introduced to each one of them should be used.

In fluidized beds, higher oxygen mole fractions in the feed could be used due to the high degree of mixing. This results in a low oxygen mole fraction in the bed. In addition, fluidized beds offer other advantages such as: better heat transfer, removal of diffusion resistance inside the catalyst particles because of their small size and better temperature control because of the mixing. The main disadvantage of fluidized bed is the possibility of catalyst loss due to attrition and the erosion of cooling tubes. These problems have been resolved in some industrial cases such as the oxidation of butane to maleic anhydride and the ammoxidation of propylene to acrylonitrile.

Many investigators have explored the use of fluidized beds for the oxidation of butane [2], ethylbenzene [3], ammoxidation of propylene to acrylonitrile [4] oxidative coupling

of methane [5,6] and o-xylene [7]. Partial oxidation was studied using different catalysts such as VPO, VO, MoVNb and B_2O_3 [8-10]. The paper of Ruth et al. [11] contains almost complete list of catalysts tested for ethane partial oxidation. The reaction kinetics for this reaction is presented by Thorsteinson et al. [8]. The hydrodynamic and transport properties are obtained from the correlation presented in ref. [2].

In this paper, the possibility of using fluidized beds for the partial oxidation of ethane is investigated and its results are compared with that obtained by those from fixed bed reactors.

2. Development of the mathematical model

To explore the possibility of using fluidized bed for the partial oxidation of ethane, a simple model is used. A two-phase model used by previous investigators [2-4] is developed in this work to take into consideration the kinetics of oxidative dehydrogenation of ethane obtained by Thorsteinson et al. [8]. This model is based on considering the bed as consisting of a bubble Phase and a dense phase. Several famous companies such as Union Carbide, British Petroleum, Rhone Poulenc and many other researchers [12,13,14] have studied this reaction. The reaction is attractive since it produces ethylene, which is a major petrochemical product, by another route than the existing thermal cracking process that suffers from high capital cost in separation of the cracked gas to get high purity ethylene.

2.1. Bubble phase balances

Mass balances for component j in the bubble phase gives:

$$\frac{N_{jb}}{Q_b} - \frac{N_{jd}}{Q_d} = (\frac{N_{jbF}}{Q_b} - \frac{N_{jd}}{Q_d}) \ e^{-ajZ} \ . \tag{1}$$

Where $aj = \dfrac{(K_{bd})_{jb}}{u_b}$. An energy balance for

the bubble phase is given by:

$$T_b = T_D - (T_D - T_F) e^{-bZ}$$

where,

$$b = \frac{H_{bd}}{u_b \rho_g Cp_g} \ . \tag{2}$$

2.2. Dense phase balances

A mass balance for component j in the dense phase is given by:

$$N_{jd} = x_{jF} N_F \frac{Q_{dF}}{Q_F} + U_b A_b (\frac{x_{jF} N_F}{Q_F} - \frac{N_{jd}}{W_{dF}})(1 - e^{-ajH})$$

$$+ V(1-\delta)(1-\varepsilon_{mf})\rho_g \sum_{i=1}^{n} \alpha_{ij} r_i \ . \tag{3}$$
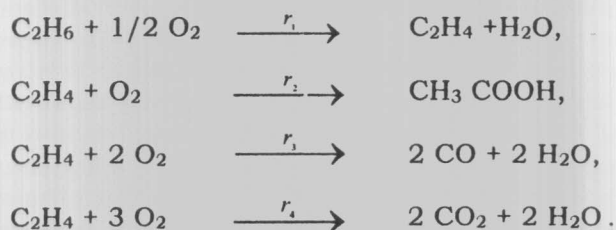
The energy balance around the dense phase is given by,

$$\rho_g Cp_g Q_{dF}(T_F - 298) - \rho_g Cp_g Q_d(T_D - 298)$$

$$+ h_w A_w(T_w - T_d)$$

$$+ u_b \rho_g Cp_g A_b(T_F - T_D)(1 - e^{-bH}) \tag{4}$$

$$+ V(1-\delta)(1-\varepsilon_{mf})\rho_p \sum_{i=1}^{n}(-\Delta H_i)r_i = 0 \ ,$$

where δ (volume fraction of bubble phase to overall bed) and A_b are given by,

$$\delta = \frac{(u_0 - u_{mf})}{u_b} \quad \text{and} \quad A_b = \delta A \ .$$

2.3. Reaction kinetics

The reactions occurring in the reactor are shown below. The rate equations, for these reactions, which were developed by Thorsteinson et al. [8], are adapted in this work.

$$C_2H_6 + 1/2 \ O_2 \xrightarrow{\ r_1 \ } C_2H_4 + H_2O,$$

$$C_2H_4 + O_2 \xrightarrow{\ r_2 \ } CH_3 COOH,$$

$$C_2H_4 + 2 \ O_2 \xrightarrow{\ r_3 \ } 2 \ CO + 2 \ H_2O,$$

$$C_2H_4 + 3 \ O_2 \xrightarrow{\ r_4 \ } 2 \ CO_2 + 2 \ H_2O \ .$$

Where

$$r_1 = \frac{-1.73 *10^3 e^{\frac{-5625}{T}} P_{C_2H_6} P_{O_2}}{(1+2.286 P_{C_2H_4} +14.63 P_{O_2})^2}, \tag{5}$$

$$r_2 = \frac{3.29*10^4 e^{\frac{-5625}{T}} P_{C_2H_4} P_{O_2} P_{H_2O}}{(1+1.84 P_{C_2H_4} +4.215 P_{O_2} +1.465 P_{H_2O})^3}, \tag{6}$$

$$r_3 = \frac{1.755*10^{11} e^{\frac{-15270}{T}} P_{C_2H_4} P_{O_2}}{(1+0.3119 P_{C_2H_6} +6.83 P_{C_2H_4})^2}, \text{ and} \tag{7}$$

$$r_4 = \frac{2.96*10^5 e^{\frac{-9318}{T}} P_{C_2H_4} P_{O_2}^{\frac{1}{2}}}{(1+3.787 P_{C_2H_4})^2}. \tag{8}$$

These kinetic equations are obtained for catalyst particles of average diameter 0.64 cm. Thus these kinetic expressions are not the intrinsic kinetics. Notice that the rates as obtained in ref. [8] are given in kg moles/kg catalyst h. Thus they need to be transformed into kg moles/kg catalyst. But fortunately for our case the intraparticle diffusion can be neglected, since the effectiveness factor is almost unity. From the work of Burch and Swarnakar [15] for the same reaction with same catalyst in form of powder, a rate constant of 0.004 s⁻¹ at 548 K and 20 atm. is estimated. The ethane effective diffusivity at 548 K and 20 atm. is estimated to be 0.002 cm²/s. Thus the generalized Thiele modulus for 0.64 cm catalyst particle is

$$\Phi = \frac{r}{3}\sqrt{\frac{k}{D}} = \frac{0.32}{3}\sqrt{\frac{0.004}{0.002}} \cong 0.15, \text{ and}$$

$$\eta = \text{effectivne ss factor} = \frac{\tanh \Phi}{\Phi}$$

$$= \frac{\tanh 0.15}{0.15} \cong 0.993 \cong 1.$$

2.4. The overall model

For the overall model the pressure should be related to the molar flow rates. These relations are given by,

$$N_F = N_{F,C_2H_6} + N_{F,O_2} + N_{F,CO} + N_{F,CO_2} + N_{F,H_2O} + N_{F,C_2H_4} + N_{F,AC.AC}, \tag{9}$$

$$N_T = \frac{N_F}{(1-0.5X_1 +0.5X_2 -1.5X_3 -0.5X_4)}, \tag{10}$$

$$P_{C_2H_6} = (\frac{N_{F,C_2H_6}}{N_T} - X_1 - X_2 - X_3 - X_4) P, \tag{11}$$

$$P_{Ac.Ac} = (\frac{N_{F,Ac.Ac}}{N_T} + X_2)P, \tag{12}$$

$$P_{CO} = (\frac{N_{F,CO}}{N_T} +2X_3)P, \tag{13}$$

$$P_{CO_2} = (\frac{N_{F,CO_2}}{N_T} +2X_4)P, \tag{14}$$

$$P_{C_2H_4} = (\frac{N_{F,C_2H_6}}{N_T} + X_1)P, \text{ and} \tag{15}$$

$$P_{O_2} = (\frac{N_{F,O_2}}{N_T} -0.5X_1 -1.5X_2 -2.5X_3 -3.5X_4)P. \tag{16}$$

Where the conversion of $C_2H_6, CH_3COOH, CO,$ and CO_2 are defined by,

$$X_1 = (\frac{N_{F,C_2H_6 - n_{C_2H_6}}}{N_{F,C_2H_6}}), \tag{17}$$

$$X_2 = (\frac{n_{CH_3COOH} - N_{F,CH_3COOH}}{N_{F,C_2H_6}}), \tag{18}$$

$$X_3 = (\frac{n_{CO} - N_{F,CO}}{N_{F,C_2H_6}}), \text{ and} \tag{19}$$

$$X_4 = (\frac{n_{CO_2} - N_{F,CO_2}}{N_{F,C_2H_6}}). \tag{20}$$

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3. Numerical solution

For an assumed dense phase temperature, the four non-linear algebraic equations representing the material balance equation (eq. (3)) with the rate equations given by eqs. [5-8] are solved using the Newton method provided by ZSPOW subroutine of IMSL library. Having obtained the concentration of different species, the conversions, selectivity, and yields could be calculated.

4. Results and discussion

The study involves modeling and simulation of a fluidized bed reactor. The reactor is used for partial oxidation of ethane into ethylene and acetic acid. The results are expressed in terms of conversion of ethane, selectivity, and yields (product of conversion and selectivity) of ethylene and acetic acid. The study involves also comparison of the performance of fixed and fluidized bed reactors. Fixing the operating conditions for both cases is the basis of the comparison. The data are for a plant that could produce about 105 kt/year of ethylene and 170 kt/year of acetic acid. table 1 depicts the design data, while table 2 shows the operating conditions. Comparison results of fixed and fluidized bed reactors are given in table 3. It is to be noticed that in case of fixed bed reactors, three reactors are used with the same constant inlet temperatures and equally distributed flowrates of oxygen. The inlet temperature of each of three fixed bed reactors is kept at 520 K in order to avoid temperature runaway.

The fluidized bed has higher conversion and selectivity towards acetic acid formation. The heat transfer area of fluidized bed is about 1/7of that of fixed bed due to higher heat transfer coefficient and higher temperature driving force. On the contrary the catalyst weight in the fluidized bed is about 4 times that in the fixed bed due to lower reaction rate because of the back mixing. If one estimates a catalyst price of 100 $/kg and one year service, the cost of catalyst annual charge for the fluidized bed becomes 48.8 million dollars and that for fixed bed case becomes 12.2 million dollars. These prices are high enough to make these processes unsuitable for economic production of ethylene and acetic acid. Thus the catalyst development program should be directed towards better catalyst activity, stability and suitable support materials.

The fixed bed reactor using the base case conditions is similar to that used for fluidized bed. Fig. 1 shows the temperature distribution along each of the three reactors used. In the first reactor there is no hot spot because the oxygen is not completely consumed, while in the second and the third reactors hot spots appear around the center of the reactor. This is because oxygen has totally reacted at the hot spot. No more reactions take place afterwards and the heat exchange with coolant serves only as to cool product gases.

Fig. 2 shows the conversion profile, while figs. 3,4 show the selectivity of both ethylene and acetic acid produced from the reactions. As we move along the reactor ethylene is converted to acetic acid. In order to check if it is possible to improve the yield from the fluidized bed by changing mole fraction, different conditions of feed other than the base case were tested.

Figs. 5-9 are obtained when a total feed input of 2506 moles, feed temperature of 473 K and total pressure of 20 atmosphere are used. As can be seen in fig. 5 the increase of dense phase temperature increases the conversion sharply up to a maximum value then starts to decrease slowly. The sharp increase in conversion or the shift of the maximum value of conversion, as the mole fraction of ethane increases, is due to the movement of steady state from the quenched state to the ignited state. The selectivity of acetic acid starts to increase to a maximum at each feed composition used then decreases due to the formation of carbon oxides as shown in fig.6. It is also noted that the maximum acid selectivity goes through optimum value depending on feed concentration (ethane mole fraction of 0.7). While ethylene selectivity decreases initially then increases, the selectivity is higher at lower feed composition. The yield of acetic
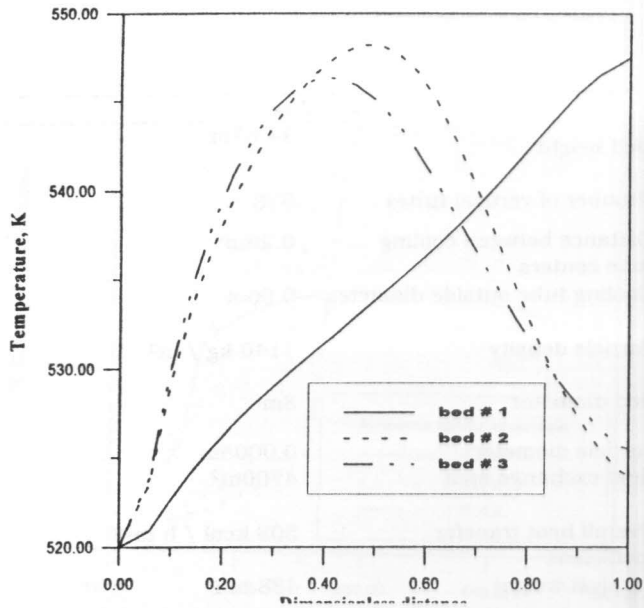
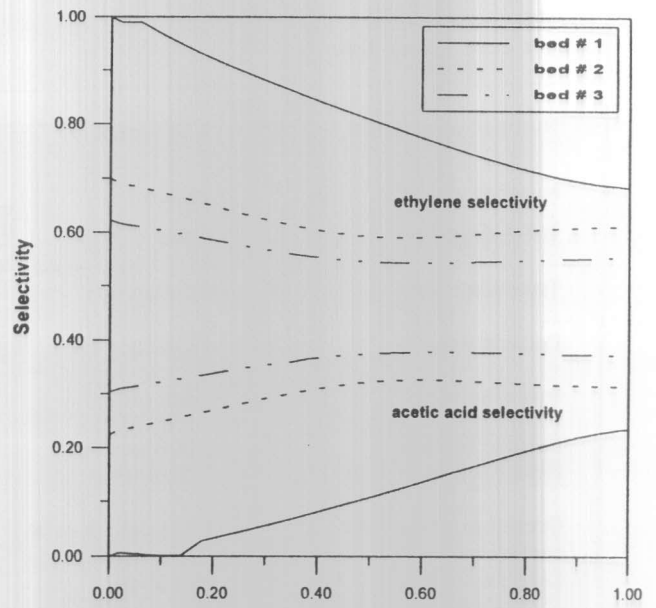Fig. 1. Temperature profile along the fixed bed reactors.

Figure 1. Temperature profile along the fixed bed reactors

Fig. 2. Conversion of ethane along the fixed bed reactors.

Fig. 3. Selectivity profile along the fixed bed reactors.

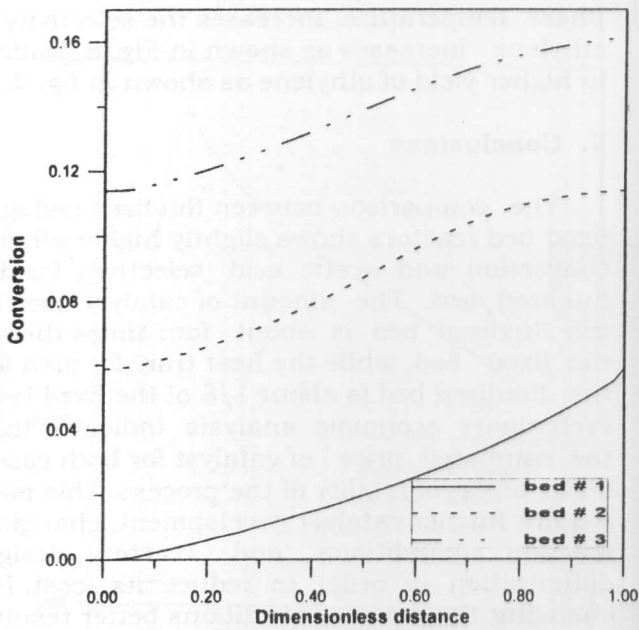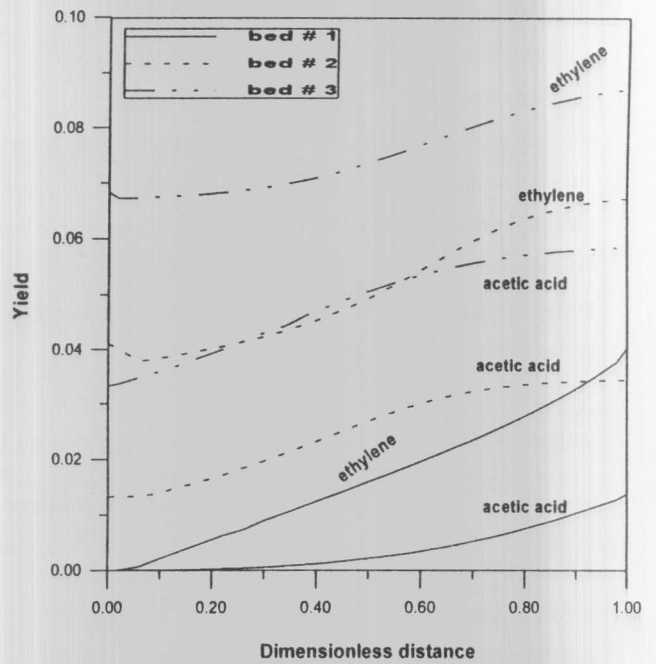**Figure 3. Selectivity profile along the fixed bed reactors**

Fig. 4. Yield profile along the fixed bed reactors.

Table 1
Base case design data

Fixed bed		Fluidized bed	
Number of reactors	3 in Series	Bed height	14.67m
Number of tubes	24660	Number of vertical tubes	858
Tube length	6.0m	Distance between cooling tube centers	0.26m
Tube diameter	0.025m	Cooling tube outside diameter	0.06m
Particle density	1140 kg / m³	Particle density	1140 kg / m³
Bed diameter	6.5m	Bed diameter	8m
Particle diameter	0.0064m	Particle diameter	0.0005m
Heat Exchange area	34862m²	Heat exchange area	4700m²
Overall heat transfer coefficient	110 kcal / h m²K	Overall heat transfer coefficient	508 kcal / h m²K
Catalyst weight	124.2 ton	Catalyst weight	488 ton

Table 2
Base case operating conditions.

Feed temperature	520K
Coolant temperature	473K
Feed pressure	20 atm
Ethane mole flow rate	1370.5 gmole / s
Ethane molar fraction (X_{C2H6})	0.820
Oxygen molar flow rate	263.694 gmole / s
Oxygen mole fraction (X_{O2})	0.158
Water molar flow rate	37.041 gmole / s
Water mole fraction (X_{H2O})	0.022

Table 3
Comparison results for fluidized and fixed bed reactors.

Results	Fixed bed	Fluidized bed
% Ethane conversion	16.5	18.2
% Acetic acid selectivity	37.2	42.0
% Ethylene selectivity	55.4	54.6
% Acetic acid yield	61.3	76.4

acid is increasing initially at lower dense phase temperature then it decreases due to the formation of carbon oxides as shown in fig. 7.

A yield of 0.13 is obtained for the case of mole fraction 0.82. The ethylene yield is low at lower dense phase temperature, however, as dense phase temperature increases the selectivity of ethylene increases as shown in Fig. 8, leading to higher yield of ethylene as shown in fig. 9.

5. Conclusions

The comparison between fluidized bed and fixed bed reactors shows slightly higher ethane conversion and acetic acid selectivity for the fluidized bed. The amount of catalyst used in the fluidized bed is about four times that of the fixed bed, while the heat transfer area for the fluidized bed is about 1/8 of the fixed bed. Preliminary economic analysis indicated that the estimated price of catalyst for both cases offset any profitability of the process. This may require further catalyst development, changing reaction conditions and reactor design optimization in order to reduce its cost. By changing the reaction conditions better results may be obtained. For the case of fluidized bed using higher feed temperature an acid yield of 0.13 can be obtained, while for the base case an acid yield of only 0.076 is obtained. For the fixed bed, the improvement of the heat transfer performance could be achieved by using
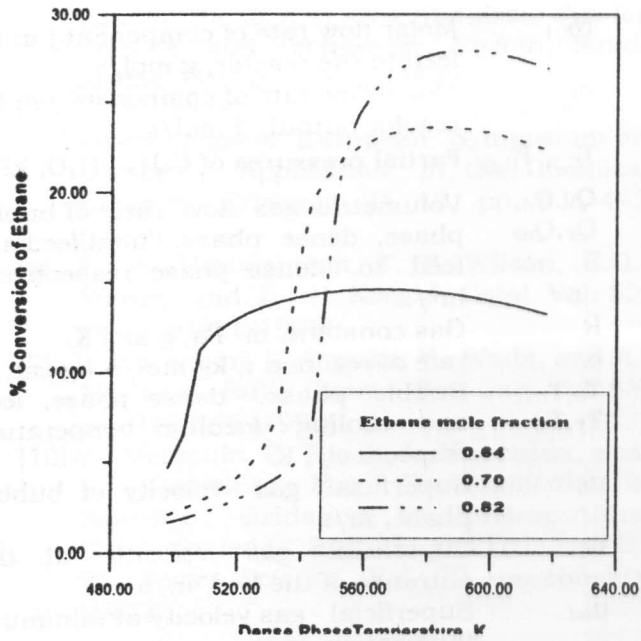
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Fig. 5. Effect of feed composition on conversion of ethane.

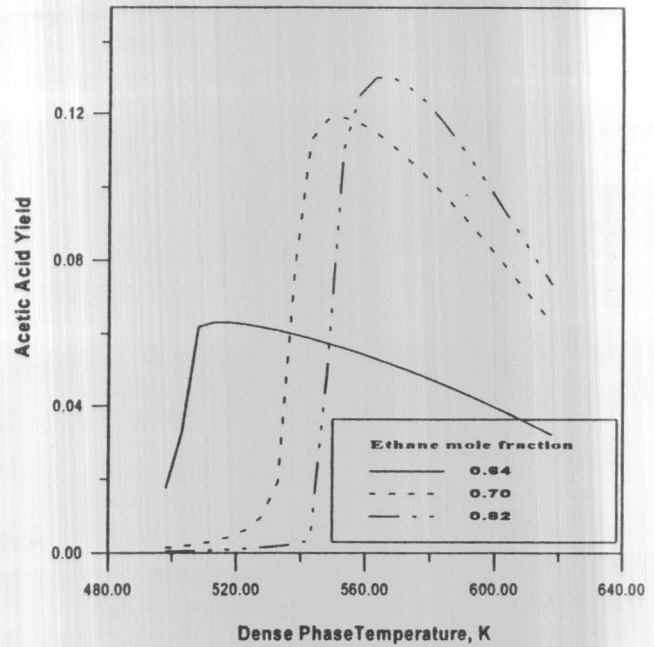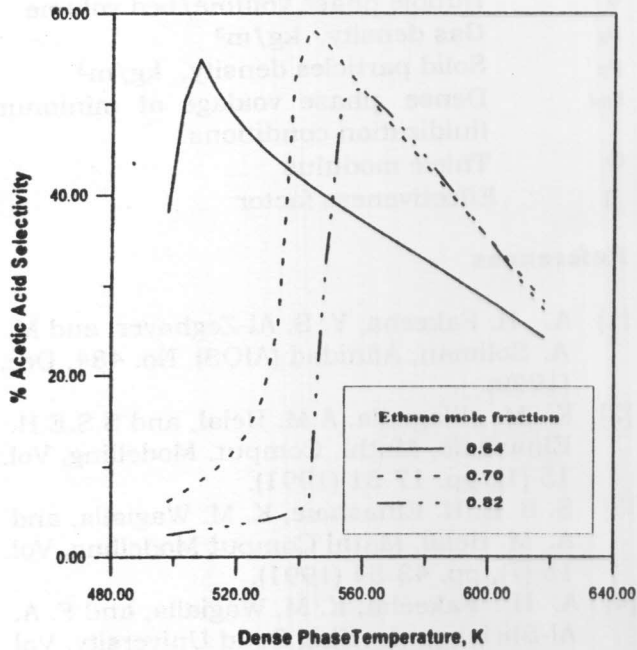Fig. 6. Effect of feed composition on acetic acid selectivity.

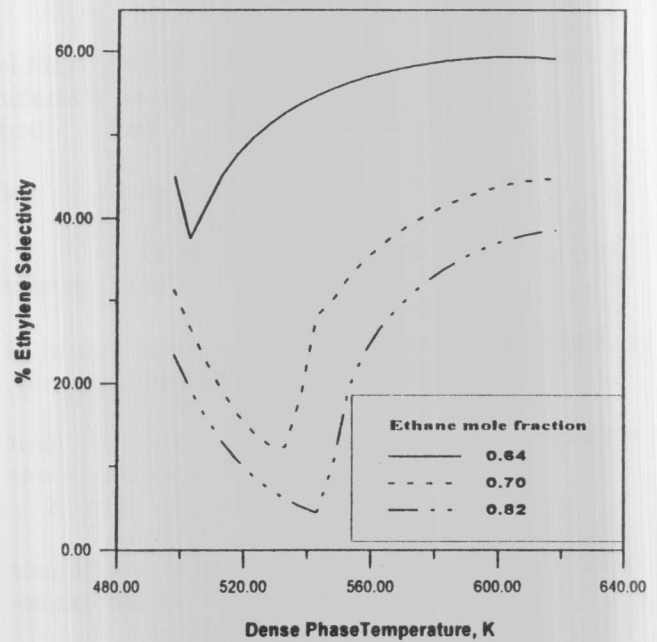Fig. 7. Effect of feed composition on acetic acid yield.

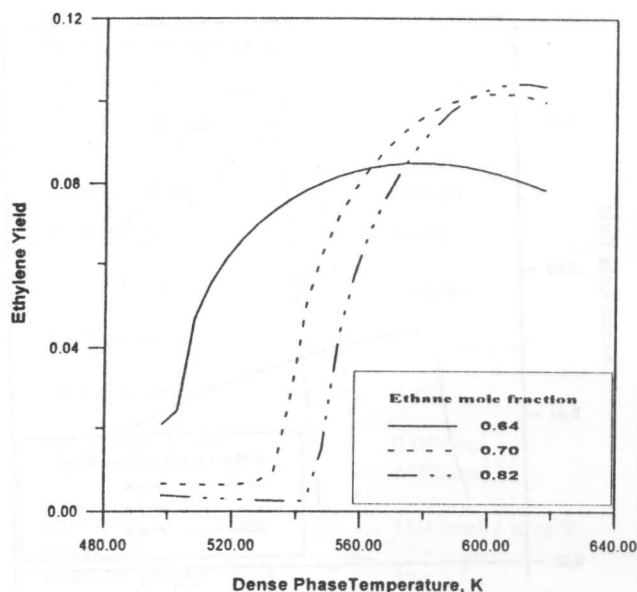Fig. 8. Effect of feed composition on ethylene selectivity.

Fig. 9. Effect of feed composition on ethylene yield.

co-current cooling. For instance, Bucala et al. [16] has shown the possibility of operating fixed bed reactors close to isothermal conditions by co-currently cooling the reactor.

Nomenclature

A, A_b, A   Cross-sectional area of bed, bubble phase and area of heat transfer between coolant and bed respectively, m^2.

a_{ij} Stoichiometric coefficient of component j in reaction, i

c_{pg} Gas heat capacity, J/kg K.

h_w Bed to cooling surface heat transfer coefficient, J/ m^2s K

H, H_{mf} Expanded bed height and height at minimum fluidization respectively, m

$(H_{bd})b$ Interphase heat transfer coefficient between bubble and dense phase based on bubble volume, J/m^3 K

$(-\Delta H)$ Heat of reaction, kcal / kmole

$(K_{bd})jb$ Interphase mass transfer coefficient between bubble and dense phase based on bubble volume, s^{-1}

N_{jb}, N_{jbF},   Molar flow rate of component j in the

N_{jd}, N_{jF} bubble phase, feed to bubble phase, dense phase and total feed respectively, g mol/s.

N_F Total molar flow rate of fresh feed to fluidized bed reactor, g mol/s.

$N_{F,j}$ Molar flow rate of component j in the feed to the reactor, g mol/s.

n_j Molar flow rate of component j in the reactor output, g mol/s.

$P_{C_2H_4}$, P_{H_2O} Partial pressures of C_2H_4 , H_2O, kPa

Q_b, Q_d,   Volumetric gas flow rate of bubble

Q_F, Q_{dF} phase, dense phase, total feed and feed to dense phase respectively, m^3/s.

R   Gas constant, m^3 Pa/g mol K.

r_i rate of reaction i, kg mol/h kg cat.

T_b, T_D,   Bubble phase, dense phase, feed

T_F, T_W and cooling medium temperature respectively, K.

u_b Superficial gas velocity of bubble phase, m/s.

u_0 Superficial gas velocity at the entrance of the bed, m/s

u_{mf} Superficial gas velocity at minimum fluidization, m/s

V   Reactor volume, m^3

X_F Feed mole fraction

X   Conversion

Z   Distance along the bed height, m

δ Bubble phase volume/bed volume

ρ_g Gas density, kg/m^3

ρ_p Solid particles density, kg/m^3

ε_{mf} Dense phase voidage at minimum fluidization conditions.

Φ Thiele modulus

η Effectiveness factor

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