

Design of Plug Flow Reactor for Dehydration of Ethanol

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Abstract: This research originates as design model for dehydration of ethanol obtained from renewable feed materials into diethyl-ether as a petrochemical feed for downstream sectors of the economy. The rate law to drive the synthetic reactions was developed by the differential method of kinetic parameters evaluation process. The reactor parameters for space velocity, space time, length of the reactor, heat generated per unit volume and the weight of the catalyst to fractional conversion were plotted showing profiles relationship on the parameters. The research considered the scaling-up of the model parameters control to full scale industrial application by adopting specific scale-up mathematical and chemical engineering rules on the shape and geometry of the tubular reactor. The resolution of the model integration process for space-velocity, space-time, length of the reactor, heat generated per unit volume, weight of catalyst to fractional conversion were evaluated using mat-lab 7.1 version. The relationship shows a progressive optimal reactor performance in the plotted graphs.

Keywords: Design model, rate law, vapour-phase-dehydration-ethanol, kinetic parameters, scaling-up

1. Introduction

Ethanol (C₂H₅OH) otherwise known as alcohol is a volatile, flammable, clear, colourless liquid. It is used as a germicide, beverage, antifreeze, fuel, depressant and chemical intermediate. Alcohols are made from either grains or biomass by first converting these materials to fermentable sugars. The sugars are then fermented, typically with yeast, to give a broth containing 6 to 12 percent ethanol along with small amounts of aldehydes, ketones, amyl alcohols, and methanol. The final step, distillation to water-free alcohol, consumes 50 to 80 percent of the energy used in a typical fermentation ethanol manufacturing process. The energy intensity of traditional distillation techniques is frequently cited in criticizing the potential of biomass-derived ethanol as a liquid fuel (Michael and George, 1982); (Dogu and Dilek, 2007); (Kupiec and Kubala, 2006); (Rajkhowa, 2011); researched on the dehydration of alcohol into many products.

An insight on the process chemistry, a dehydration reaction is usually the act of chemical reaction that involves the loss of a water molecule from the reacting molecule. Dehydration reactions are a subset of condensation reactions, because the hydroxyl group (-OH) is a poor leaving group, having a bronsted acid catalyst often helps by protonating the hydroxyl group to give the better leaving group, OH₂⁺ (Brent and

Roberts, 2011). In recent years the ever increasing value of fossil hydrocarbon liquids and gases has directed attention to the possibilities of employing bio-mass materials for fuel purposes. In particular, attention has been directed to the possibilities for employing fermentation derived ethanol alone or in a mixture with gasoline fraction hydrocarbons for automotive fuel purposes, the mixture of 90% hydrocarbon and 10% ethanol (Abowei and Ogoni, 1988) model for the heat generated per unit volume of reactor was adopted to quantify the heat generated in the envisaged reactor.

Nauman, (2001) Scale up parameters of length, diameter, volume and heat generated per unit volume, q ; was developing using fully turbulent for plug flow reactor since the reaction is gas-phase. The model developed were simulated using version 7.1 of matlab and the various results for the parameters: space time (τ), space velocity (S_v), volume of reactor (V_R), weight of the catalyst, length of the reactor, diameter of the reactor and heat of generated per unit volume, were tabulated, various plots were obtained and figures 4 to 6 results of the plots accordingly discussed. Finally, the scaling-up was broadened to accommodate different aspects of the reactor operations such as for isothermal operation, packed bed, tubular gas flow, laminar liquid flow, tubular liquid flow, tubes in series and tubes in parallel as shown in Table 2. This makes room for design flexibility to practically install.

2. Materials and Methods

To develop specific rate law model that is appropriate to drive the dehydration of ethanol to diethyl ether in a tubular reactor and simulate model for parameters control of the reactor performance, thereby applying the findings from distillation data into large scale production (Nigeria Local Content, 2004).

The dehydration of ethanol to form di-ethyl-ether (desire product) and water is carried out in the catalytic bed reactor. Material and energy balances, rate law application and kinetic data and thermodynamic data are the analytical material components.

Feed Storage:

A 95% solution of ethanol (5% water) feed is stored at atmospheric pressure and temperature in a 1MM gallon, floating-roof storage tank. This volume is large enough to hold a one month supply of ethanol and will be replenished by the ethanol plants located conveniently in the area. The large

Table 1
 Physical properties of diethyl ether

Property	Value
CAS number	60-29-7
Molecular weight	74.14 gm/mol
Freezing point	-116°C
Boiling point	35°C
Density at 20°C, g/ml	0.71
Heat of formation	(-65.2) kcal/mole
Viscosity at 200C, mPas	0.23 cp
Color	Colorless
Solubility	Moderately soluble in water (6.9ml/100ml) and soluble in alcohol.
Auto ignition temperature	180°C
Flash point	-45°C (closed cup)
Surface tension at 20°C, dyne/cm	17.3 dyne/cm
Heat of vaporization, kJ/mol	6.215 kcal/mole

Table 2
 Name and number of equipment in the flow sheet

Number	1	2	3	4	5
Name	Reactor	Heat exchanger	Distillation column	Distillation column	Flash vessel
6	7	9	10	11	12
Heat exchanger	Flash vessel	Heat exchanger	Heat exchanger	pump	Heat exchanger

volume of storage allows the plant to continue operation.

A. Method

The analytical techniques design model.

1) Stoichiometrically balance model



A = CH₃CH₂OH

B = C₂H₅-O- C₂H₅

Where, A = ethanol, B = desired product DEE

2) Reaction Kinetics

Generally, chemical kinetics relates to the studies of the rates and mechanism at which chemical processes occur, and factors on which these rates depend and the molecular acts involved in reaction mechanisms (Kayode, 2001). Reaction kinetics is the branch of chemical process that quantifies rates of reaction which corresponds to a stoichiometrically equation.

$$\frac{dC_A}{d\tau} = -k_1 C_A^2 \quad (2)$$

$$\frac{dC_B}{d\tau} = k_1 C_A^2 \quad (3)$$

In-terms of fractional conversion, α we get for the desired product as thus;

$$(r_B) = \frac{dC_B}{dt} = k_1 C_{A0}^2 \{(1 - \alpha_A)^2\} \quad (4)$$

$$k_1(T) = A_0 e^{E_a/RT} \quad (5)$$

Rearranging and integrating equation (2) with Boundary Conditions: $\tau = 0$; $C_A = C_{A0}$; $\tau = \tau$ and $C_A = C_A$ gives:

$$\int \frac{dC_A}{C_A^2} = k_1 \int d\tau \quad (6)$$

$$C_A = \frac{C_{A0}}{1 + C_{A0} k_1 \tau} \quad (7)$$

For desired product DEE, equation (3) is used, rearranged and integrated with boundary conditions to get:

$$\frac{dC_B}{d\tau} = k_1 \left\{ \frac{C_{A0}}{1 + C_{A0} k_1 \tau} \right\}^2 \quad (8)$$

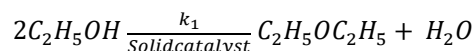
$$dC_B = k_1 \left\{ \frac{C_{A0}}{1 + C_{A0} k_1 \tau} \right\}^2 d\tau$$

$$\int_{C_{B0}}^{C_B} dC_B = k_1 \int_0^\tau \left\{ \frac{C_{A0}}{1 + C_{A0} k_1 \tau} \right\}^2 d\tau$$

$$C_B = \frac{C_{A0}^2 \tau}{1 + C_{A0} k_1 \tau} \quad (9)$$

3) Determination of rate law

Determination of an appropriate rate law and kinetic constants for the gas-phase dehydration reaction process kinetically represented as follows,



This utilizes the following kinetic data from a constant-volume batch reactor.

Table 3
 Vapour-phase dehydration of ethanol experimental data
 [Michael & George, 1982]

W(g)	P _{A0} (tm)	P _{E0} (atm)	P _{W0} (atm)	- r × 10 ⁴ (mol/gcat. min)
14.3	1.000	0.000	0.000	1.347
14.3	0.947	0.053	0.000	1.335
14.3	0.877	0.123	0.000	1.288
14.3	0.781	0.219	0.000	1.360
14.3	0.471	0.529	0.000	0.868
14.3	0.572	0.428	0.000	1.003
14.3	0.704	0.289	0.000	1.035
14.3	0.641	0.35	0.000	1.068
22.6	1.000	0.000	0.000	1.220
22.6	0.755	0.000	0.245	0.571
22.6	0.552	0.000	0.448	0.241
22.6	0.622	0.175	0.203	0.535
22.6	0.689	0.000	0.000	1.162

4) *Propounding reactor design model*

Taking a balance from first principles at steady state process in words and mathematics;

$$\left\{ \begin{array}{l} \text{Rate of input} \\ \text{of 1 mole of feed} \\ \text{material} \end{array} \right\} - \left\{ \begin{array}{l} \text{Rate of output} \\ \text{of 1 mole of feed} \\ \text{material} \end{array} \right\} - \left\{ \begin{array}{l} \text{Rate of depletion} \\ \text{of 1 mole of feed} \\ \text{material} \end{array} \right\} = 0 \quad (10)$$

Mathematically, stated as;

For 1mole of the feed material, we have;

$$F_{DEE}W - F_{DEE}(W + \Delta W) + (r_B)\Delta W = 0 \quad (11)$$

Re-arranging Equation (11) and dividing through by ΔW , yields:

$$-\left[\frac{F_{DEE}(W + \Delta W) - F_{DEE}(W)}{\Delta W} \right] = r_B \quad (12)$$

The left-hand side of Equation (12) is compared to the first principles derivative approach, given as:

$$\lim_{\Delta x \rightarrow 0} \left[\frac{f(x + \Delta x) - f(x)}{\Delta x} \right] = \frac{df}{dx} \quad (13)$$

Hence Equation (12) becomes

$$\lim_{\Delta W \rightarrow 0} \left[\frac{F_{DEE}(W + \Delta W) - F_{DEE}(W)}{\Delta W} \right] = -\frac{dF_{DEE}}{dW} \quad (14)$$

Combining the right hand side of Equation (12) and Equation (14) yields:

$$\frac{-dF_{DEE}}{dW} = r_B \quad (15)$$

Expressing equation (12) in terms of molar feed rate (flow-rate) for 1mole species

$$F_{DEE} = F_{DEE,0} - F_{DEE,0} \alpha_B \quad (16)$$

Rearranging equation (16) and differentiating gives:

$$dF_{DEE} = -F_{DEE,0} d\alpha_B \quad (17)$$

Substituting equation (17) into equation (12) yields

$$F_{DEE,0} \frac{d\alpha_B}{dW} = r_B \quad (18)$$

Re-arranging Equation (18) yields:

$$dW = F_{DEE,0} \frac{d\alpha_B}{r_B} \quad (19)$$

Equation (19) is integrated applying the boundary conditions for catalyst decay in the pack bed reactor to get.

$$\begin{aligned} W : 0 &\rightarrow W \text{ And} \\ \alpha : 0 &\rightarrow \alpha_{B,f} \\ W = \rho_{Cat} \cdot V &= F_{DEE,0} \int_0^{\alpha_{B,f}} \frac{d\alpha_B}{(r_B)} \end{aligned} \quad (20)$$

$$L = \frac{F_{DEE,0}}{\rho_{Cat} \cdot \pi r^2} \int_0^{\alpha_{B,f}} \frac{d\alpha_B}{(r_B)} \quad (21)$$

Design equations for heat generated per unit volume

From the works of (Abowei, 1988); heat generated for flow reactors is,

$$Q = F_{A0}(-\Delta H_R) \alpha_A \quad (22)$$

$$q = \frac{Q}{V_R} = \frac{\rho_{Cat} \cdot F_{A0}(-\Delta H_R) \alpha_A}{F_{DEE,0} \int_0^{\alpha_{B,f}} \frac{d\alpha_{DEE}}{(-r_{DEE})}} \quad (23)$$

3. Scaling-up of tubular reactors

[Nauman, 2001], There are three conceptually different ways of increasing the capacity of a tubular reactor:

- Add identical reactors in parallel. The shell-and-tube design used for heat exchangers is a common and inexpensive way of increasing capacity.
- Make the tube longer. Adding tube length is not a common means of increasing capacity, but it is used. Single-tube reactors exist that are several miles long.
- Increase the tube diameter, either to maintain a constant pressure drop or to scale with geometric similarity. This

Table 4
 Scale up factors for liquid-phase tubular reactors [Nauman, 2001]

Flow regime	General Scale up Factor	Series Scale up	Geometric Similarity	Constant Pressure drop Scale up
Fully Turbulent				
D	S_R	1	$S^{1/3}$	$S^{11/27}$
L	S_L	S	$S^{1/3}$	$S^{5/27}$
L/D	$S_L S_R^{-1}$	S	1	$S^{-1/9}$
ΔP	$S^{1.75} S_R^{-4.75} S_L$	$S^{2.75}$	$S^{1/2}$	1
Aext	$S_R S_L$	S	$S^{2/3}$	$S^{0.59}$
H	$S^{0.8} S_R^{-1.8}$	$S^{0.8}$	$S^{0.2}$	$S^{0.07}$
h Aext	$S^{0.8} S_R^{-0.8} S_L$	$S^{1.8}$	$S^{0.87}$	$S^{0.66}$
ΔT	$S^{0.2} S_R^{0.8} S_L^{-1}$	$S^{-0.8}$	$S^{0.13}$	$S^{0.34}$

means keeping the same length-to-diameter ratio L/d_t upon scale up, scaling with a constant pressure drop with the lower L/d_t ratio, if the flow is turbulent.

The first two of the three methods are preferred when heat transfer is important. The third is cheaper for adiabatic reactors.

The scaling up allows for the number of tubes, the tube radius, and the tube length to be changed upon scale up (Nauman, 2001).

A. Process technical sequence

The process begins with a 1MM gallon feed storage tank. A tank of this size can hold a one-month supply of ethanol. The feed is then pumped to a high pressure, vaporized and passed through a packed bed isothermal reactor. The reaction products are sent through a separation train designed to purify the diethyl ether. The product is 99.5% + pure. The diethyl ether product stream is sent directly into storage tanks available. The separation train also produces a waste stream of costly water, which is sent directly to an off-site waste treatment facility.

4. Results and discussion

A. Reactor model simulated results.

Dependence on fractional conversion, rate of reaction, space time and space velocity, length of reactor, heat generated, Q and heat generated per unit volume, q and weight of catalyst.

Table 5
Reactor model simulated results

α_A	r_B	S_p	S_r	L	Q	q	W
0.1	0.81	0.013	7.63	0.368	0.03	0.04	0.01
0.2	0.64	0.0058	17.17	0.482	0.06	0.035	0.015
0.3	0.49	0.0034	29.47	0.577	0.09	0.031	0.02
0.4	0.36	0.00218	45.92	0.669	0.12	0.026	0.025
0.5	0.25	0.00145	69.05	0.766	0.15	0.022	0.03
0.6	0.16	0.0010	100.03	0.878	0.18	0.017	0.035
0.7	0.09	0.0006	163.3	1.02	0.21	0.0128	0.05
0.8	0.04	0.00035	2865.3	1.23	0.24	0.084	0.07
0.9	0.01	0.00014	7131.6	1.67	0.27	0.004	0.14

Table 6
Summary of the Research Values at X=0.9

Control Parameters	S.I Unit	Industrial Unit
L	1.67m	1670mm
D	0.500m	500mm
V_R	70m ³	70000L
Q	0.03g/ m ³	3J/L
W	0.35g	0.35g

Table 7
Summary of Scale-up Values at X=0.9

Control Parameters	Research value	Scale-up factor	Scale-up value
L	1670mm	S	1670mm
D	500mm	S	500mm
V_R	70,000L	$V^{2/3}$	1698.5L
q	3J/L	$q^{0.8}$	2.4J/L
W	0.35g	$W^{2/3}$	0.5g

The above Table 5 showed that the control parameters (length, L; diameter, D; volume of reactor V_R ; heat exchange per unit volume q, and weight of catalyst W) for the model tubular reactor at fractional conversion of 0.9, were converted

from the S.I Unit to Industrial unit (research values) to enable for the scaling up process of the tubular reactor

The control parameters of the research values (industrial values) obtained in Table 5 was scale up to obtain the scale up values as showed in Table 6 above, which is the realistic values for the fabrication of the tubular reactor for per pass production of DEE upon scale up. The reactors volume determines the amount of acetaldehyde that will be produced per pass.

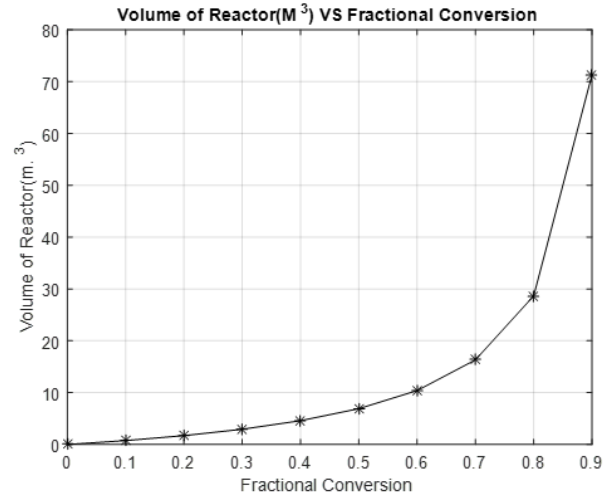


Fig. 1. Variation of volume of reactor (m³) against fractional Conversion

The figure 1 shows how volume of reactor is affected with fractional conversion. From the plot, the volume increases in an exponential manner to the increase of fractional conversion. The figure shows that when the volume is at 0m³, the fractional conversion of zero (0) and increases to volume of 71m³ at maximum conversion of 0.9.

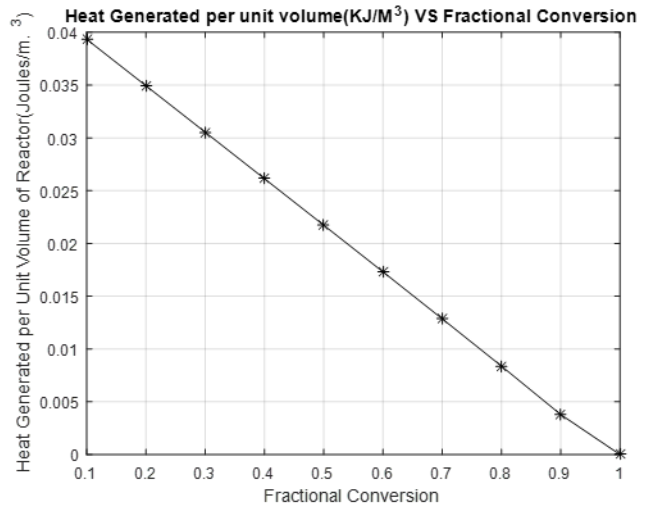


Fig. 2. Variation of heat generated per unit volume reactor against (J/m³) against fractional conversion

The figure depicts the fact that the heat generated per unit volume, q varies inversely to the fractional conversion. At higher values of q, say q=0.04 J/m³, $\alpha = 0.1$ and drops to Q=0

J/m^3 but conversion is at maximum of 0.9. This shows that at higher conversion, the heat generated per unit volume reduces to a minimum value when conversion is at maximum.

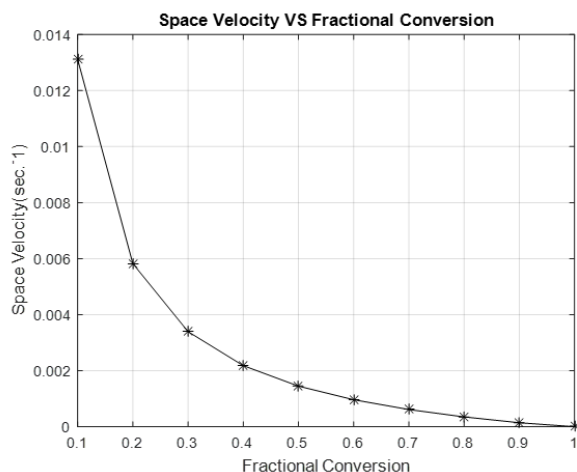


Fig. 3. Variation of space velocity (s^{-1}) versus fractional conversion

The figure above shows that space velocity is a function of fractional conversion as indicated by the models developed. The relation is exponentially and space velocity varies inversely. At lower conversion of 0.1, the space velocity is at maximum of $0.0135s^{-1}$ and then drops exponentially to $0s^{-1}$ when the conversion is 0.9.

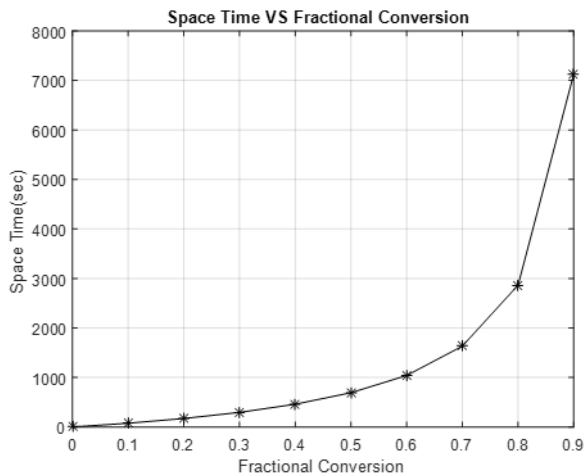


Fig. 4. Plot of space time (s) against fractional conversion

The plot shows the variation of space time against fractional conversion. The figure indicates that space time varies exponentially with fractional conversion starting from 0s at conversion of 0 to 7000s at conversion of 0.9.

In the figure 5, the weight of the catalyst (g) is a function of fractional conversion. The relation varies exponentially from 0g weight of the catalyst at 0% fractional conversion to a maximum weight of 0.35g at 90% conversion.

The weight of the catalyst (g) is related to the length of the reactor (m). The weight of catalyst from the plot increases from 0g at 0m to 0.35g at 1.7m.

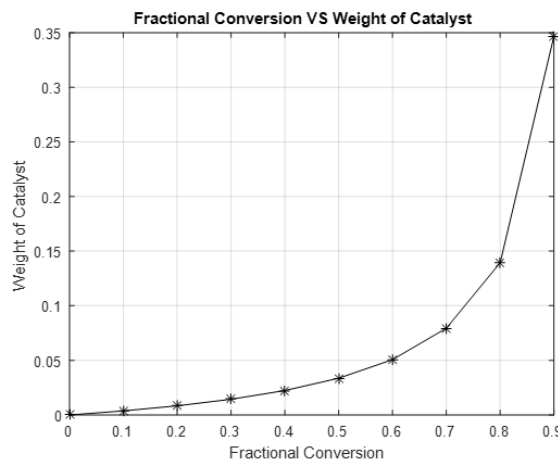


Fig. 5. Variation of weight of catalyst versus fractional conversion

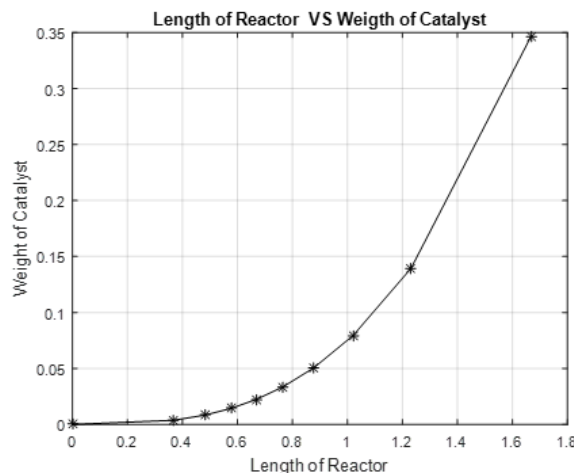


Fig. 6. Plot of Weight of Catalyst (g) against Length of Reactor (m)

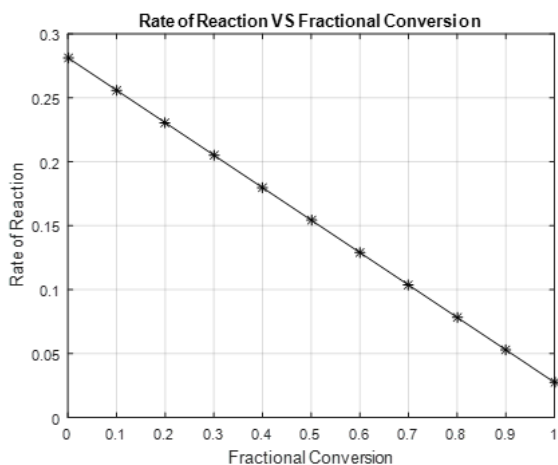


Fig. 7. Variation of rate of reaction against fractional conversion

The rate of reaction is also affected by the fractional conversion. From figure 6 the rate of reaction is highest at very low fractional conversion, i.e. rate of reaction of 0.28 at conversion of 0 and drops to $r=0.03$ at conversion of 100%.

5. Conclusions

The research successfully developed model for dehydration of ethanol into diethyl ether petrochemical precursors for other sectors of the economy. Nigeria is seriously importing ethanol for many industrial and medicinal applications, such as solvent or extractant for oils, perfumes, resins, dyes, fuels and anesthetic in surgery and production of drugs.

The significance of the product explains the necessity of the development of the design model with appropriate qualitative rate law to drive the reactors with the process conditions.

Nomenclature

k_1 = specific reaction rate constant.

A = Frequency factor (Arrhenius constant)

E_a = Activated energy (J/mol)

R = Universal gas constant (8.314 J/mol)

T = Absolute temperature (K)

DEE= Di-ethyl ethanol

$\rho_{cat.}$ = density of the catalyst, Kg/m³]

r = radius of the reactor, meters

F_{DEE} = molar flow rate, mols/s

Q= Heat generated or retained, J

q=heat generated per unit volume J/m³

S = the scale up factor for throughput

G_o = Superficial Velocity, m/s

ρ = density of the system/fluid, Kg/m³

ΔH_r = Heat of the reaction J/mol

U = Overall coefficient of heat, W/m²K

T_h =

Temperature of the hot fluid entering system, K

T = Temperature within the fluid, K

C_p = Specific heat capacity of the system/fluid, J/mol.K

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