

## SERIES-OXIDATION OF ETHANOL TO ACETALDEHYDE PETROCHEMICAL IN TUBULAR REACTOR

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### ABSTRACT

The model for the series-oxidation of ethanol feed into acetaldehyde a precursor petrochemical product is presented in these studies. A unimolecular feed  $C_2H_5OH$  stoichiometric balance equation  $A \rightarrow B \rightarrow C$  at steady state process was fundamentally investigated with its kinetic principles of batch reactor. The results from the kinetic studies were applied to establish the appropriate rate law. The trajectories of the control parameters show progressive optimum performance of the reactor. Finally, research showed three conceptual ways to scaling-up a tubular reactor throughput into a full scale industrial process which suffices, adding identical reactors in parallel, making the tube longer and increasing the tube diameter. The scaling-up on the throughput was fundamentally based on  $S = S_{Tubes} S_R^2 \frac{[P_{in}^3 - P_o^3]_2 \beta_1}{[P_{in}^3 - P_o^3]_1 \beta_2}$ . The scaling-up model is design for both series and parallel tubes with a corresponding cost elements of \$40,000, dollars (N14, 232, 498.00).

**Keywords:** Model, stoichiometric-equations, rate law, series-oxidation-ethanol, Acetaldehyde, cost-estimates, scaling-up.

### 1. INTRODUCTION

Acetaldehyde trivial named ethanal is an organic chemical compound with the formula  $CH_3CHO$ , sometimes called Me CHO (Methyl) by chemist. Acetaldehyde is a ubiquitous chemical which is found from two natural feed sources renewable and fossil i.e natural coffee, ripe fruits, various plants, vegetables, and petroleum fractions. The detailed physical properties of acetaldehyde according to (Jyrki, 2000); (Mikael, 2003) stated in table 1.

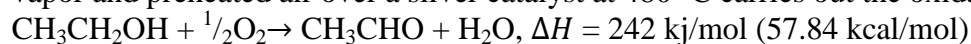
This chemical application is wide ranging from petrochemical, pharmaceutical, perfumes, dyes and drugs, as a flavoring agent (PubChem, 2015). Therefore, it can be naturally harnessed and also synthetically produced from these two process feeds.

There are copious literature existing on the origin, pharmaceutical activities, and industrial applications available according to the researchers [(Sharma, 2006); (Higham, 2007); (Budavari, 1996); (Verschueren, 1996); (Hagemeyer, 1991); (Jira et al, 1985); (Hagemeyer, 1991); (United State National Library of Medicine, 1998); (Johanna, 2010); (Chiang, 2008); (Mikael, 2003)].

Therefore, the present work is tailored to utilizing the research & development data from the kinetic studies to applying the chemical and petrochemical engineering concepts design of a reactor which will produce or synthesize 1mmtons of this desire product (acetaldehyde) to Nigeria and the global communities. Consequently, this will reduce the foreign exchange drift and self-sufficiency of the product. It is our hope that research will get to the Federal Government and private sectors initiatives (Local Content Board, 2004) expectations. Model for maximum yield of the desire product at an optimum time  $t_{opt}$  are generated. In many chemical processes transformation of feed or reactants into products, only the disappearance of the reactants and appearance of the final products may be observed (Sharma, 2006).

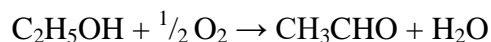
**Acetaldehyde production**

Acetaldehyde is produced commercially by the catalytic oxidation of ethyl alcohol. Passing alcohol vapor and preheated air over a silver catalyst at 480 °C carries out the oxidation

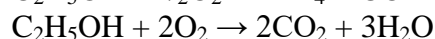
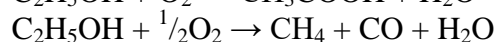
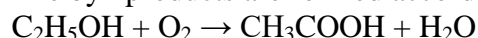


With a multi-tubular reactor, conversions of 74 – 82% per pass can be obtained while generating steam to be used elsewhere in the process.

The main reaction stoichiometric ratio is,



The by-products are formed according to the following reactions:



Chiang (2008) said that the ethanol conversion, acetaldehyde selectivity and yield, and contact time were calculated according to the following formulae.

$$\text{EtOH Con. (\%)} = \frac{\text{Moles of reacted EtOH}}{\text{Moles of EtOH in feed}} \times 100$$

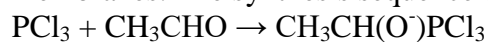
$$\text{AcH Sclc. (\%)} = \frac{\text{Moles of produced AcH}}{\text{Moles of EtOH in feed}} \times 100$$

$$\text{AcH Yield (\%)} = \frac{\text{Moles of produced AcH}}{\text{Moles of EtOH in feed}} \times 100$$

$$\text{Contact Time (W/F)} = \frac{\text{Catalyst Weight (g)}}{\text{Total EtOH feed rate (ml/min)}}$$

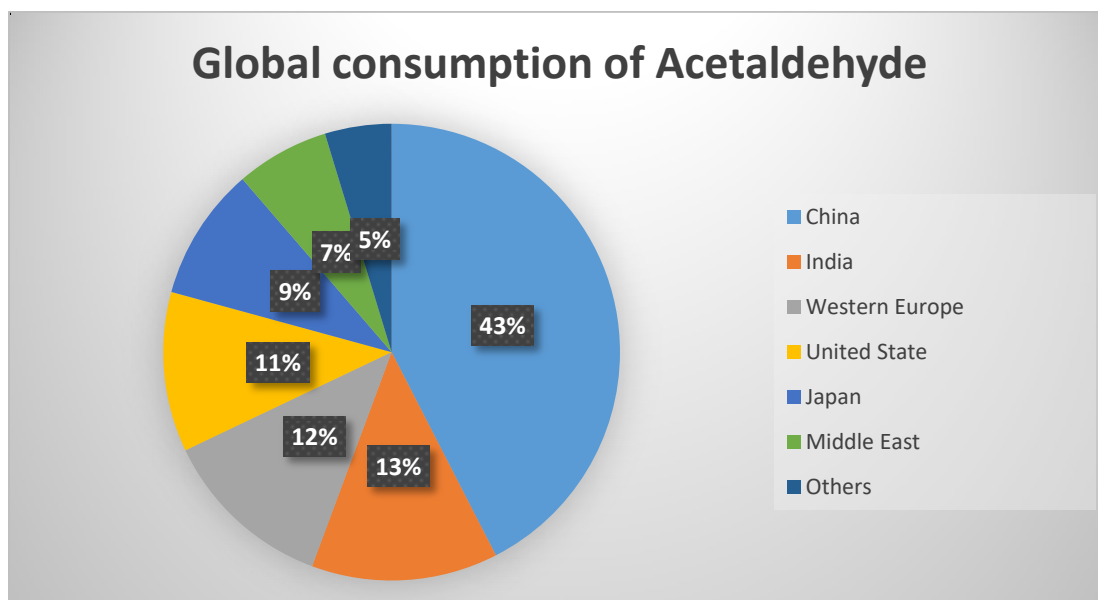
**Acetaldehyde Precursors**

Acetaldehyde is a precursor to Vinylphosphoric acid which is used to make adhesive and ion conductive membranes. The synthesis sequence begins with a reaction with phosphorus tri-chloride.



Major use has been the production of acetic acid. Other uses such as pyridine and pentaerythritol are expected to grow faster than acetic acid. Pyridine bases are very important raw materials in the production of agricultural chemicals.

According to (Markit, 2016), acetaldehyde is a chemical intermediate, pyridine 34%, pentaerythritol 23%, acetic acid 18% and acetate esters 10% respectively of 2016 global acetaldehyde consumption. Pyridine bases are very important raw materials in the production of agricultural chemicals.



**Figure 1:** Global consumption of acetaldehyde petrochemical (Markit, 2016)

## 2. MATERIALS AND METHOD

### 2.1 MATERIALS

The series oxidation of ethanol to form acetaldehyde is investigated in a catalyst of 4wt% Cu – 2wt% Cr  $\text{Al}_2\text{O}_3$ . The reaction carried out in a threefold excess of oxygen and in dilute concentrations. The volume change of the reaction in a batch reactor was neglected in this process (Wordu and Ozurumba, 2016).

### Physical Properties

According to (Ullmann, 2007) acetaldehyde,  $\text{C}_2\text{H}_4\text{O}$ , Mol. mass 44.054, is a colorless liquid with a pungent suffocation odor that is slightly fruity when diluted

**Table 1:** Detailed physical properties of acetaldehyde (Jyrki, 2000); (Mikael, 2003);

Bp at 101.3 kPa	20.16°C					
Mp	-123.5°C					
Critical temperature $t_{\text{crit}}$	181.5 °C					
Critical pressure $p_{\text{crit}}$	6.44 MPa					
Relative density	$d_4 = 0.8045 - 0.001325.t$ ( $t$ in °C)					
Refractive index	$d_D = 1.34240 - 0.0005635.t$ ( $t$ in °C)					
Molar volume of the gas at 101.3 kPa and 20.16°C	23.40 L/mol					
at 25.0°C	23.84 L/mol					
Specific volume of the vapor at 20.16°C	0.531 m <sup>3</sup> /kg					
At 25.0°C	0.541 m <sup>3</sup> /kg					
Vapor density (air = 1)	1.52					
Vapor pressure						
$t$ , °C	-20	-0.27	5.17	14.76	50	100
$p$ , kPa	16.4	43.3	67.6	82.0	279.4	1014.0
Viscosity of liquid $\eta$						
At 9.5 °C	253 mPa · s					

t 20 oC	21 mPa · s
viscosity of vapor η t 25°C	5 × 10 <sup>-6</sup> mPa · s
surface tension γ at 20°C	1.2 × 10 <sup>-2</sup> mN cm <sup>-1</sup>
dipole moment (gas phase)	69 ± 2% D
dielectric constant of liquid at 10°C Of vapor at 20.16°C, 101.3 kPa	1.8 0.216
heat capacity of liquid t 0°C t 20°C t -80°C	18 J g <sup>-1</sup> K <sup>-1</sup> 38 J g <sup>-1</sup> K <sup>-1</sup> 24 J g <sup>-1</sup> K <sup>-1</sup>
heat capacity of vapor 25°C, 101.3 kPa	24 J g <sup>-1</sup> K <sup>-1</sup>
thermal conductivity of liquid at 20°C	174 J m <sup>-1</sup> s <sup>-1</sup> K <sup>-1</sup>
cubic expansion coefficient per K (0 – 20°C)	0.0169
heat of combustion at constant p	168.79 (1166.4) KJ/mol
heat of solution in water (infinite dilution)	7906J/mol
latent heat of fusion	246.3J/mol
latent heat of vaporization at 20.2°C	5.73KJ/mol
heat of formation ΔH from the element at 25°C gaseous acetaldehyde	66.47 KJ/mol
Gibbs free energy of formation ΔG from element at 25°C for gaseous acetaldehyde	33.81 KJ/mol
entropy for gaseous acetaldehyde at 25°C	65.9 J mol <sup>-1</sup> K <sup>-1</sup>
entropy for liquid acetaldehyde at 20.16°C	72.9 J mol <sup>-1</sup> K <sup>-1</sup>
entropy of vaporization at 20.16°C	1.57 J mol <sup>-1</sup> K <sup>-1</sup>
first ionization potential	0.5 eV
dissociation constant at 0°C	7 × 10 <sup>-14</sup> mol/L

### 3.2 Method

This research takes *experimental cum analytical techniques*.

#### 3.2.1 Experimental Technique

The ethanol was obtained through research and development a prerequisite to concurrent oxidation into acetaldehyde petrochemical.

#### 3.2.2 Analytical Techniques - Reaction kinetics

##### 3.2.2 Stoichiometric balance equation (McCabe, 1983)



$K_1 \gg K_2$  a necessary constraint for desire product model formulations



A = CH<sub>3</sub>CH<sub>2</sub>OH feed, B = CH<sub>3</sub>CHO desire product, C = CO<sub>2</sub> unwanted product,

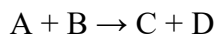
D = H<sub>2</sub>O process water with trace of contaminants,

Reactions process being a series reaction type yielding the species balance equations (2) and (3)

$$\frac{dC_A}{dt} = -k_1 C_A \quad (2)$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B \quad (3)$$

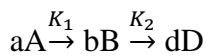
Generally, chemical kinetics relates to the studies of the rates at which chemical processes occur, and factors on which these rates depend and the molecular species involved in reaction mechanisms (Wordu, 2009); (Kayode, 2001). It quantifies rates of reaction which corresponds to a stoichiometric equation as stated below:



And, reaction rate defined mathematically as;

$$-r_A = K_1 C_A C_B \quad (4)$$

Where, k = specific reaction rate constant.



Differentiating

$$r_A = -\frac{dc_A}{dz} = K_1 C_A \quad (5)$$

Rearranging

$$\int \frac{dC_A}{C_A} = K_1 \int dz \quad (6)$$

Boundary conditions

$$\text{BC: } \tau = 0; C_A = C_{A0}$$

$$\tau = \tau; C_A = C_A$$

Hence,

$$\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = -K_1 \int_0^\tau d\tau \quad (7)$$

$$\ln C_A = \int_{C_{A0}}^{C_A} = \ln C_A - \ln C_{A0} = \ln C_A / C_{A0} = -K_1 \tau \quad (8)$$

$$\frac{C_A}{C_{A0}} = e^{-K_1 \tau} \quad (9)$$

$$C_A = C_{A0} e^{-K_1 \tau} \quad (10)$$

**Rate law for desired product acetaldehyde**

$$(-r_B) = \frac{-dC_B}{d\tau} = -K_1 C_A + K_2 C_B \quad (11)$$

$$\frac{dC_B}{d\tau} = K_1 C_A - K_2 C_B \quad (12)$$

Rearranging

$$\frac{dC_B}{d\tau} + K_2 C_B = K_1 C_A \quad (13)$$

Where,  $C_A = C_{A0} e^{-k_1 \tau}$

$$\frac{dC_B}{d\tau} + K_2 C_B = K_1 C_{A0} e^{-K_1 \tau} \quad (14)$$

Applying I.F

$$e^{sk_2 d\tau} = e^{k_2 \tau}$$

Multiply equation (14) by  $e^{k_2\tau}$  gives

$$e^{k_2\tau} \left[ \frac{dC_B}{d\tau} + K_2 C_B \right] = K_1 C_{AO} e^{-K_1\tau} \cdot e^{k_2\tau}$$

Hence,

$$e^{k_2\tau} \frac{dC_B}{d\tau} + e^{k_2\tau} K_2 C_B = K_1 C_{AO} e^{(K_2-K_1)\tau} \quad (15)$$

Integrate equation (15)

$$\int \frac{d}{de} [C_B e^{k_2\tau}] de = K_1 C_{AO} \int e^{(k_2-k_1)\tau} d\tau$$

$$C_B e^{k_2\tau} = \frac{K_1 C_{AO}}{K_2-K_1} e^{(k_2-k_1)\tau} + C \quad (16)$$

Putting B.C. in equation (16)

$$\tau = 0; C_B = C_{B0} = 0$$

$$\tau = \tau; C_B = C_B$$

$$C_{B0} e^{k_2(0)} = \frac{K_1 C_{AO}}{K_2 - K_1} e^{(k_2-k_1)(0)} + C$$

$$0 = \frac{K_1 C_{AO}(1)}{K_2-K_1} + C$$

Therefore:

$$C = \frac{K_1 C_{AO}}{K_2-K_1} \quad (17)$$

Substituting equation (17) into equation (16) yields

$$C_B e^{k_2\tau} = \frac{K_1 C_{AO}}{K_2-K_1} e^{(k_2-k_1)\tau} - \frac{K_1 C_{AO}}{K_2-K_1} \quad (18)$$

Rearranging Equation (15) gives

$$C_B e^{k_2\tau} = \frac{K_1 C_{AO}}{K_2-K_1} [e^{(k_2-k_1)\tau} - 1] \quad (19)$$

Divide Equation (3.16) by  $e^{k_2\tau}$

$$C_B = \frac{K_1 C_{AO}}{K_2-K_1} [e^{(k_2-k_1)\tau} e^{-k_2\tau}]$$

Where,

$$\frac{1}{e^{k_2\tau}} = e^{-k_2\tau}$$

$$C_B = \frac{K_1 C_{AO}}{K_2-K_1} [e^{-k_1\tau} - e^{-k_2\tau}] \quad (20)$$

Equation (20) is the concentration profile of the desire product acetaldehyde.

### **Model for optimizing the desire product B**

At optimum, yield  $\frac{dC_B}{d\tau} = 0$

Differentiating equation (20) with respect to space time ( $\tau$ ) gives

$$\frac{dC_B}{d\tau} = \frac{K_1 C_{AO}}{K_2-K_1} [-K_1 e^{-k_1\tau} - (-k_2) e^{-k_2\tau}]$$

Equating to zero

$$0 = \frac{K_1 C_{AO}}{K_2-K_1} [-K_1 e^{-k_1\tau} + k_2 e^{-k_2\tau}] \quad (21)$$

Multiply equation (21) by  $(k_2 - k_1)$  and divide by  $K_1 C_{AO}$  yields:

$$0 = -K_1 e^{-k_1\tau} + K_2 e^{-k_2\tau} \quad (22)$$

Re-arranging equation (22) to obtain the optimum space time  $\tau_{opt}$  yields:

$$k_1 e^{-k_1 \tau_{opt}} = k_2 e^{-k_2 \tau_{opt}}$$

Therefore,

$$e^{(k_2 - k_1) \tau_{opt}} = \frac{k_2}{k_1} \quad (23)$$

Taking ln on both  $\tau_{opt}$  sides of equation (23) gives

$$\begin{aligned} \ln [e^{(k_2 - k_1) \tau_{opt}}] &= \ln \frac{k_2}{k_1} \\ (k_2 - k_1) \ln e &= \ln \frac{k_2}{k_1} \end{aligned} \quad (24)$$

$$\ln e = 1$$

$$(k_2 - k_1) \tau_{opt} = \ln \left( \frac{k_2}{k_1} \right)$$

$$\therefore \tau_{opt} = \ln \left( \frac{\frac{k_2}{k_1}}{k_2 - k_1} \right) \quad (25)$$

### Reaction optimum time

Substituting equation (25) into equation (20)

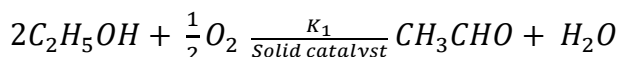
$$\begin{aligned} C_B &= \frac{K_1 C_{AO}}{K_2 - K_1} [e^{-k_1 \tau_{opt}} - e^{-k_2 \tau_{opt}}] \\ C_B &= \frac{K_1 C_{AO}}{K_2 - K_1} \left[ e^{-k_1 \left[ \ln \frac{(k_2/k_1)}{k_2 - k_1} \right]} - e^{-k_2 \left[ \frac{(k_2/k_1)}{k_2 - k_1} \right]} \right] \end{aligned}$$

$$\left[ \frac{C_B}{C_{AO}} \right] = \frac{k_1}{k_2 - k_1} \left[ e^{-\frac{k_1}{k_2 - k_1} \ln \frac{k_2}{k_1}} - e^{-\frac{k_2}{k_2 - k_1} \ln \frac{k_2}{k_1}} \right]$$

$$\left[ \frac{C_B}{C_{AO}} \right]_{max} = \left[ \frac{K_1}{K_2} \right] \frac{K_2}{K_2 - K_1}$$

### Development of Rate law model

Appropriate rate law and kinetic constants for gas-phase oxidation reaction process kinetically represented as,



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

### Stepwise Solution

1. Proposing a generalized rate expression for testing the data. Analysis of rate data by the differential method involves utilizing the entire reaction-rate expression to find reaction order and the rate constant. Since the data have been obtained from batch reaction, a general rate expression of the following form may be applied:

$$(-r_A) = \frac{dC_A}{dt} = -K_1 C_A \quad (26)$$

Where, K and  $\alpha$  are the reaction rate constant and reaction order to be defined.

2. Convert the rate expression to units of pressure since the data are in the form of total pressure versus time, the rate expression to be tested must also be in the form of total pressure versus time.

Assuming ideal – gas behavior,

$$PV = nRT, \quad (27)$$

Therefore:

$$C_i = \frac{n_i}{V} = \frac{P_i}{RT} \quad (28)$$

Where,  $P_i$  = partial pressure of species i. Thus, the rate expression becomes:

$$\frac{1}{RT} = \frac{dP_A}{dt} = - \left( \frac{1}{RT} \right)^\alpha \cdot K P_A^\alpha \quad (29)$$

Now, partial pressure of species A must be related to total system pressure. This may be done easily by a general mole balance on the system, resulting in the following relationships.

a. For any reactant feed material,

$$P_R = P_{R,O} - \frac{r}{\Delta n} (\pi - \pi_o) \quad (30)$$

b. For any product,

$$P_S = P_{S,O} + \frac{s}{\Delta n} (\pi - \pi_o) \quad (31)$$

Where,  $P_{R,O}$  and  $P_{S,O}$  are initial partial pressures of reactant feed R and product S, r and s are molar stoichiometric coefficients on R and P,  $\pi$  is the total pressure,  $\pi_o$  is initial total pressure, and  $\Delta n$  is change in number of moles, equating total moles of products minus total moles of reactant feed. In the present case, r for the reactant A equals 1, s for the product B equals 2, and  $\Delta n$  equals  $(2-1) = 1$ . Using the data, and the relationship between partial pressure and total pressure for a reactant, the form of the rate expressions to be tested may be derived.

$$P_A = P_{A,O} - \frac{1}{2-1} (\pi - \pi_o) \quad (32)$$

From the data,  $\pi_o = 132.74 \text{ kPa}$

3. Linearize the rate expression by taking logs, and plot the data. The proposed rate expression may be linearized by taking, logs resulting in the following expression.

$$\begin{aligned} \ell_n \left( \frac{d\pi}{dt} \right) &= \ell_n K^{1+\alpha} + \ell_n (234.87 - \pi) \\ \ell_n \left( \frac{d\pi}{dt} \right) &= \ell_n K^{1+\alpha} + \ell_n (234.87 - \pi) \end{aligned} \quad (33)$$

This expression indicate that if  $\ell_n \left( \frac{d\pi}{dt} \right)$  versus  $\ell_n (234.87 - \pi)$  a straight line obtained with slope  $\alpha$  and y intercepting at  $\ell_n K_1$ .

Thus, to complete the rate-data analysis, the derivative  $\frac{d\pi}{dt}$  must be evaluated.

Three methods are commonly used to estimate this quantity:

1. Slopes from a plot of  $\pi$  versus t.
2. Equal–area graphic differentiation, or
3. Taylor series expansion.

The derivative as found by equal area graphic differentiation and other pertinent data are shown in the table below:

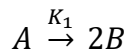


**Table 2:** Kinetic data

Time (h)	$\pi$	$234.87 - \pi, KPa$	$d\pi/dt$
0	132.74	102.13	45
0.5	151.99	82.88	34
1	167.19	67.68	26
1.5	178.33	56.54	19.5
2	186.44	48.43	15
2.5	192.52	42.35	11
3	197.58	37.29	9
3.5	201.64	33.23	7.5
4	205.18	29.69	6.5
5	210.76	24.11	4.5
6	214.81	20.06	3.5
7	217.85	17.02	2.5
8	220.38	14.49	1.5

$d\pi/dt$  Versus  $234.87 - \pi, KPa$

Plotting  $\ell_n(d\pi/dt)$  versus  $\ell_n(234.87 - \pi)$  yields an essentially straight  $\ell_n$  with a slope of 1.7 and an intercept of 0.0165. Thus, an appropriate rate expression for this reaction process.



is given by

$$d\pi/dt = 0.0165 (234.87 - \pi)^{1.7} \quad (34)$$

$$-\frac{dP_A}{dt} = 0.0165 P_A^\alpha \quad (35)$$

### 3.2.5 Propounding reactor model

Plug flow reactor equations were developed from first principles of material balance at steady state process.

Mathematically, stated as follows:

For 1mole of the feed material, we have

$$F_{EtOH}W - F_{EtOH}(W + \Delta W) + (-r_{EtOH})\Delta W = 0 \quad (36)$$

Re-arranging equation (36) and dividing through by  $\Delta W$ , yields:

$$-\left[\frac{F_{EtOH}(W + \Delta W) - F_{EtOH}(W)}{\Delta W}\right] = -r_{EtOH} \quad (37)$$

The left-hand side of equation (37) is compared to the first principles derivative approach, given as:

$$\lim_{\Delta x \rightarrow 0} \left[\frac{f(x + \Delta x) - f(x)}{\Delta x}\right] = \frac{df}{dx} \quad (38)$$

Hence Equation. (3.37) becomes

$$\lim_{\Delta x \rightarrow 0} \left[\frac{F_{EtOH}(W + \Delta W) - F_{EtOH}(W)}{\Delta W}\right] = -\frac{dF_{EtOH}}{dW} \quad (39)$$

Combining the right hand side of Equation (37) and Equation (39) yields:

$$\frac{-dF_{EtOH}}{dW} = -r_{EtOH} \quad (40)$$

Expressing Equation.(40) in terms of molar feed rate (flow-rate) for 1mole species

$$F_{EtOH} = F_{EtOH,0} - F_{EtOH,0} \alpha_{EtOH} \quad (41)$$

$$F_{EtOH} = F_{EtOH}(1 - \alpha) \quad (42)$$

Differentiating equation.(42) yields,

$$dF_{EtOH} = -F_{EtOH,0} d\alpha \quad (43)$$

Substituting equation. (43) into equation(40) yields

$$F_{EtOH,0} \frac{d\alpha}{dW} = -r_{EtOH} \quad (44)$$

Rearranging equation(44) yields:

$$dW = F_{EtOH,0} \frac{d\alpha}{-r_{EtOH}} \quad (45)$$

Eqn.(45) is integrated applying the boundary conditions for catalyst decay in the pack bed reactor

$$W : 0 \rightarrow W \quad \text{and} \alpha : 0 \rightarrow \alpha_f$$

$$\int_0^W dW = \int_0^{\alpha_f} F_{EtOH,0} \frac{d\alpha}{-r_{EtOH}} \quad (46)$$

$$W \int_0^W = F_{EtOH,0} \int_0^{\alpha_f} \frac{d\alpha}{-r_{EtOH}} \quad (47)$$

$$W = F_{EtOH,0} \int_0^{\alpha_f} \frac{d\alpha}{-r_{EtOH}} \quad (48)$$

$$W = \frac{V}{\rho_{Cat.}} = F_{EtOH} \int_0^{\alpha_f} \frac{d\alpha}{(-r_{EtOH})} \quad (49)$$

$$\frac{\pi r^2 l}{\rho_{Cat.}} = F_{EtOH} \int_0^{\alpha_f} \frac{d\alpha_A}{(-r_{EtOH})} \quad (50)$$

$$L = \frac{\rho_{Cat.} F_{EtOH}}{\pi r^2} \int_0^{\alpha_f} \frac{d\alpha_A}{(-r_{EtOH})} \quad (51)$$

## 4 RESULTS AND DISCUSSIONS

### 4.1 RESULTS

**Table 3:** Predicted kinetic data for the series-oxidation of ethanol.

$r_H(\mu m)$	ace Time ( $\tau$ )	$\frac{\Delta C_{EtOH}}{\Delta \tau} \times 10^{-6}$	$\ln \left[ \frac{-\Delta C_A}{d\tau} \right]$	$\ln C_A$
0	0	4.0	-12.43	0
2	0.5	0.4	-14.73	-13.12
2.2	1.0	4.0	-12.43	-13.03
3	1.2	2.5	-12.90	-12.72
5	2.0	1.0	-13.82	-12.21
8	5.0	7.2	-11.84	-11.74
44				10.03

**Table 4:** Kinetic data for the oxidation of ethanol.

$C_2H_5OH$	$CH_3CHO$	$\tau$	$\frac{\Delta C_{EtOH}}{\Delta \tau}$	$\frac{\Delta C_{AcH}}{\Delta \tau}$	$\ln C_{EtOH}$	$\ln C_{AcH}$	$\ln \left[ \frac{-dC_{EtOH}}{d\tau} \right]$	$\ln \left[ \frac{-dC_{AcH}}{d\tau} \right]$
1.0	0	-1.625	0.05	-1.05	-3.91	-0.486	-0.05	
0.35	0.02	0.4	-1.4	0.1	-2.66	-3.22	-0.336	
0.07	0.04	0.6	-0.2	0.4	-3.51	-2.12	1.61	
0.03	0.12	0.8	-0.125	0.35	-5.30	-1.66	2.08	
0.005	0.190	1.0	-0.025	0.1	-9.21	-1.56	3.69	
0.000	0.21	1.2						

Table 4 and 4.2 above showed the rate constant calculated values for rate law predicted kinetic data for the oxidation of ethanol, and the order of the reaction 1.

**Table 5:** MATLAB Simulated Results.

$\chi_A$	$r_B$	L	$S_V$	$S_T$	W	Q	q	$V_R$
0.1	0.256	0.69	0.0107	9.354	0.008	0.068	0.0363	1.87
0.2	0.2305	0.887	0.00508	19.689	0.018	136	0.0345	3.94
0.3	0.20516	1.035	0.00320	31.24	0.022	204	0.0327	6.25
0.4	0.1798	1.163	0.002256	44.32	0.03	272	0.0307	8.86
0.5	0.1544	1.282	0.00168	59.41	0.044	340	0.0286	11.9
0.6	0.129	1.399	0.00130	77.24	0.0615	408	0.0264	15.5
0.7	0.1036	1.520	0.00101	99.05	0.08	476	0.0240	19.8
0.8	0.0783	1.6520	0.000786	127.17	0.10	544	0.0214	25.4
0.9	0.05288	1.8087	0.00060	166.89	0.135	612	0.0183	33.4
1.0	0.0275	2.031	0.000423	236.17	0.19	680	0.0144	47.2

Table 5 above showed the result obtained from the simulation of performance equations for reactions, in respect to the reactors functional parameters of rate of reaction ( $r_B$ ), space time ( $S_T$ ), weight of the catalyst (W), heat per unit volume (q), length of the reactor (L), heat of reaction (Q), space velocity ( $S_V$ ), and volume of the reactor ( $V_R$ ) at different fractional conversion intervals from 0.1 to 1.0.

**Table 6:** Summary of the research values at  $\chi_A = 1.0$ 

Control Parameters	Small scale	Design capacity
L	2.031m	2031mm
D	0.6093m	609.3mm
$V_R$	47.2m <sup>3</sup>	47200L
Q	0.0144g/ m <sup>3</sup>	14.4J/L
W	0.19g	0.19g

Table 6 shows the control parameters of length L, diameter D, volume of reactor  $V_R$ , heat exchange per unit volume q, and weight of catalyst W for the tubular reactor at maximum fractional conversion of 1.0.

**Table 7: Summary of Scale-up Values at  $X = 1.0$** 

Control Parameters	Research Values	Scale-up Factors	Scale-up Values (per hr)
L	2031mm	S	2031mm
D	609.3mm	S	609.3mm
$V_R$	47200L	$V^{2/3}$	1306.1L
Q	14.4J/L	$q^{0.8}$	8.4J/L
W	0.19g	$W^{2/3}$	0.33g

The control parameters of the research values obtained in Table 6 was scaled-up to obtain the scale-up values as shown in Table 7 which is the realistic values for the fabrication of the tubular reactor for per pass production of acetaldehyde.

**Table 8: Summary of Reactor Throughput S**

Scale-up values (l)	Per pass (hrs.)	Day(s)	Hours	Throughput
1306.1			24	31,346.4
1306.1		300	7200	9,403,920
1306.1		Shift		10,448.8

Table 8 shows the actual amount of acetaldehyde that will be produced perday, in a year and in a normal working industrial operation of eight (8) hours per shift per day). The tubular reactor will produce 31,346.4liters of acetaldehyde in a day at its per pass production rate of 1306.1liters, and if there is no interruption in its operation for 300days of the year 9, 403,920liters of acetaldehyde will be produced at 31,346.4liter of acetaldehyde per day.

**Table 8 Summary of the Reactor Feed Consumption.**

Actual feed pass (l/hr.)	Per pass (hrs.)	Day(s)	Hours	Real Feed consumption
1966.6			24	47,198.4
1966.6		300	7200	14,159,520
1966.6		Shift		15,732.8

Table 8show actual feed supplied to the tubular reactor per pass is 1966.6liters, amounting to 47,198.4liters of ethanol for the daily operation of the reactor. 14,159,520liters of ethanol is need for 300days operation of the reactor, at the feed supply rate of 47,198.4liters per day. This is because the reaction in the tubular reaction is a consecution reaction in series, where both desired and undesired product will be form from the feed.

**Table 9 Cost Estimate of the Reactor.**

Materials	Units				Amount (₦)
	S. I. Unit (m)		Industrial Unit (ft)		
	L	D	L	D	
Oxygen Cylinder	4.2	0.96	14	3.2	1,800,000
Tank Volume	9.75	2.92	32	8.7	2,500,000
Tube	2.13	0.64	7	2	600,000
Chromium					18,300
Copper					204,960
Aluminum Oxide					21,350
Industrial Oxygen					2,007,888
Ethanol					7,080,000
TOTAL			US \$40,000		₦ 14,232,498

Table 9 show monetary cost for fabrication and production of the reactor for industrial operation is fifteen 15 million naira only. That at fabrication and start-up operation of the tubular reactor for the production of acetaldehyde fifteen 15 million naira.

## 4.2 DISCUSSIONS

### 4.2.1 Variation of the Reactor Volume with Fractional Conversion.

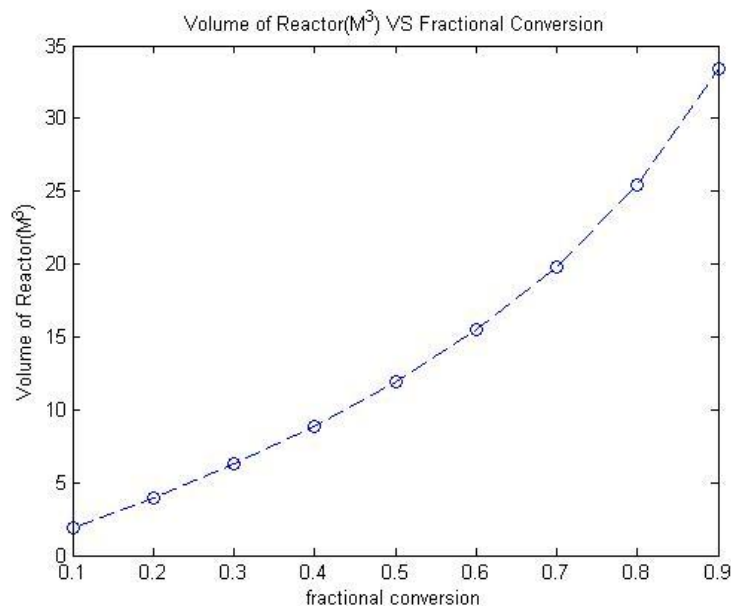


Figure 1: Plot of the Volume of Reactor with Fractional Conversion.

Figure 1 plot of volume in  $\text{m}^3$  of the reactor to the fractional conversion. The volume of the reactor as a function of fractional conversion showed that the fractional conversion increases to a maximum of 90% as volume increases to  $33.4\text{m}^3$ . This showed the negligence of the reactor volume change with respect to the reaction taking place in the tubular reactor and confirms that the actual feed to the reactor as seen in Table 4.7 at a fractional conversion of 1.0.

#### 4.2.2 Variation of Heat Generated per Unit volume with Fractional Conversion

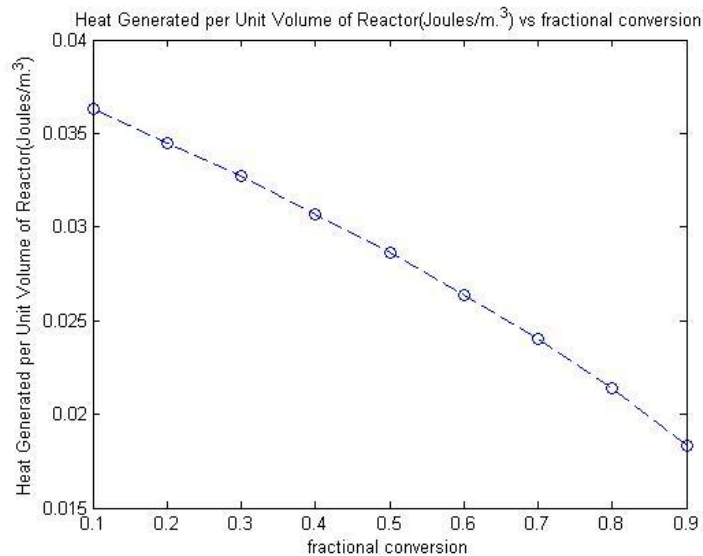


Figure 2: Plot of Heat Generated per Unit Volume against Fractional Conversion.

The heat generated per unit volume is highest at 0.15 fractional conversion i.e.  $0.036 \text{ J/m}^3$ . Then as fractional conversion increases, heat generated per unit volume ( $q$ ) drops parabolically to a minimum value of  $0.018 \text{ J/m}^3$  of 0.9 fractional conversions; implies that the rate of reaction is greatly influenced by temperature and concentration of the reacting feed in the tubular reactor.

#### 4.2.3 Variation of Space Velocity with Fractional Conversion

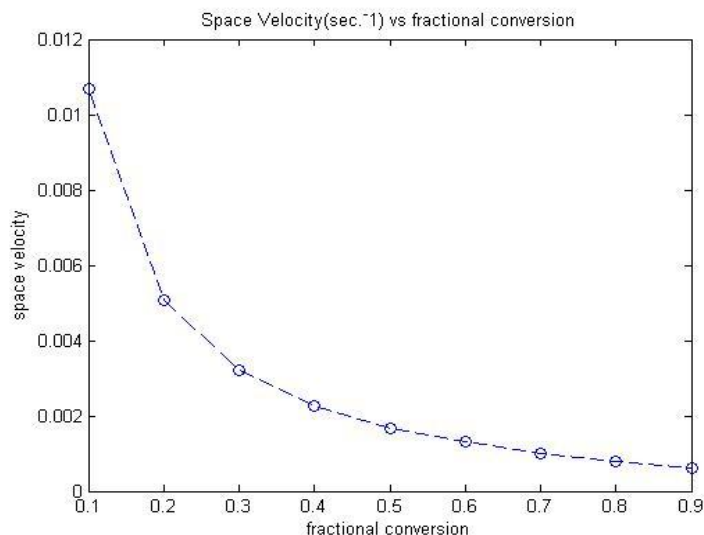


Figure 3: Plot of Space Velocity with Fractional Conversion.

The figure 4.3 above depicts the fact that space velocity varies with fractional conversion along the flow reactor. The variation is exponentially, starting from the highest space velocity value of  $0.0104 \text{ s}^{-1}$  at 0.1 fractional conversion and decreases to almost zero ( $0$ )  $\text{s}^{-1}$  at 0.9 fractional conversion. This showed that the conversion of ethanol in the tubular reactor can be increased by obtaining the data point at different space velocities.

#### 4.2.4 Variation of Space Time and Fractional Conversion.

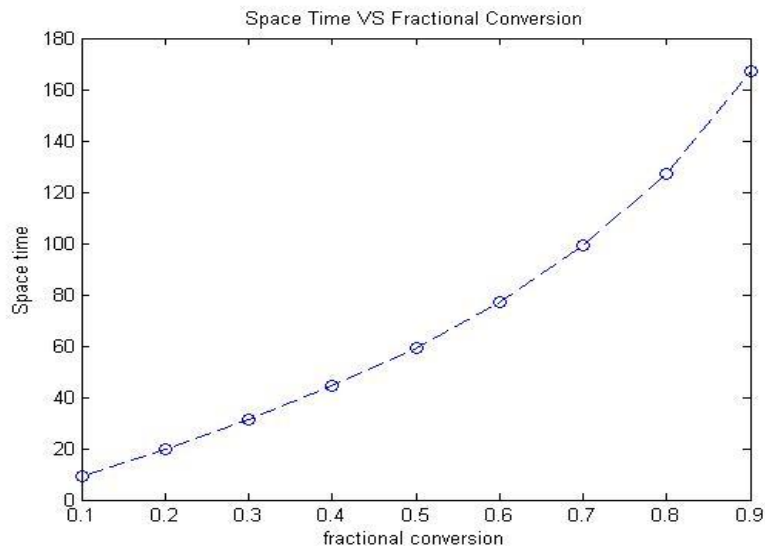


Figure 4: Plot of Space Time against Fractional Conversion.

The figure 4 depicts that there is direct exponential variation of space time with fractional conversion. As the conversion is 0.9, the space time is 168s and as conversion decreases to 0, the space time drops exponentially to 0, showing that for series consecutive reactions in the tubular reactor that time factor is important and shows the concentration of acetaldehyde as a function of space time.

#### 4.5 Variation of Weight of Catalyst with Fractional Conversion

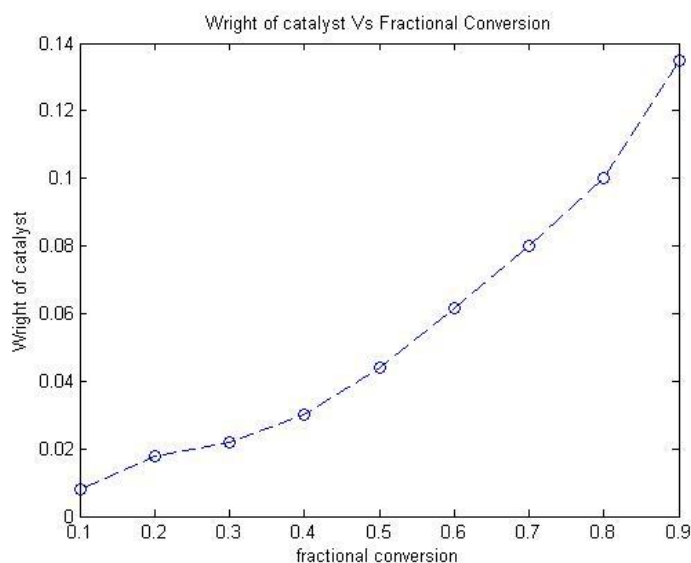


Figure 5: Plot of Weight of Catalyst versus Fractional Conversion.

The plot shows the variation of weight of catalyst with fractional conversion. The weight is 0g at fractional conversion of 0 and exponentially increases to 0.135g at fractional conversion 0.9. This showed the catalyst stability which is important for acetaldehyde commercial production. It was seen that the catalyst was constant at first, but the deactivation of the catalyst was observed at a fractional conversion of 0.2 and a catalyst weight of 2%.

#### 4.6 Variation of Weight of Catalyst to Length of Reactor.

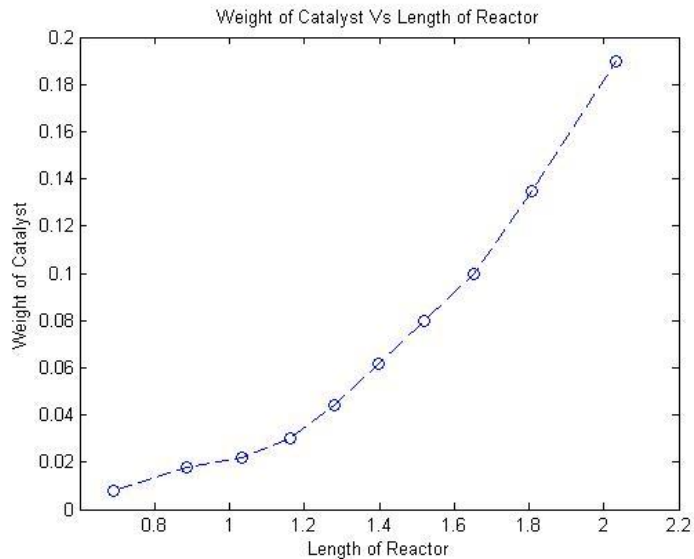


Figure 6: Plot of Weight of Catalyst versus Length of Reactor.

Figure 6 shows that as reaction increases along the length of the tubular reactor catalyst function maximally to an optimum point and will begin to decrease exponentially to a minimum point.

#### 4.7 Variation of Rate of Reaction with Fractional Conversion.

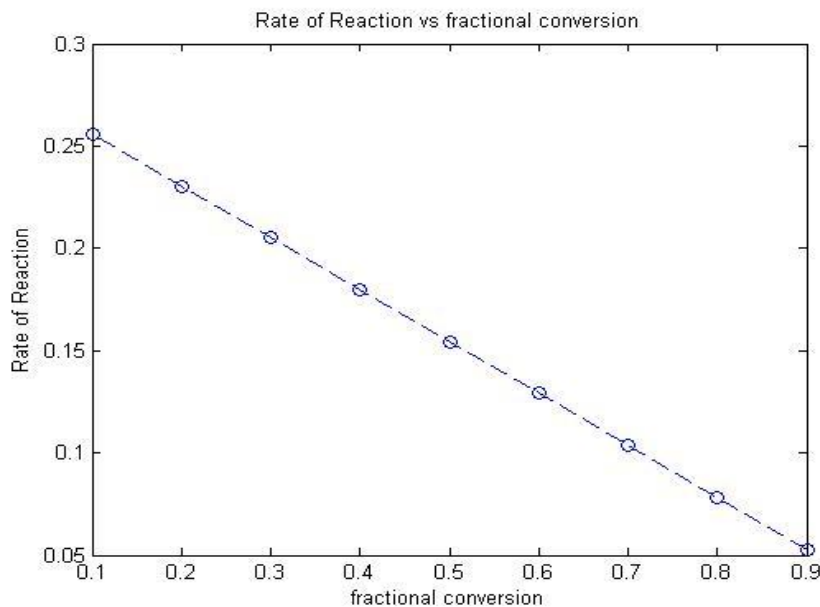


Figure 7: Plot of Rate of Reaction versus Fractional conversion.



The plot shows that rate of reaction decreases exponentially from 0.255 to 0.051 at a fractional conversion of 0.9. This showed the yield of acetaldehyde in the tubular reactor as a function of the conversion of the feed, and the reaction is a first order series reaction.

#### 4.8 Variation of Rate of Reaction versus Heat Exchanged per Unit Volume

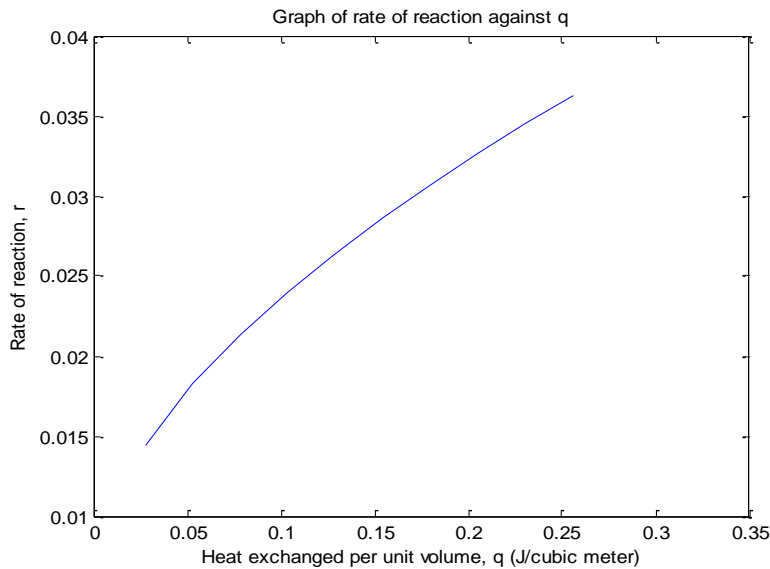


Figure 8: shows that the rate of reaction and heat exchange per unit increases exponentially.

The rate of reaction increased from 0.014 to 0.037 as heat exchange increases to 0.27, which showed that the reaction progressed at steady state process in the tubular reactor.

#### 4.9 Variation of Fractional Conversion against Reaction Time

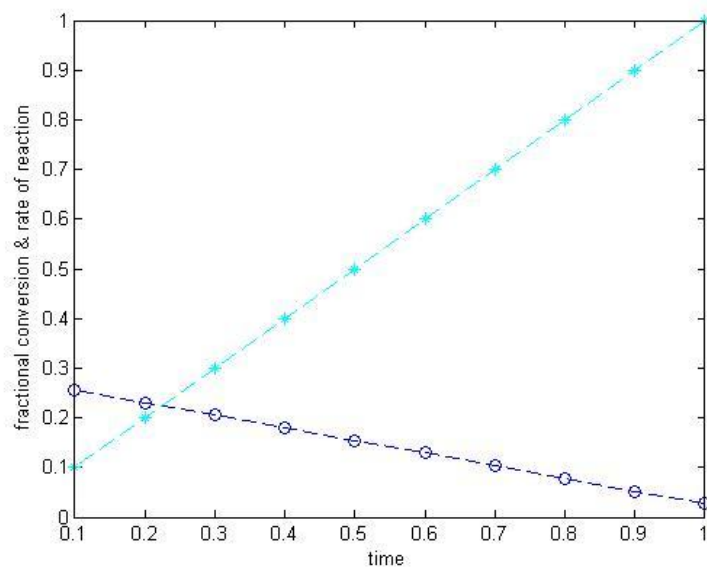


Figure 9: Plot of Fractional Conversion against Reaction Time.

Figure 9 shows fractional conversion against rate of reaction versus time (g min/ml) showed that between 0.23 to 0.3, there is a variation in the variables as well as change in the reactors operation. Since rate of reaction decreases with time.

**4.10 Variation of Space Velocity & Volume of Reactor with Fractional**

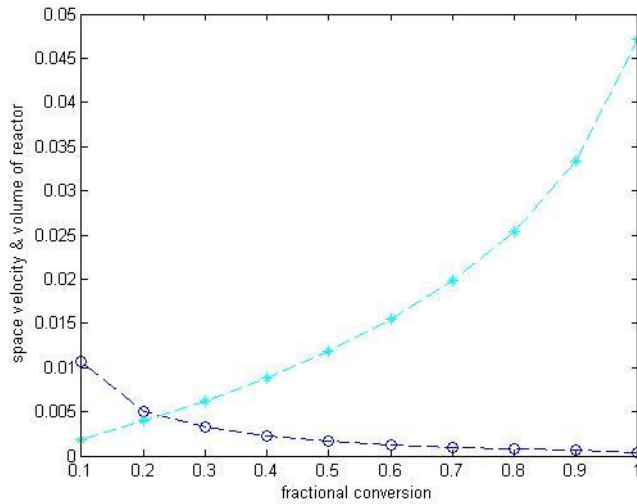


Figure 10: Plot of Space Velocity and Volume of Reactor against Fractional Conversion.

Figure 10 shows space velocity against volume of reactor versus fractional conversion showed that there is a variation between 0.23 to 0.3 which altered flow as well as change in the operation of the reactor. Since an increase in feed flow rate decreases the residence time of the reactants in the reactor.

**4.11 Variation of Heat Exchange & Rate of Reaction with Fractional**

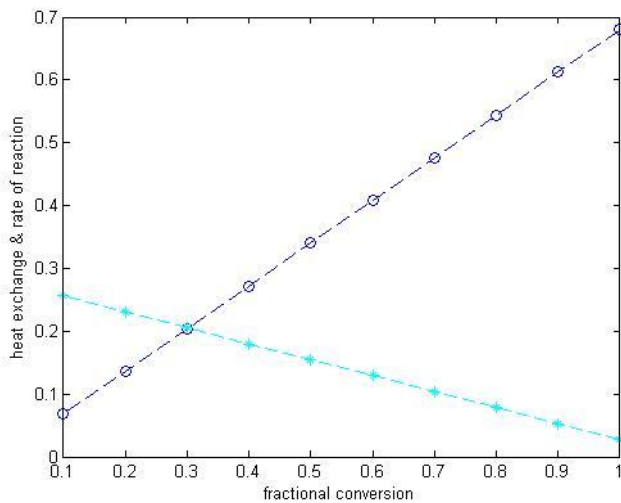


Figure 11: Plot of Heat Exchange and Rate of Reaction versus Fractional Conversion

The plot of heat exchange & rate of reaction versus fractional conversion showed that at 0.3 fractional conversion all variables in the reactor remains constant and the reactor operation is at a steady state, as shown in figure 8.

### 4.3 Reactor Dead Time ( $\theta_p$ )

The dead time of the reactor which is delay due to change in reaction for the reactor to achieve steady state process is obtained between 0.23 and 0.3 fractional conversion as shown in figure 9 and 10. The reactor model shows that at 0.3 fractional conversions the reactor will run at a steady state process as shown in figure 11 and 8.

## CONCLUSION

The research model is suitable for private sector consultancy and Nigerian government local content utilization for acetaldehyde production. Therefore, a daily production of output of 30,810.9 L/day can be achieved with a corresponding cost element of \$40,000 dollars equivalent of N14,000,000 only.

## Nomenclature

MeCHO = Methyl aldehyde	$\omega$ = frequency factor
CH <sub>3</sub> CHO = Acetaldehyde	$E_a$ = Activated energy
$t_{p.opt.}$ = Optimum Time	R = Universal gas constant
C <sub>2</sub> H <sub>5</sub> O = Ethanal	T = Temperature
H <sub>2</sub> = Hydrogen	$-r_A$ = Rate of disappearance
O <sub>2</sub> = Oxygen	$\tau_{opt.}$ = Optimum space time
H <sub>2</sub> /O <sub>2</sub> = Hydrogen to Oxygen ratio	$C_B$ = Concentration of product
C <sub>2</sub> H <sub>6</sub> = Methane	$F_{EtOH}$ = molar flow rate of ethanol
C <sub>2</sub> H <sub>5</sub> = Methyl	$\mu m$ = Micrometer
H = Hydrogen atom	$\alpha_{EtOH}$ = Fractional conversion of ethanol
C <sub>2</sub> H <sub>4</sub> O = Acetaldehyde	$dF_{EtOH}$ = Change in molar flow rate of ethanol
Bp = Boiling Point	$d\alpha_{EtOH}$ = Change in fractional conversion of ethanol
KPa = Kilo Pascal	$L/d_t$ = Length to diameter ratio
Mp = Melting Point	S = Throughput scale-up factor
$d_4$ = Relative density	$N_{tubes}$ = Number of tubes
$d_D$ = Refractive index	$S_{Tubes}$ = Scale – up factor for tubes
l/mol = liter per mole	$S_R$ = Scale – up factor for radius
m <sup>3</sup> /kg = Cubic meter per kilogram	$S_L$ = scale – up factor for length
mPa · s = mmpascal per second	$\alpha_A$ = Fractional conversion
$\eta$ = Viscosity of vapor	$r_B$ = Rate of Reaction
$\gamma$ = Surface tension	$S_V$ = Space Velocity
mN cm <sup>-1</sup> = mm Newton per centimeter	$S_\tau$ = Space Time
J g <sup>-1</sup> K <sup>-1</sup> = Joule per gram per Kelvin	$V_R$ = Volume of Reactor
J m <sup>-1</sup> s <sup>-1</sup> K <sup>-1</sup> = Joule per meter per seconds	L = Length of Reactor
Kelvin	W = Weight of Catalyst
KJ/mol = Kilo-Joule per mole	Q = Heat Exchange
J/mol = Joule per mole	q = Heat Exchange per unit Volume
J mol <sup>-1</sup> K <sup>-1</sup> = Joule per mole per Kelvin	D = Diameter
mol/l = Mole per liter	
NFPA = National Fire Protection Agency	
C <sub>2</sub> H <sub>5</sub> OH = Ethanol	

<p> <math>CH_3COOH</math> = Ethanoic acid  <math>H_2O</math> = Water  <math>CH_4</math> = Methane  <math>CO_2</math> = Carbon dioxide  <math>\Delta H</math> = Enthalpy  Cu = Copper  Co = Cobalt  <math>Cr_2O_3</math> = Chromium (III) oxide  wt% = Percent weight of catalyst  Ni = Nickel  Ni/SnO<sub>2</sub> = ratio of Nickel to Silicate oxide  W/F = Contact time ratio   <i>EtOH Con. (%)</i> = Ethanol conversion  <i>AchSelc. (%)</i> = Acetaldehyde Selective  <i>AchYield (%)</i> = Acetaldehyde Yield  PCl<sub>3</sub> = phosphorus trichloride.  HCL = Hydrochloric acid  Cr Al<sub>2</sub>O<sub>3</sub> = Chromium Aluminum oxide  <math>C_{A0}</math> = Initial concentration flow rate  K = specific reaction rate constant  A </p>	<p> <math>\theta_p</math> = Reactor dead time  <math>\Delta P</math> = Change in pressure  U = Overall coefficient of heat  <math>A_{ext}</math> = Heat transfer area  H = inside coefficient  <math>\Delta T</math> = Driving force  <math>G_o</math> = Superficial Velocity  <math>\rho</math> = density of the system/fluid  <math>\rho_{Cat.}</math> = Catalyst density  <math>\Delta H_r</math> = Heat of the reaction  <math>T_h</math> = Temperature of the hot fluid entering system  T = Temperature within the fluid  <math>C_p</math> = Specific heat capacity of the system/fluid  <math>R_e</math> = Reynolds number.  A = CH<sub>3</sub>CH<sub>2</sub>OH, B = CH<sub>3</sub>CHO,  C = CO<sub>2</sub>, D = H<sub>2</sub>O, A = ethanol, B = desired product  C = undesired product </p>
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