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PERFORMANCE EVALUATION OF PFR AND CSTR 1- REACTOR TANK FOR FORMALDEHYDE PETROCHEMICAL PRODUCTION

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ABSTRACT

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CSTR 1-reactor tank and PFR plug flow reactor for the production of formaldehyde are two reactors subjected to performance studies. The research models were derived from the fundamental principles of conservation of mass and energy balance; and qualitative kinetic optimum model for the determination of yields for the dehydrogenation and partial oxidation of methanol in the two reactors at 600-6500C. The data obtained for model evaluation were statistically regressed to adopt it as engineering data which is adequate for applications in the evaluation process. The design models for the CSTR 1-reactor tank and PFR plug flow reactor reactors were appropriately solved. The results obtained on the two reactors parameters are given as follows: CSTR 1-reactor tank volume 2.85m3, Height 5.69m, Space-time 0.12hr, Space-velocity 0.67/hr, pressure drop and heat generated per unit volume 2.34*107J/m3. Similarly, PFR volume 1.26m3, Height 12.58m, Space-time 0.225hr, Space-velocity 0.182/hr, pressure drop 3.73*10-8 and heat generated per unit volume 1.17*108 J/m3, And, innovatively, results of optimal yields Yopt calculation for CSTR 1-reactor tank and Plug flow reactor PFR showed that the yields obtained for the two reactors are 69% and 87% and compare favorably with operational yields of the production process which stood at 78.5% and 80.1%. From the results PFR provide a better volume for the production of formaldehyde at 87% conversion of 1.26m3. Hence, the PFR has a better performance for the production of formaldehyde with 87% feed conversion.

Contribution/Originality: Research originates detailed derivations of formulas for reactor performance models and also applying calculus function for the optimum yields Yopt. calculation for the rate of depletion of feed in reactors into desired products as a detailed theoretical concepts of calculating yields of products in advance manner in chemical reaction engineering.

1. INTRODUCTION

Formaldehyde is an organic compound of the aldehydes group of compound and has a chemical formula of HCHO. It acts as the base for other petrochemical compounds like phenol-formaldehyde, urea-formaldehyde and melamine-resin. It is applied in process industries in many ways; with a world production rate of about 10 million metric tons annually.

The areas of applications are in engineering, plastics, resin and also in making rubber, Paper, fertilizers, explosives and preservatives Bahmanpour, et al. [1].

At room temperature, pure formaldehyde is colorless with a pungent, suffocating odor. As population increased the demand for formaldehyde also increased. Waterhouse, et al. [2] posited that production of formaldehyde amounted to 32.5 million tons per year, due to the application of formaldehyde in chemical synthesis.

Several attempts have been made to produce HCHO by non-catalytic oxidation of several compounds such as propane, (C_3H_8) and butane (C_4H_{10}), however, several products were produced which required a complicated and cost separation system. And so partial oxidation had an advantage over the other processes.

The sequence of HCHO production is made in three stages; firstly, natural gas is reformed which leads to the production of synthesis and it is converted to CH_3OH through CH_3OH synthesis or hydrogenation of CO and finally partial oxidation of CH_3OH leads to the production of HCHO. HCHO is industrially produced via two reactions in commercial units.

Reaction I

Dehydrogenation

$$CH_3OH \longrightarrow CH_2O + H_2 \qquad \Delta\tilde{H}\dot{r} = +85\,\mathrm{KJ.mol}^{-1} \tag{1}$$

Reaction 2

Partial Oxidation

$$CH_3OH + {}^{1}\!/_{2}\,O_2 \longrightarrow CH_2O + H_2O \qquad \Delta\tilde{H}\dot{r} = -159\,\mathrm{KJ.mol}^{-1} \tag{2}$$

Formaldehyde HCHO is produced from the endothermic dehydrogenation and exothermic partial oxidation of methanol according to the reaction kinetics Equations model 1 and 2 with enthalpies.

These two reactions occur simultaneously in commercial units in a balanced reaction, called auto thermal because the oxidative reaction releases heat to effect dehydrogenation to take place. About 50 to 60 percent of HCHO is formed by the exothermic reaction. The oxidation reaction requires about $1.6m^3$ of air per kilogram of methanol reacted, a ratio that is maintained when passing separate streams of these two feed materials forward rate process.

The products (HCHO and process water) leave the converter at 620^0C and at 34 to 69 kpa absolute. About 65 percent of methanol is converted per pass and the operational yield from the reaction is 85 to 90 percent. Literature showed that in 1982 USA produced about $2.2 * 10^6$ tons of 37 percent solution (formalin) at a price of 19 to 20 cents per kilogram, HCHO is industrially produced currently from CH_3OH using the silver contact process which is also known as the air deficient process of silver process. In this particular process the methanol (CH_3OH) under dehydrogenation and partial oxidation reaction to give formaldehyde (process used by BASF, Borden, Degussa, Bayer, DuPont, Mitsubishi, and Mitsui).

Wachs and Madix [3] worked on oxidation of methanol on silver (110) catalyst. Methanol oxidation in a packed bed reactor using Ag catalyst at process conditions of 250K, 300K and 340K to give formaldehyde. The adsorption takes place on the surface of the silver catalyst for increase productivity and efficient performance of the catalyst. The rate expression was predicated as first order kinetic through the various intermediates studied. The rate constant was estimated to $(2.4 \pm 2.0) \times 10^{11} \exp(-14.0 \pm \mathrm{kcal/mol.RT})\,\mathrm{sec}^{-1}$.

Schotborgh, et al. [4] worked on analysis of the multi tubular reactor for Formaldehyde production by one-dimensional models. The oxidation of methanol in a packed bed catalytic reactor was studied and steady state models for the temperature and mass (mole) were derived using principles of conservation of mass and energy. The developed models were solved using 4th-order Runge-Kutta Algorithm and profiles of temperature and moles fraction. The kinetic expressions followed that of Cozzolino, et al. [5] and Tesser, et al. [6]. The results indicate that Tesser, et al. [6] kinetic expression was satisfactory and gives a good description of the system than others.

Jilesh and Linesh [7] worked on implementation of cleaner production principles in Formaldehyde production. The dehydrogenation process is exothermic and oxidation route which is highly endothermic. Route III was proposed and carried out which was environmentally friendly and combined the two routes in reactor with minimal energy required which approximates to zero. Thus, Formaldehyde in this route is aimed at conserving energy than the other routes.

These two process routes are demonstrated below;

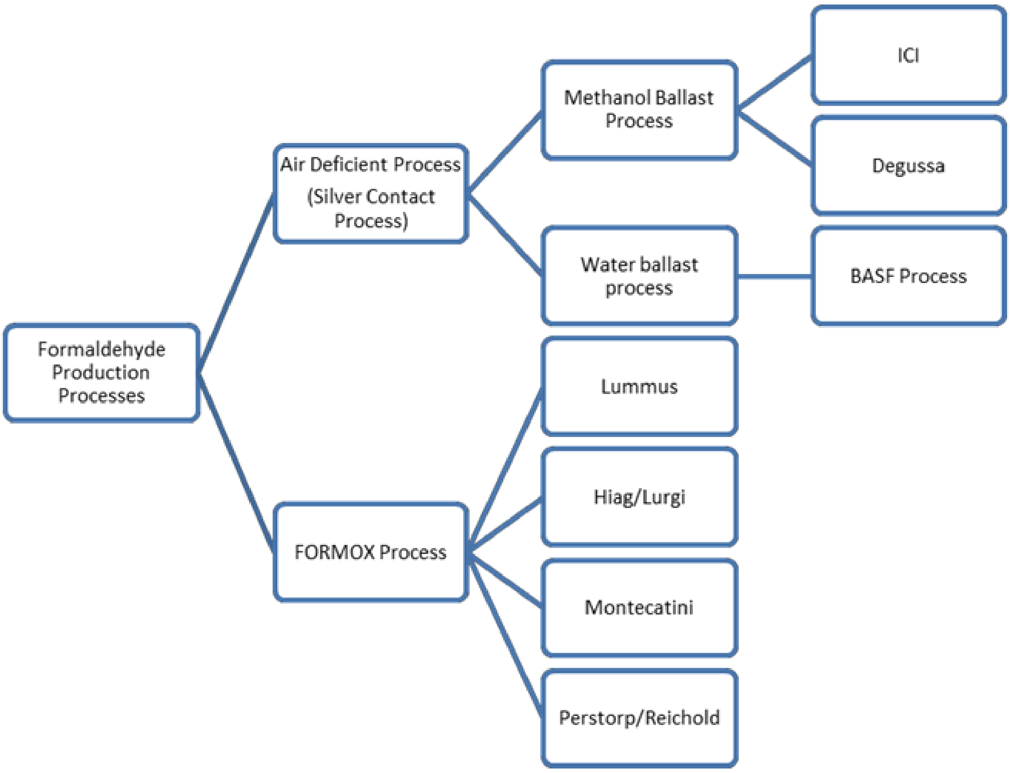

Figure-1. Schematics of industrial production of formaldehyde.
Source: Bahmanpour, et al. [1].

Figure 1 represents tree diagram for the formaldehyde production.

The currently used two main processes for formaldehyde production from methanol are silver contact process and the oxide process. The silver contact process can be further grouped into two types the methanol ballast process and BASF [1].

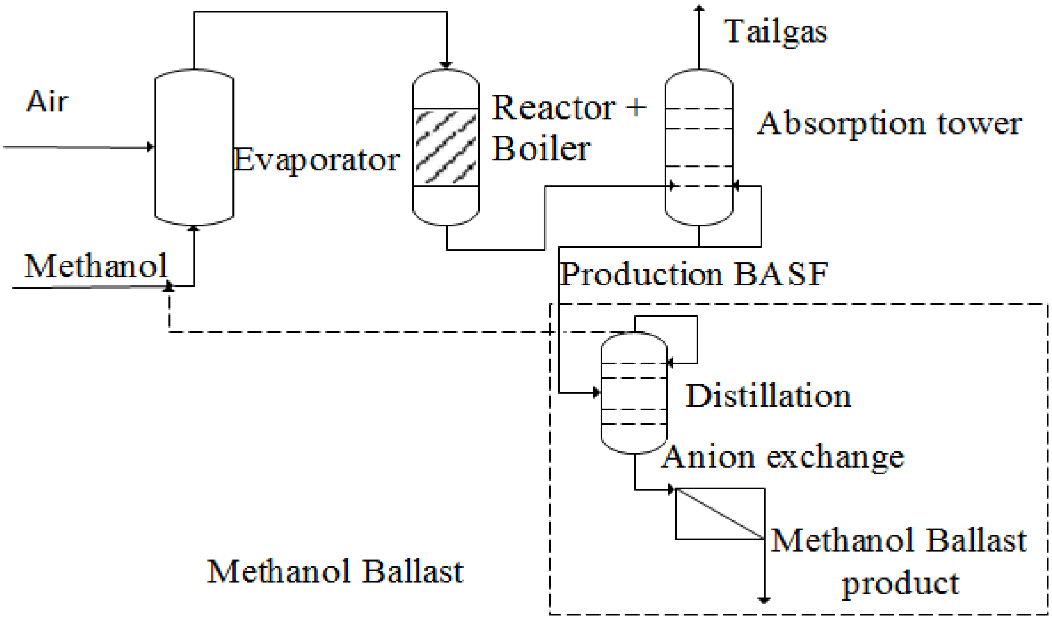

Figure-2. A Schematic overview of the silver process.
Source: Ase [8].

1.1. Research Focus

The research thrives to investigate two reactors performance for HCHO production; develop performance models, feed physical and chemical properties; and the rigorous mathematical optimal kinetic model for the dehydrogenation (rate constant K_1) and partial oxidation (rate constant K_2) cum qualitative model treatments for the effectual yields of the desired product HCHO and undesired product process water.

The reactors are PFR and 1-reactor tank CSTR. The performance models were developed from the fundamental principles of material balance and kinetic optimal model qualitative treatment to determine the optimum yields for the two processes. HCHO productions are prevalent but the optimal model for yields determination and reactor comparison is rare.

Finally, taking dehydrogenation and partial oxidation kinetic literature data [7] to test the validity of the optimal kinetic model for the reactors thereby making an inference from the yields obtained from production process and that of theoretical model qualitative treatment. This action is lacking and also complementary to the two reactors sizes and relevant performance control parameters.

2. MATERIALS AND METHODS

2.1. Materials

The analytical materials applied are:

Design model of CSTR 1- reactor tank and PFR, Stoichiometric balance equations, First-order kinetic process, Energy balance (temperature effects); Dehydrogenation and Partial oxidation kinetic literature data [7].

2.2. METHODS

2.2.1. Design Model CSTR 1 - Reactor Tank

2.2.1.1. Theoretical Concepts/Constraints

The process is at steady state conditions.

The composition of the reacting mixture is uniform.

Balancing was taken on the entire volume of reactor.

The reaction mixture is well stirred.

The composition of the exit stream is the same as that within the reactor.

No conversion of feed prior to flow into the reactor volume.

The feeds entering of reactor immediately assumes a final uniform composition throughout the reactor due to assumed perfect mixing.

2.2.1.2. Reaction Kinetics of the Process

The kinetics according to Equations 1 and 2 above are two main process for formaldehyde production; dehydrogenation and partial oxidation reactions according to Jilesh and Linesh [7] kinetic literature data adapted for the research.

Rate $\alpha\ C^n$, i.e. the rate of reaction for the dehydrogenation process is proportional to the concentration of the methanol index the order of the dehydrogenation process Equation 3.

(a) Dehydrogenation Rate Equation is

$$(r_B)_1 = k_1 C_{CH_3OH} \qquad (3)$$

Equation 3 is expressing the rate law or rate equation for feed A depletion with a speed constant K_1 in the reactor Suppose methanol is designated as species A, and formaldehyde is species B.

$$(r_B)_1 = k_1 C_A = k_{10} \exp\,[-E_A/RT]\; C_{A,O}\,(1-X_A) \qquad (4)$$

Equation 4 represents the coupling of the Arrhenius model with rate equation w.r.t fractional conversion of feed A for formaldehyde production in reaction 1.

Where: $k_1 = k_{10} \exp\,[-E_A/RT]$

(b) Partial oxidation Process rate equation is .

$$(r_B)_2 = k_2 \exp\,[-EA/RT] C_{A_o}(1 - X_A) \qquad (5)$$

Equation 5 represents the coupling of the Arrhenius model with rate equation w.r.t fractional conversion of feed A for formaldehyde production in reaction 2.

Where;

$$k_2 = k_{2,o} \exp\,[-EA/RT] \qquad (6)$$

Equation 6 represents the Arrhenius model.

k_2 = Rate constant of partial oxidation process, S^{-1}

2.2.1.3. Volume of 1 - Reactor Tank CSTR

Taking a material balance for the process is given as:

$$Input - Output + Depletion\ of\ feed \ = Accumulation \qquad (7)$$

Equation 7 is couched mathematically to give Equation 8;

$$\frac{d}{dt}(C_A V_R) \ = \ F_{AO} - [F_{AO}(1 - X_A)] - (-r_A)V_R \qquad (8)$$

At steady state process we have,

$$\frac{d}{dt}(C_A V_R) = 0 \qquad (9)$$

Equation 9 is the rate of accumulation is equals zero

$$\therefore \ \ 0 = F_{AO} - [F_{AO}(1 - X_A)] - (-r_A)V_R \qquad (10)$$

Equation 10 is the steady state process model via Equation 11 to yield Equation 12 which is the volume of the reactor

$$0 = F_{AO} - F_{AO} + F_{AO}X_A - (-r_A)V_R$$

$$0 = F_{AO}X_A - (-r_A)V_R$$

$$V_R \ = \ \frac{F_{AO}X_A}{(-r_A)} \qquad (11)$$

Substituting rate law $f(C_i\,T)$ into Equation 11 yields Equation 12

$$V_R \ = \ \frac{F_{AO}X_A}{Ae^{-E/RT} C_{AO}(1 - X_A)} \qquad (12)$$

2.2.1.4. Height of 1-Tank Reactor CSTR

Since the reactor is cylindrical, volume of a cylindrical reactor is given as

$$V_R = \pi R^2 L_R \tag{13}$$

And, radius of a cylinder is half its diameter, i.e.

$$R = \frac{D_R}{2} \tag{14}$$

Combining Equation 13 and 14 yields Equation 15 the volume of CSTR

$$V_R = \pi \left(\frac{D_R}{2}\right)^2 L_R \tag{15}$$

For a CSTR, whose configuration is cylindrical

$$\text{Let } \frac{L_R}{D_R} = 2 \tag{16}$$

$$D_R = \frac{L_R}{2}$$

(17)

Combining Equation 15 and 17 yields

$$V_R = \frac{\pi \left(\frac{L_R}{2}\right)^2 L_R}{4}$$

$$V_R = \frac{\pi L^3{}_R}{16}$$

$$\therefore \; L_R = \left(\frac{16 V_R}{\pi}\right)^{1/3}$$

(18)

Substituting Equation 12 into 18 yields

$$L_R = \left[\frac{16 \; F_{AO} X_A}{\pi . A_e{}^{-E/RT} C_{AO} \left(1 - X_A\right)}\right]^{1/3} \tag{19}$$

Equation 19 represents the length of the reactor in (meters)

2.2.1.5. Diameter of 1- Reactor Tank (CSTR)

From Equation 17

$$D_R = \frac{L_R}{2}$$

Substituting Equation 18 into 16 yields

$$D_R = \frac{\left[\dfrac{16\ F_{AO}X_A}{\pi.A_e^{-E/RT}C_{AO}\left(1-X_A\right)}\right]^{1/3}}{2} \tag{20}$$

Equation 20 is known as the diameter of the reactor

2.2.1.6. Space Time

Ratio of reactor volume to volumetric flow rate of feed

$$\tau_{CSTR} = \frac{V_R}{v_O} \tag{21}$$

Substituting Equations 12 into 21 yields Equation 22

$$\tau_{CSTR} = \frac{\dfrac{F_{AO}X_A}{A_e^{-E/RT}C_{AO}\left(1-X_A\right)}}{v_O}$$

(22)

$$F_{AO} = C_{AO}v_O \tag{23}$$

Substituting F_{AO} in Equation 23 into Equation 22 yields equation (24)

$$\tau_{CSTR} = \frac{X_A}{A_e^{-E/RT}\left(1-X_A\right)} \tag{24}$$

2.2.1.7. Space Velocity 1- Reactor Tank S_V

This is the reciprocal of space time.

$$S_V = \frac{1}{\tau_{CSTR}} \tag{25}$$

Equation 25 is the space velocity model for reactor, which is the reciprocal of space time τ_{CSTR}

Substituting Equations 22 into 24 yields Equation 26

$$S_V = \frac{A_e^{-E/RT}\left(1-X_A\right)}{X_A} \tag{26}$$

Equation 26 is the space velocity model for reactor with its complementary parameters for evaluation

2.2.1.8. Quantity of Heat 1- Reactor Tank Q

The quantity of heat generated is mathematically given as

$$Q = \Delta H_R \; F_{AO} X_A$$

(27)

Equation 27 is the quantity of heat released in the reactor

2.2.1.9. Heat Generated Per Unit Volume 1- Reactor Tank

This can be obtained by dividing the quantity of heat generated by the volume of the reactor (V_R)

$$\frac{Q}{V_R} = \frac{\Delta H_R \; F_{AO} X_i}{V_R}$$

(28)

Equation 28 represents quantity of heat per unit volume

$$q = \frac{\Delta H_R \; F_{AO} X_A}{V_R} \tag{29}$$

Equation 29 is the quantity of heat generated per unit volume of the reactor

Where q = quantity of heat generated per unit volume of the reactor

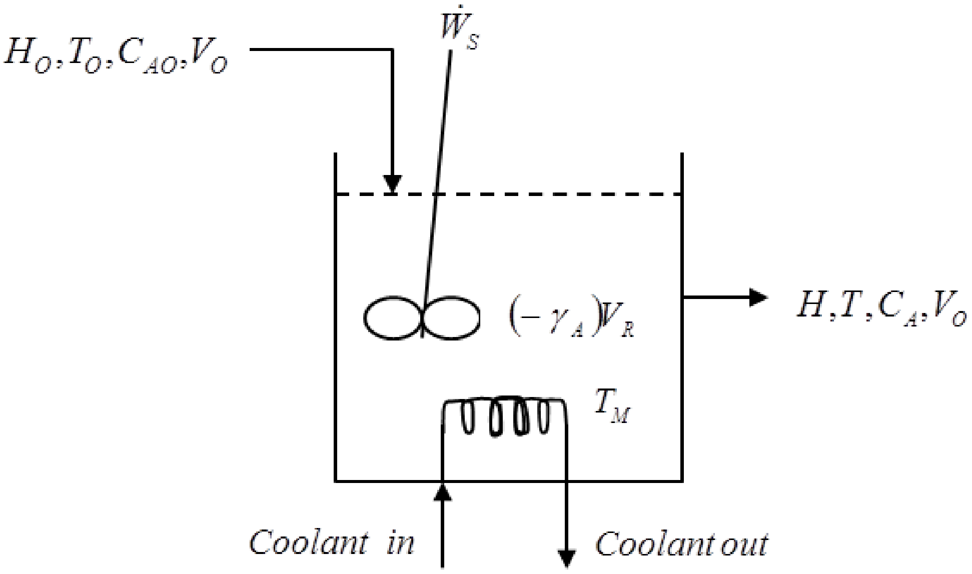

Figure-3. Sketch of typical CSTR 1- Reactor tank with heat effect.

Source: John [9].

2.2.1.10. Heat/Energy Balance with Heat Transfer Surface

Taking a balance for a 1-Reactor tank CSTR reactor volume V. measured over an element of time $d\tau$ is given as;

$$\begin{pmatrix}\text{Rate of heat}\\ \text{inflow}\\ \text{into}\\ \text{volume element}\end{pmatrix} - \begin{pmatrix}\text{Rate of heat outflow}\\ \text{from}\\ \text{volume element}\end{pmatrix} \pm \begin{pmatrix}\text{Rate of heat released or}\\ \text{absorbed due to chemical}\\ \text{reaction within volume element}\end{pmatrix} \pm$$
$$\begin{pmatrix}\text{Rate of heat transfer or removed}\\ \text{to and from}\\ \text{volume element}\end{pmatrix} + \begin{pmatrix}\text{Shaft work by}\\ \text{the stirrer}\end{pmatrix} =$$
$$\begin{pmatrix}\text{Rate of accumulation}\\ \text{of feed as products within}\\ \text{the reactor}\end{pmatrix}$$

(30a)

Equation 30a is constrain under heat transfer and steady state process; the algebraic sum of all the heat flows into and from the reactor is zero i.e.

$$Q_{in} - Q_{out} \pm Q_r \pm Q_1 = 0$$

When heat transfer takes place in the reactor operation, we have;

$$\boldsymbol{Q_1 = UA\Delta T}$$

$$\boldsymbol{v_o C_{P,O} \rho_O T_O - v C_P \rho T - \Delta H_R r_{feed} v \pm U_{ht} A_{ht} \Delta T_{ht} = V \frac{d(\rho C_P T)}{d\tau}} \qquad (30b)$$

Equation 30b therefore, is mathematically couched as Equation 31 below

$$\rho V_O C_p \frac{dT}{d\tau} = \rho V_O C_p T_o - \rho V_O C_p T - (-r_A) V_R (\Delta H_R) - UA_C (T - T_C) + W_S$$

(31)

At steady state process, we have,

$$\frac{dH}{d\tau} = \rho C_p V \frac{dT}{dt} = 0$$

Neglecting the Shaft Work W_s

Equation 31 becomes

$$0 = \rho V_O C_p T_o - \rho V_O C_p T - (-r_A) V_R (\Delta H_R) - UA_C (T - T_C)$$

Rearranging and factorization

$$\rho V_O C_p (T - T_0) = -(-\gamma_A) V_R (\Delta H_R) - UA_C (T - T_C)$$

Dividing through by $\rho V_O C_p$

$$T - T_O = -\frac{(-r_A)V_R(\Delta H_R)}{\rho v_O C_p} - \frac{UA_C(T - T_C)}{\rho v_O C_p} \tag{32}$$

Simplifying Equation 32 yields Equation 33

But $\frac{V_R}{v_O} = \tau\,(space\,time)$

$$T - T_O = \tau\frac{-\Delta H_R r_A}{\rho C_p} - \frac{UA_C(T - T_C)}{\rho v_0 C_p} \tag{33}$$

Equation 33 can be rearranged to give Equation 34

$$T = \frac{\tau\ \Delta H_R r_A V_O + UA_C T_C + \rho V_O C_P T_O}{\rho V_O C_P + UA_C} \tag{34}$$

Equation 34 is the reactor temperature model

2.2.1.11. Design Model Plug Flow Reactor (PFR)

Model Constraints

Reactor is operated at steady state.

Composition of the reacting mixture is uniform in the axial direction.

Balance is taken on differential volume of reactor.

No conversion of feed prior to flow into the reactor volume.

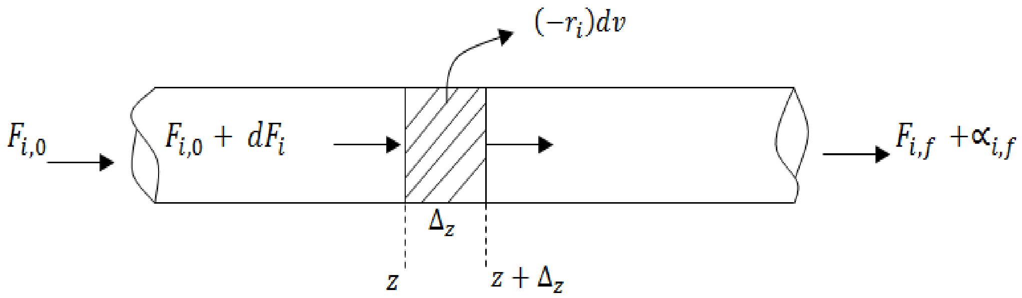

Figure-4. PFR differential volumes.

Source: Wordu [10].

Where i = species A

$$F_{i,0} - (F_i + dF_i) - (-r_i)dF_i = \frac{dN_i}{d\tau}$$

(35)

Equation 35 is the material balance taken on the differential volume in Figure 4

$$F_{i,0} - (F_i + dF_i) + (-r_i)dV_p = \frac{dN_i}{d\tau}$$

$$-dF_i + (-r_i)dV_p = \frac{dN_i}{d\tau} \qquad (36)$$

Equation 36 is a consequence upon simplification of the material balance.

In terms of fractional conversion, $\propto_A$

$$F_i = -F_{Ao} \propto_A$$

Integrating with boundary conditions;

$$\propto_A = o;\ V_p = o \quad \propto_A = \propto_{A,F};\ V_p = V_{PFR}$$

$$\int_o^{V_{PFR}} dV_p = \int_o^{\propto_{A,f}} \frac{F_{Ao}\, d\propto_A}{k_0(1-\propto_A)}$$

$$V_{PFR} = F_{AO} \int_O^{\propto_{A,f}} \frac{d\propto_A}{k_0(1-\propto_A)} \qquad \textbf{(37)}$$

Equation 37 is the result of integrating reactor model equation for the volume of PFR.

2.2.1.12. Space Time of PFR

This is mathematically stated as:

$$\tau_p = \frac{V_{PFR}}{v_o} = \frac{F_{AO} \int_O^{\propto_{A,f}} \frac{d\propto_A}{k_0(1-\propto_A)}}{v_o}$$

(38)

Equation 38 is the design model equation for space-time of PFR.

2.2.1.13. Space Velocity

The space velocity of the PFR is expressed mathematically as:

$$S_{VP} = {}^{V_o}/_{V_{PFR}} = \frac{1}{\tau_p}$$

(39)

Equation 39 is the design model equation for space-velocity of PFR

2.2.1.14. Length of the PFR

The length of the PFR is given by:

$$L_{PFR} = \frac{V_{PFR}*4}{\pi D^2}$$

(40) Equation 40 represent a reactor whose configuration is cylindrical in shape

Also; ${}^{L}/_{D} = 2.5$

$$D = \frac{L_{PFR}}{2.5} \tag{41}$$

Equation 41 is the diameter of the reactor obtained from Equation 40 above

2.2.1.15. Heat Generated Per Unit Volume of PFR

The heat generated per unit volume is given by:

$$q_p = \frac{Q}{V_p} = \frac{(-\Delta H_r)F_{A,0}\propto_A}{V_{PFR}} \tag{42}$$

Equation 42 is the quantity of heat generated per unit volume.

$$q_{PFR} = \frac{(-\Delta H_r)\propto_A}{\int_0^{\propto_{A,f}} \frac{d\propto_A}{k_0(1-\propto_A)}}$$

(43)

Equation 43 is the quantity of heat generated in the reactor.

2.2.1.16. Pressure Drop along PFR

It is calculated for plug flow reactor since it deals with gaseous species and is the major characteristics of the reactor. Hence, pressure drop in a tubular flow system is expressed as:

$$\Delta p = \frac{8fl\rho u^2}{2D} = \frac{4fl\rho u^2}{D}$$

Where $f = \frac{0.04}{(Re)0.16}$ (44)

But, $Re = \frac{\rho u D}{\mu}$ (45)

Equation 45 is for calculation of Reynolds number

Combining the 3 equations gives Equation 46

$$\Delta P = \frac{0.16L\rho^{0.84}u^{1.84}\mu^{0.16}}{D^{1.16}} \tag{46}$$

Equation 44 becomes:

$$\Delta P = \frac{0.16L_{PFR}\rho^{0.84}\mu^{0.16}u^{1.84}}{D^{1.16}} \tag{47}$$

Equation 47 represents the actual mathematical value of pressure drop in the tubular reactor

2.17. Heat / Energy Balance PFR

The steady state heat balance in words is given as Equation 48;

$$\begin{pmatrix} Rate\ of\ heat \\ inflow \\ into \\ volume\ element \end{pmatrix} - \begin{pmatrix} Rate\ of\ heat\ outflow \\ from \\ volume\ element \end{pmatrix} \pm \begin{pmatrix} Rate\ of\ heat\ released\ or \\ absorbed\ due\ to\ chemical \\ reaction\ within\ volume\ element \end{pmatrix} \pm \begin{pmatrix} Rate\ of\ heat\ transfer\ or\ removed \\ to\ and\ from \\ volume\ element \end{pmatrix} = \begin{pmatrix} Rate\ of\ accumulation \\ of\ feed\ as\ products\ within \\ the\ reactor \end{pmatrix} \tag{48}$$

$$0 = UA_T \rho CpT_Z - UA_t \rho C_p T_{Z+DZ} + A_t \Delta H_R (-r_i)\, dz + 0 \tag{49}$$

Equation 48 is couched mathematically as Equation 49 established as heat/energy balance model.

At Adiabatic Process Operation of Reactor, we have;

$$T = T_c = 0$$

$$0 = UA_T \rho Cp(T_{Z+\Delta z} - T_Z) + A_t\ \Delta H_R (-r_i)\, dz$$

$$0 = UA_T \rho Cp \frac{dT}{dZ} + A_t\ \Delta H_R (-r_i)\, dz$$

$$\frac{dT}{dZ} = \frac{1}{u\rho C_p} (\Delta H_R)(-r_i) \tag{50}$$

Equation 50 establishes the temperature model of the reactor with which to study the effects of temperature of the reaction process.

2.2.1.18. Optimal Kinetic Model PFR and 1- Reactor Tank CSTR

Yields for both reactors, optimum model for the PFR and CSTR are derived as follows:

$$\begin{pmatrix} Rate\ of\ accumulation \\ of\ feed\ as\ products\ within \\ the\ reactor \end{pmatrix} = \begin{pmatrix} Rate\ of\ inflow\ of \\ feed\ into \\ the\ reactor \end{pmatrix} - \begin{pmatrix} Rate\ of\ outflow\ of \\ feed\ from \\ the\ reactor \end{pmatrix} - \begin{pmatrix} Rate\ of\ depletion\ of \\ feed\ due\ to \\ chemical\ reaction \\ within\ the\ reactor \end{pmatrix} \tag{51}$$

Equation 51 is material balance stated in words

2.2.1.19. Kinetic Model Qualitative Treatment- 1- Reactor Tank CSTR

$$CH_3OH \xrightarrow[k_1]{-H_2} HCHO$$

Dehydrogenation process (52)

$$CH_3OH \xrightarrow[k_2]{O_2} HCHO$$

Partial oxidation (53)

Equations 52 and 53 are the established kinetic model for the study/research

Suppose, A = CH_3OH; B = HCHO

Taking a balance on CSTR 1-reactor tank

For species A

$$V_0C_{AO}-V_0C_A+(-kC_A)V_R=o \tag{54}$$

Equation 54 expresses CSTR 1-reactor tank species A balance

$$C_{AO}-C_A-k_1C_A\ \frac{V_R}{V_0}=o \tag{55}$$

let $\dfrac{V_R}{V_0}=\tau_m$ (56)

Equation 56 represent the space time parameter in the material balance Equation 55 which is simplified to give Equation 57.

$$\Rightarrow C_A(1+(1+k_1\tau_m)=-C_{AO} \tag{57}$$

$$C_A=\frac{C_{AO}}{1+k_1\tau_m} \tag{58}$$

Equation 58 is the solution model for evaluating concentration of species A in the reactor.

2.2.1.20 For Species B Desired Product

Taking a material balance, at steady state process.

$$V_0C_{SO}-V_0C_B+(-r_B)V_R=0 \tag{59}$$

Equation 59 is material balance taken w.r.t species A i.e. formaldehyde produced.

Substituting rate law of species B desired product HCHO the depletion of feed in the reactors, at Concentration of

$$C_{BO}=0$$

But,

$$r_B = K_2C_BV_R + K_1C_AV_R$$

$$-V_0C_B-k_2C_SV_R+k_1C_AV_R\quad =O \tag{60}$$

Dividing through by the volumetric flow rate V_o

And, noting that $\frac{V_R}{V_O} = \tau_M$

$$-C_B - k_2 C_B \tau_m + k_1 C_A \tau_M \quad = 0 \tag{61}$$

$$-C_B(1 + k_2\tau_m) = -k_1 C_A \tau_m \tag{62}$$

$$C_B = \frac{k_1 \tau_m C_A}{1 + k_2 \tau_m} \tag{63}$$

Simplifying Equation 59 via Equations 60, 61 and 62 gives Equation 63 which represents solution model for species B i.e. formaldehyde product.

Substituting Equation 58 into 63 yields Equation 64 .

$$C_B = \frac{k_1 \tau_m C_{AO}}{(1 + k_2 \tau_m)(1 + k_1 \tau_m)} \tag{64}$$

For optimum value, applying calculus quotient rule of differentiation we have,

$$\frac{dC_B}{d\tau_m} = 0$$

$$C_B = \frac{k_1 \tau_m C_{Ao}}{1 + k_1 \tau_m + k_2 \tau_m + k_1 k_2 \tau_m{}^2} \tag{65}$$

Opening the brackets in Equation 64 yields Equation 65

$$\frac{dC_B}{d\tau_m} = \frac{\frac{VdU}{d\tau_m} - \frac{UdV}{d\tau_m}}{V_2} \tag{66}$$

Equation 66 is invoked from calculus quotient rule for application in Equation 65

Where : $U = k_1 \tau_m$

$$\frac{dU}{dt_m} = k_1$$

$$V = 1 + k_1 \tau_m + k_2 \tau_m + k_1 k_2 \tau_m{}^2 \tag{67}$$

$$\frac{dV}{d\tau_m} = k_1 k_2 + 2 k_1 k_2 \tau_m \tag{68}$$

Equations 67 and 68 are the numerator and the denominator of Equation 65 subjected to optimum differentiation of

Equation 65 above yields Equation 69

$$\frac{dC_B}{d\tau_m} = 0 = \frac{(1+k_1\tau_m+k_2\tau_m+k_1k_2\tau_m{}^2)(k_1) - k_1\tau_m(k_1+k_2+2k_1k_2\tau_m)}{(1+k_1\tau_m+k_2\tau_m+k_1k_2\tau_m{}^2)^2} \tag{69}$$

$$(1+k_1\tau_m+k_2\tau_m+k_1k_2\tau_{m\,2})(k_1) - k_1\tau_m(k_1+k_2+2k_1k_2\tau_m{}^2) = 0 \tag{70}$$

Simplifying Equations 69 and 70 in successions yields Equation 71

$$\Rightarrow \tau_m(k_1+2k_2+k_1k_2\tau_{m\,2}) = 1+k_1\tau_m+k_2\tau_m+k_1k_2\tau_m{}^2 \tag{71}$$

$$k_1k_2\tau_m{}^2 = 1 \tag{72}$$

Equation 72 is solved for tau maximum/optimum to give Equation 73

$$\tau_{opt} = \sqrt{\frac{1}{k_1k_2}} = \sqrt{\frac{k_1k_2}{k_1k_2}} = \sqrt{\frac{1}{k_1k_2}} \tag{73}$$

Equation 73 is the τ_{opt} model developed from the application of quotient rule of calculus.

2.2.1.21. *The Optimum Yield*

$$\left(\frac{C_B}{C_{AO}}\right)_{opt} = Y_{B,opt} = \frac{k_1\tau_{opt}}{(1+k_2\tau_{opt})(1+k_1\tau_{opt})} \tag{74}$$

$$Y_{B,OPT} = \frac{\dfrac{k_1\sqrt{k_1k_2}}{k_1k_2}}{\left(1+k_2\dfrac{\sqrt{k_1k_2}}{k_1k_2}\right)\left(1+k_1\dfrac{\sqrt{k_1k_2}}{k_2k_1}\right)} \tag{75}$$

Equations 74 and 75 was derived by substituting optimum model 73 into model 65

$$Y_{B,OPT} \quad \frac{1}{\left[1+\left(\frac{k_1}{k_2}\right)^{\frac{1}{2}}\right]^2} \qquad \textit{1- REACTOR TANK CSTR} \tag{76}$$

Equation 76 was derived by simplifying Equation 75

2.2.1.22. *Kinetic Model Qualitative Treatment PFR*

The rate expressions:

$$(-r_A) = k_1 C_A \tag{77}$$

Equation 77 represents the rate equation for species A

$$\frac{-dC_A}{d\tau} = k_1 C_A \tag{78}$$

Equation 78 is the component balance to species A

$$\frac{-dC_A}{C_A} = k_1 d\tau \tag{79}$$

Equation 79 is separating variables and integrating

$$\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = k_1 \int_0^{\tau} d\tau \tag{80}$$

$$\ln {}^{C_A}/_{C_{AO}} = -k_1\tau \tag{81}$$

Equation 81 is the result of integrating Equation 80

$$C_A = C_{A0}\, e^{-k_1\tau} \tag{82}$$

Equation 82 is the solution kinetics to Equation 78 i.e. species A kinetic balance

$$(-r_B) = k_1 C_{A-} k_2 C_B \tag{83}$$

Equation 83 is the rate equation for species A and B depletion in the reactor

$$\frac{dC_B}{d\tau} = k_1 C_{A-} k_2 C_B \tag{84}$$

Re-arranging Equation 84, we get

$$\frac{dC_B}{d\tau} + k_2 C_B = k_1 C_{A0}\, e^{-k_1\tau} \tag{85}$$

Since C_A is known, integrating Equation 85 with respect to τ_p, gives C_B desired product:

Using integrating factor,

$$\text{I.F} = e^{\int k_2 d\tau} = e^{k_2\tau}$$

Multiply Equation 85 throughout I.F

$$e^{k_2\tau}\left(\frac{dC_B}{d\tau} + k_2 C_{B=}\right) = e^{k_2\tau}.C_{AO}\, e^{-k_1\tau} \tag{86}$$

Equation 86 is the result of multiplying with integrating factor, e^{-k_1t} and subsequently integrating and factoring out C_B yields Equation 87

$$\int \frac{d}{d\tau}\left(C_B e^{K_2\tau}\right) = C_{Ao} \int e^{(K_2-K_1)\tau} d\tau$$

$$C_B e^{k_2\tau} = \frac{C_{AO}}{k_2-k_1}\, e^{(k_2-k_1)\tau} + C \qquad (87)$$

Equation 87 is the result of integrating Equation 86

Boundary conditions: At $\tau = 0$; $C_B = C_{B0} = 0$

$$C_B = \frac{C_{AO}}{k_2-k_1}\, e^{0} + C$$

$$C = -\frac{C_{AO}}{k_2-k_1} \qquad (88)$$

Equation 88 is solution for the constant C which is substituted into Equation 87 to give Equation 89

$$C_B e^{k_2\tau} = \frac{C_{AO}}{k_2-k_1}\, e^{(k_2-k_1)\tau} - \frac{C_{AO}}{k_2-k_1}$$

$$C_B = \frac{C_{AO}}{k_2-k_1}\, e^{(K_2-K_1)\tau} - \frac{C_{AO}}{k_2-k_1} \qquad (89)$$

Equation 89 is the model for calculation of C_B i.e. (formaldehyde) desired product.
Applying calculus mathematical function for maximum yield of formaldehyde, we have,

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

Application of calculus function to the kinetic model Equation 89 to evaluate maximum yield of desired product B (formaldehyde). Therefore, the following mathematical derivations commencing from Equations 89 to 98 ensues to achieve optimum yield Equation 98.

$$\frac{dC_B}{d\tau} = 0 = \frac{C_{AO}}{k_2-k_1}\left[-k_1 e^{-k_1\tau} + k_2 e^{-k_2\tau}\right] \qquad (90)$$

$$\frac{0(k_2-k_1)}{c_{Ao}} = -k_1 e^{-k_1\tau} + k_2 e^{-k_2\tau}$$

$$k_1 e^{-k_1\tau} + k_2 e^{-k_2\tau} = 0 \qquad (91)$$

Equations 91 is achieved by cross multiplying k1-k2 and separating the constants K_1 and K_2 in Equations 91 to give Equation 92

$$k_1 e^{-k_1\tau} = k_2 e^{-k_2\tau}$$

$$\frac{k_1}{k_2} = e^{-k_2\tau}\ e^{-k_1\tau} \tag{92}$$

$$\frac{k_1}{k_2} = e^{(k_1-k_2)\tau}$$

$$\text{In}\left({}^{k_1}/_{k_2}\right) = (k_1 - k_2)\tau_{opt} \tag{93}$$

Taking ln of both sides of preceding equation gives Equation 93 which implies mathematically the optimum value for the formaldehyde product

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

$$\tau_{opt} = \frac{1}{\frac{k_1-k_2}{In\left({}^{k_1}/_{k_2}\right)}} \tag{94}$$

Equation 94 is obtained by simplifying preceding tau model

$$\tau_{opt} = \frac{1}{k_{log}} \tag{95}$$

Equation 95 establishes tau optimum and it is equated to the kinetic model of the right hand side of Equation 96 as shown below;

2.2.1.23. Optimum Model for PFR.

$$C_B = \frac{C_{AO}}{k_1-k_2}\left(e^{-k_1\tau} - e^{-k_2\tau}\right) \tag{96}$$

$$\left({}^{C_B}/_{C_{AO}}\right)_{opt} = y_{B,opt} = \frac{1}{k_2-k_1}\left(e^{-k_1\tau_{opt}} - e^{-k_2\tau_{opt}}\right) \tag{97}$$

$$= \frac{1}{k_2-k_1}\left(e^{-{}^{k_1}/_{k_{log}}} - e^{{}^{k_2}/_{k_{log}}}\right)$$

Equation 97 is the model for calculating optimum yield of formaldehyde product, Y_B,opt.

$$y_{B,opt} = \left[\frac{k_1}{k_2}\right]^{\frac{k_1}{[k_2-k_1]}} \tag{98}$$

Equation 98 represents the derived optimum model for PFR

$$y_{B,CSTR} = \frac{1}{\left[1+\left(\frac{k_1}{k_2}\right)\right]^2} \quad \textit{Optimum model for CSTR} \tag{99}$$

$$y_{B,PFR} = \left[\frac{k_1}{k_2}\right]^{\frac{k_1}{[k_2-k_1]}} \quad \textit{Optimum model for PFR} \tag{100}$$

Equations 99 and 100 specifies models for calculation of optimal yields the reactors.

2.2.1.24. Cost of Reactors

Considering jacketed, agitated reactors (CSTR & PFR), the estimated cost according to Sinnott and Towler [11] is given by:

$$Ce = a + b(V)^n \tag{101}$$

Equation 101 is model for costing for the reactors

Where,

A=\$177, b=\$93.3, n=0.8 and V= volume of reactors in m^3

3. SOLUTION TECHNIQUES

The input data for simulation of reactors functional parameters presented in Table 1.

Table-1. Computer program data.

Parameters	Value	
Initial concentration, $C_{AO}\,(mol\ m^{-3})$	0.2050	
Volumetric flow rate, $v_O\,(m^3/s)$	4.4663	Calculated
Heat of Reactor, $\Delta H_r\,(KJ/mol)$	-159	
Temperature (k)	600	
Mean viscosity, $\mu(N_s/m^2)$	1.6782×10^{-5}	
Molar flow rate, F_{AO}, (mol/s)	0.915625	Calculated
Activation Energy, ϵ_a, (kj/mol)	86082.5	
Pre-exponential-constant, $k_o(m^6/mol^2.s)$	800000.72	

4. RESULTS AND DISCUSSIONS

The research focus has been achieved adequately by the applications of the optimal kinetic model for determination of the effectual yields $Y_{B,,opt}$ 69% and 87% compare favorably with the operational yield 78.5% and 80% formaldehyde HCHO production by the dehydrogenation and partial oxidation reactions process.

The design results for two reactor types are shown in Table 2 and 3.

Table-2. Performance Results of PFR and 1 - Reactor Tank CSTR Parameters at 90% conversion of Methanol 1 - reactor Tank CSTR.

PARAMETERS	CSTR	PFR
Conversion	0.90	0.90
Diameter (m)	2.85	5.03
Volume (m^3)	2.85	1.26
Length (m)	5.69	12.58
Space Time (hr)	0.102	0.225
Space Velocity (hr^{-1})	0.673	0.182
Heat Gen. per volume (J/m^3)	2.64E07	1.17E08
Operational Yield (%)	78.5	80.1
Pressure Drop (Pa)	N.A	3.73E-08

Table-3. Cost of Reactors per annum.

Reactor	Cost ($)	Cost (N)
CSTR	1041	374,760.00
PFR	1013	364,680.00

From Table 2 continuous stirred tank reactor shows a high cost due to high volume, since the cost estimate is a function of volume 2.85m³ and 1.26m³for CSTR & PFR respectively.

4.1. Comparison of Temperature Profiles of Continuous Reactors with Length

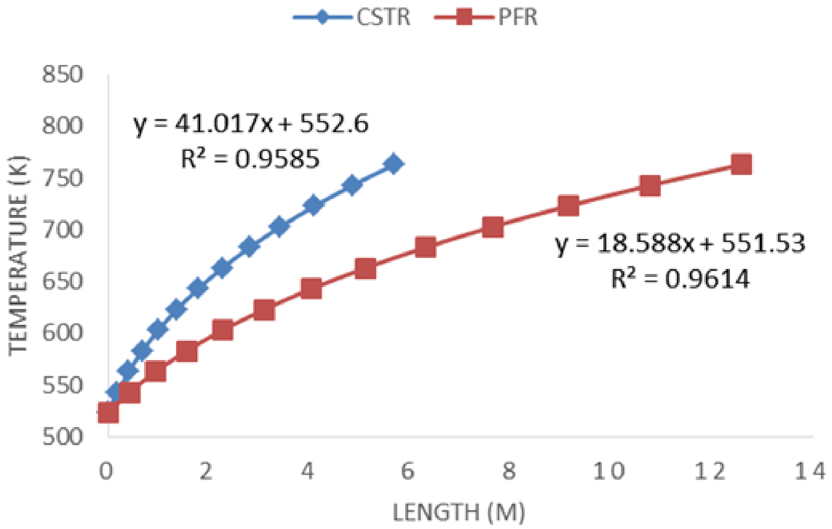

Figure-6. Variation of temperature for flow reactors versus length.

Figure 6 depicts the variation of temperature profiles of flow reactors with length. There is exponential increase of the temperature profiles of the flow reactors for CSTR and PFR with increase in the length of the flow reactors. The reliability of the process is such that temperature value of the PFR is fairly close to the CSTR. Both flow reactors are of order 1 meaning that the data and results are reliably acceptable and good for the production of formaldehyde.

4.2. Comparison of Temperature Profiles of Continuous Reactors with Space Time

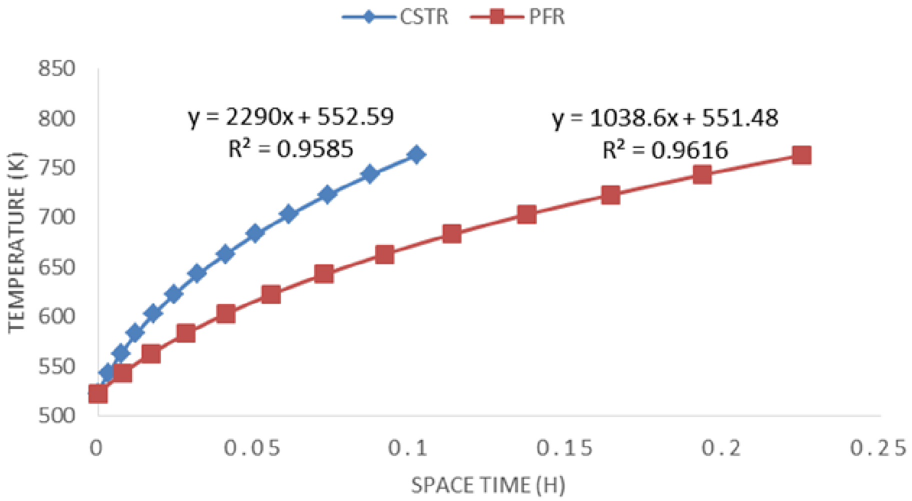

Figure-7. Variation of temperature for flow reactors versus space time.

Figure 7 shows the variation of temperature profiles with space time of the continuous reactors. The reliability of the process is confirmed since coefficient of determination, $R^2_{PFR} > R^2_{CSTR}$. The order of reactions of both reactors are first order, thus the literature data used was acceptable. The equation of the line is $y_{PFR} = 1038.6x + 551.48, R^2_{PFR} = 0.9616 \; and \; y_{CSTR} = 2293x + y_{PFR} = 1038.6x + 551.48, R^2_{CSTR} = 0.9585.$

There is exponential increase of temperature with increase in space-time.

4.3. Comparison of Reactor Volumes of the Continuous Reactors with Conversion

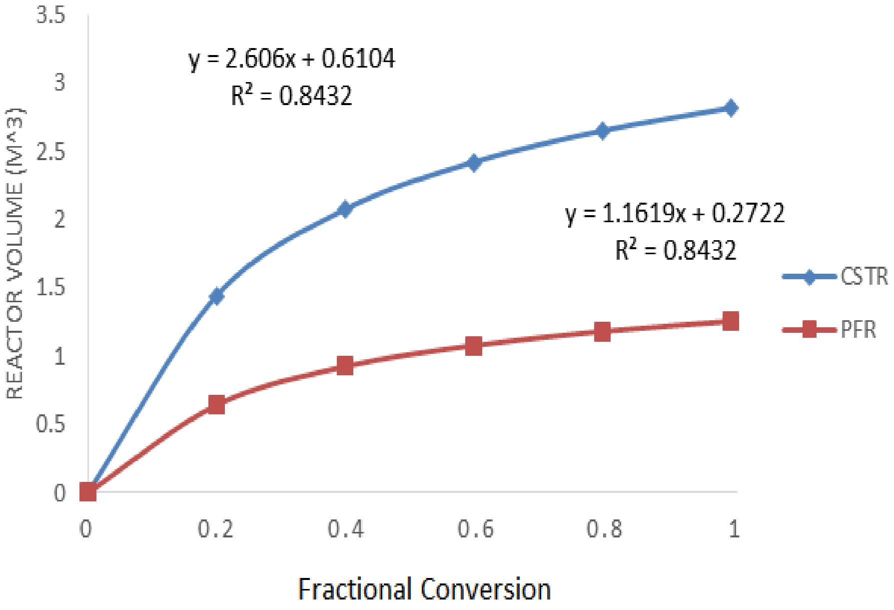

Figure-8. Variation of Volume of flow reactors versus conversion.

Figure 8 depicts the variation of volume of the flow reactors with conversion. The equation of the lines of best fit is respectively; $y_{PFR} = 1.162x + 0.2722$ and $R^2 = 0.8432$ and $y_{CSTR} = 2.606x + 0.6104$ and $R^2 = 0.8432. R^2_{CSTR} = R^2_{PFR}$, The process for production of formaldehyde is reliable and acceptable. From 8, the volume of the flow reactors increases exponentially as conversion increases. The slopes of the equation of the lines are respectively. $M_{CSTR} = 2.606; M_{PFR} = 1.162$ While the intercepts of the flow reactors are respectively; $C_{CSTR} = 0.61 \; and \; C_{PFR} = 0.27$. Since both reactors have $R^2 - \text{value}$ above 50%, the process is reliable and good enough. Also from the plot, a large volume is required for CSTR compared to PFR. This obviously gives an insight of the reactor type to be used in practice after considering costing of the overall process.

4.4. Comparison of Reactor Length of the Continuous Reactors with Conversion

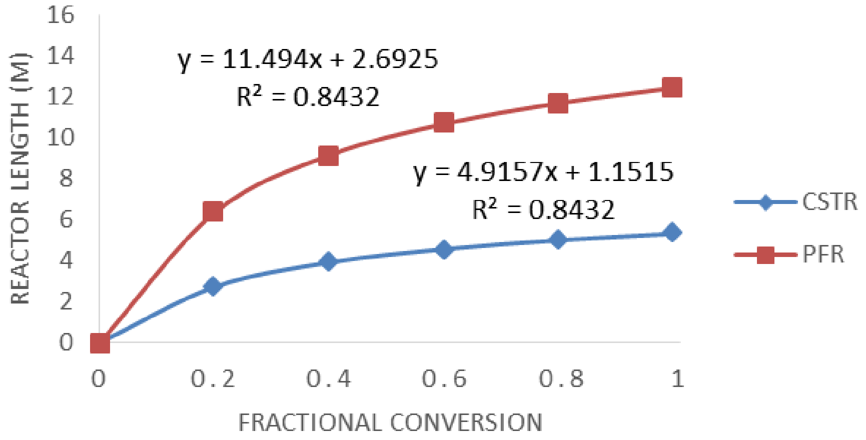

Figure-9. Variation of length of flow reactors versus conversion.

Figure 9 shows the variation of the length of the flow reactors with conversion. The equations of the lines of best fit are respectively $y_{CSTR} = 4.9157x + 1.1515\ and\ R^2_{CSTR} = 0.8432$ and $y_{PFR} = 11.494x + 2.6925$ and$R^2_{PFR} = 0.8432$.The process is reliable and acceptable due to the fact that$R^2 = values$ for both reactors are same. The process is first order thus it is acceptable. There is an exponential increase in the flow reactors as the conversion increases from 0-1. The length of the PFR is more compared to CSTR. The larger the values of the length, the larger the volume of the reactor since volume is a function of the length of the reactor. For the same production capacity, the length of reactor is very important functional parameter since it will affect cost of fabrication of these reactors.

4.5. Comparison of Reactor Space Time of the Continuous Reactors with Conversion

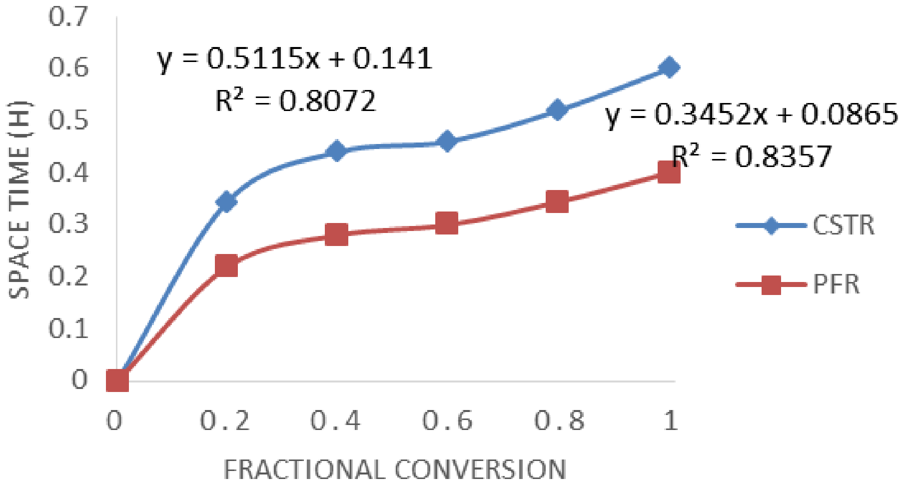

Figure-10. Variation of Space Time of Flow Reactors versus Conversion.

Figure 10 depicts the variation of space time of the flow reactors with conversion. The equations of the lines of best fit are respectively $y_{CSTR} = 0.5115x + 0.141\ and\ R^2_{CSTR} = 0.8072$ and

$y_{PFR} = 0.34524x + 0.0865$ and $R^2_{PFR} = 0.8357. R^2 values$ for both is above 50% hence the process is acceptable. The process for the plug flow reactor is more reliable than that of CSTR since $R^2_{PFR} > R^2_{CSTR}$. The equations of the lines are both first order meaning that the process and the data used is reliable and acceptable. The space time increases exponentially as the conversion increases.

4.6. Comparison of Reactor Space Velocity of the Continuous Reactors with Conversion

Figure 11 shows the relationship between the variation of the space velocity and the conversion. The space velocity is a function of conversion and decreases exponentially as conversion increases. The reliability of the space velocity for the plug flow reactor is more compared to that of the continuous stirred tank reactor (CSTR). This is because $R_p^2 = 0.8245 > R_c^2 =$ values are 50% and above. The process is first order for the flow reactor since the equation of the best fit is of order 1. This order shows that the data and value predicted is acceptable and reliable. It can be concluded that the conversion is inversely proportional to the space velocities of the reactors.

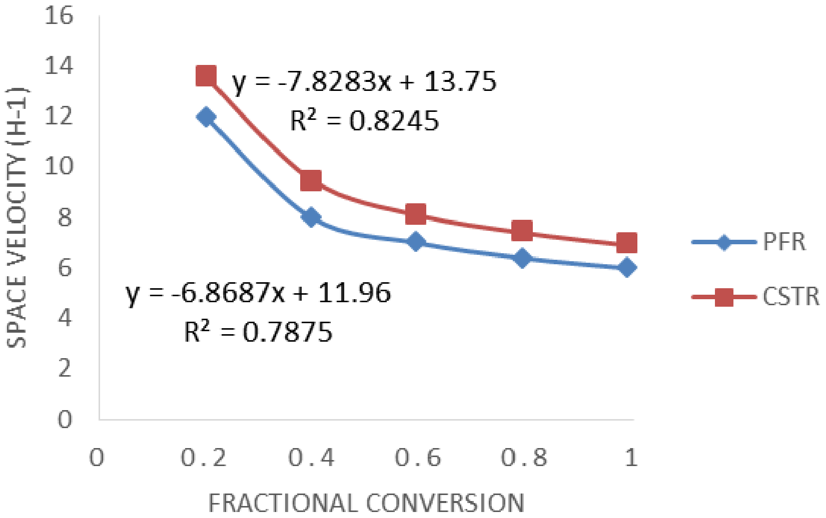

Figure-11. Variation of space velocity of flow reactors versus conversion.

4.7. Comparison of Reactor Heat Generated per Volume of the Continuous Reactors with Conversion

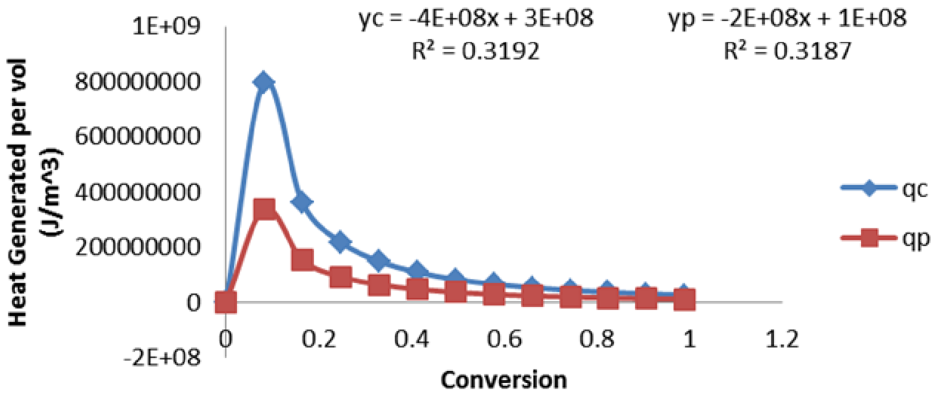

Figure-12. Variation of heat generated per volume of flow reactors versus conversion.

Figure 12 depicts the relationship between the heats generated per unit volume varying with conversion. Both reactions progressed from initial condition to a maximum point and starts decline to a steady state process, as the heat generated per unit volume reduces with increase in fractional conversion.

4.8. Comparison of Reactor Diameter of the Continuous Reactors with Conversion

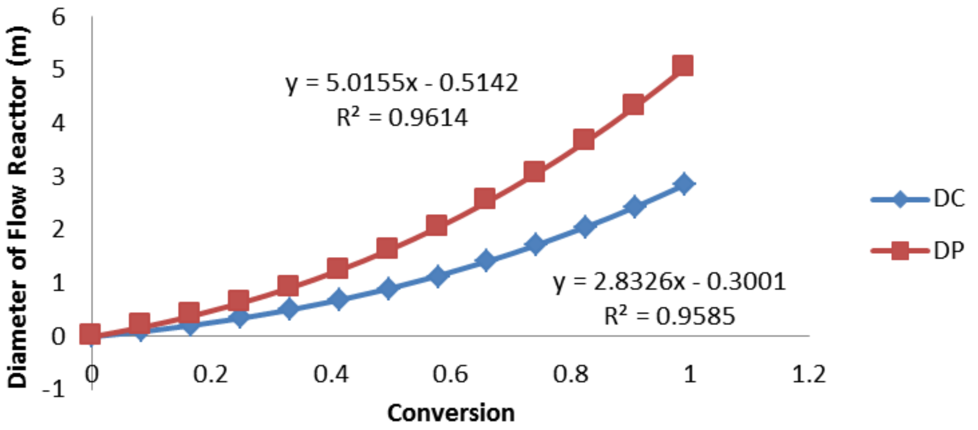

Figure-13. Variation of Diameter of Flow Reactors versus Conversion.

Figure 13 shows the variation of the diameter of the flow reactors varying with fractional conversion. There an exponential increase of the diameter of the flow reactors as the conversion increases from initial condition. The process is highly reliable since R^2-values are up t0 90% and $R_{PFR}^2 = 0.9614 > R_{CSTR}^2 = 0.9585, thus,$ diameter of the plug flow reactor is more reliable than continuous flow reactor. The processes are both first order as a result of the equations of the lines as shown as thus: $y_{CSTR} = 2.83x - 0.30 \; and \; y_{PFR} = 5.016x - 0.5142.$

4.9. Comparison of Reactor Diameter of the Continuous Reactors with Conversion

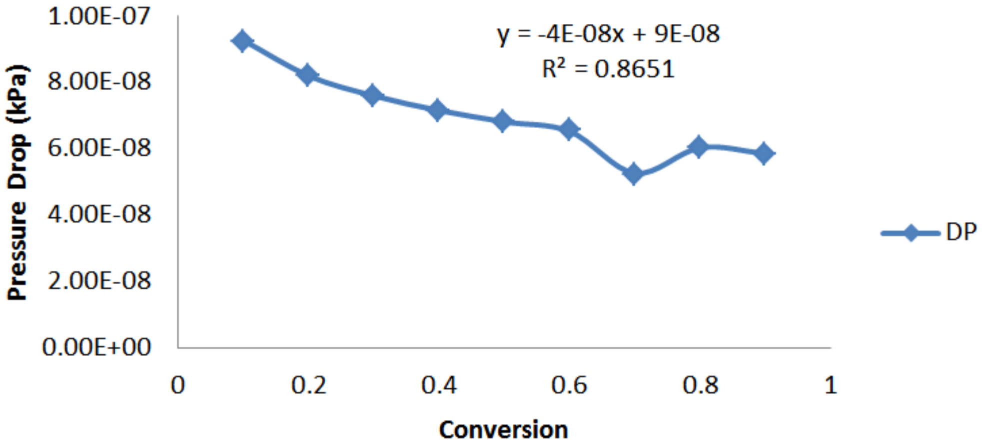

Figure-14. Variation of pressure drops of flow reactor versus conversion.

Figure 14 shows the variation of pressure drop with conversion. This parameter is only affected by packings along the tubular flow of the reactor, not continuous stirred tank reactor. The pressure drop variation is due to configuration of the plug flow reactor. The pressure drop decreases as fractional conversion increases.

5. CONCLUSION

From the study of the two reactors, production of formaldehyde is more achieved using a plug flow reactor. The models were derived from the fundamental principles of conservation of mass and energy balance; and kinetic optimum model for the determination of effectual yields for dehydrogenation and partial oxidation of methanol in the two reactors.

The results of optimal kinetic model yields Y_{opt} of CSTR 1 - reactor tank and Plug flow reactor PFR showed that the yields obtained for the two reactors are 69% and 87% and compare favorably with operational yields of the production process which stood at 78.5 and 80.1 percent. From the results PFR provide a better volume for the production of formaldehyde at 87% conversion. The cost of the reactors was also developed to obtain the results and MATLAB program was used to simulate the design models developed.

Nomenclature

V_R = Volume of reactor (m^3)
R = Radius of reactor (m)
L_R = Height of reactor (m)
π = Constant

$\rho = density\ of\ the\ flowing\ material, [kg/m^3]$

$D = Diameter\ of\ the\ PFR, [m]$

$L = Length\ of\ the\ PFR, [m]$

$\mu = main\ fluid\ viscosity\ [Ns/m^2]$\

$u = Mean\ superficial\ velocity, [m/s]$

$\Delta P = change\ or\ pressure\ drop\ per\ bars, [KP_a]$

D_R = Diameter of Reactor (m).
Q = Quantity of heat (J/k)

ΔH_R = Heat of reaction (KJ/mol)

F_{AO} = Flow Rate of Species (mol/s)

X_A = Fractional Conversion of Species

K_1 = Rate constant, S^{-1}

E_A = Activation energy, KJ/mol

K_{10} = Pre, exponential constant S^{-1}

R = Gas constant, KJ/mol K; T = temperature, k.

C_{AO} = Initial concentration, $mol/_{L}$

V_O=Total Volumetric Flow Rate of Reactants m^3/S

C_{AO}=Initial Concentration		mol/m^3
f_{AO}	Initial Molar Flow Rate	mol/m^3
P_O	Initial Pressure of Feed	N/m^2
T_O	Initial Temperature of Feed	K
R	Gas Constant	$Nmmol^{-1}K^{-1}$
A	Frequency Factor	S^{-1}
E	Activation Energy	Kj/mol
K_I	Rate Constant of Reaction	S^{-1}
r_A	Reaction Rate	$mol/m^3/s$
X_A	Fractional Conversion	Dimensionless
T_C	Coolant Temperature	K
C_P	Specific Heat Capacity	J/mol k
ΔC_P	Change in Specific Heat Capacity	J/mol k
ΔH_R	Change in Enthalpy of Reaction	J/mol

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