Research Paper   Open Access

Modeling Slurry Reactor Plug Flow For Catalytic Nitrobenzene Hydrogenation Process

WORDU, A. A& Chinah, J. E
Department Of Chemical, Petrochemical Engineering Rivers State University, Nkpolu, Oroworokwo, Port Harcourt, Nigeria
Corresponding Author: WORDU, A. A

ABSTRACT: *The research developed a typical 3-phase system kinetic rate laws for the gas-liquid-solid-phase for nitrobenzene hydrogenation process applying Material-component, Henry's law and SvanteAhrrenius functions to develop the non-linear rate model with respect to temperature and concentration f(T, C_i) for iterative process. The resistances of the gas, liquid and solid films mass transfer co-efficient for the process were coupled to give overall rate law which expresses the fundamental mole balance equation for the hydrogenation process, which couples with temperature model for evaluation. Model profiles plot exhibit trends typical of plug flow reactor configuration given in figures 1, 2, 3 and 4.*

Keywords: Three-phase-systems, mass transfer co-efficient, Henrys law, plug flow-Slurry-reactor, Arrhenius model, hydrogenation.

I. INTRODUCTION

The plug flow-slurry reactors are three-phase reactor which implies that reaction takes place in solid, liquid and gas simultaneously. They usually consist of catalyst solid suspended in a liquid-phase through which a gas is bubbled through [Fogler, 1998]; [Butt, 2000]; [Octave, 2007]. The catalytic hydrogenation of nitro-benzene to aniline in a slurry reactor is a complex chemical process involving the reduction of nitro-benzene with hydrogen over fixed catalyst [Rihani, Narayanan and Doraiswamy 1995].

The research focused on development of plug-flow-slurry reactor equations for hydrogenation of specialty chemicals such as aniline and biological systems. The principal difficulty in slurry bed operation is the efficient separation of catalyst, typically in the form of a fine particulate. Catalyst in a slurry reactor can be suspended by stirring or bubbling gas up through the liquid. Since the process conditions of the process, laws and /or principle governing the process are comprehensible enough; mathematical modeling depicting plug flow-slurry reactor is hereby presented. Principally, some literature data from batch-slurry reactor studies [Landert and Scubia, 1995], [Octave Levenspiel, 2007], [Torres, Sanchez, Dalmon, Bernauer, Lieto, 1994], [Rylander, 1967], [Rylander, 1973] were put to fruition.

II. MATERIALS

The fundamental materials research comprises of a plug flow reactor equation, balanced stoichiometric equation 1:3 hydrogenation process, thermodynamic equations, and literature data, physical and chemical data.

2.1 Mechanism and Process Chemistry

$$C_6H_5NO_2 + 3H_2 = C_6H_5NH_2 + 2H_2O \qquad (1)$$

Equation [1] is the chemical reaction between molecules of hydrogen and Nitrobenzene in the presence of a catalyst with a stoichiometric ratio of 1:3

2.2 Mechanism of process
Aniline is an important derivative of benzene that can be synthesized in two

Steps by nitration to nitrobenzene which in situ is catalytically hydrogenatedto aniline as product and two moles of waste water sent for treatment.

Synthetically, the nitration of benzene with mixed acids HNO_3/H_2SO_4 is an electrophilic aromatic substitution which involves the nitronium ion intermediate as the attacking species for the process. This synthetic route replaced the Fe-acid reduction process that is considered non-viableeconomically.

In this work, complete modeling of a catalytic plug flow-slurry reactor for a 3-phase model reaction figure 1 nitrobenzene hydrogenation is presented.
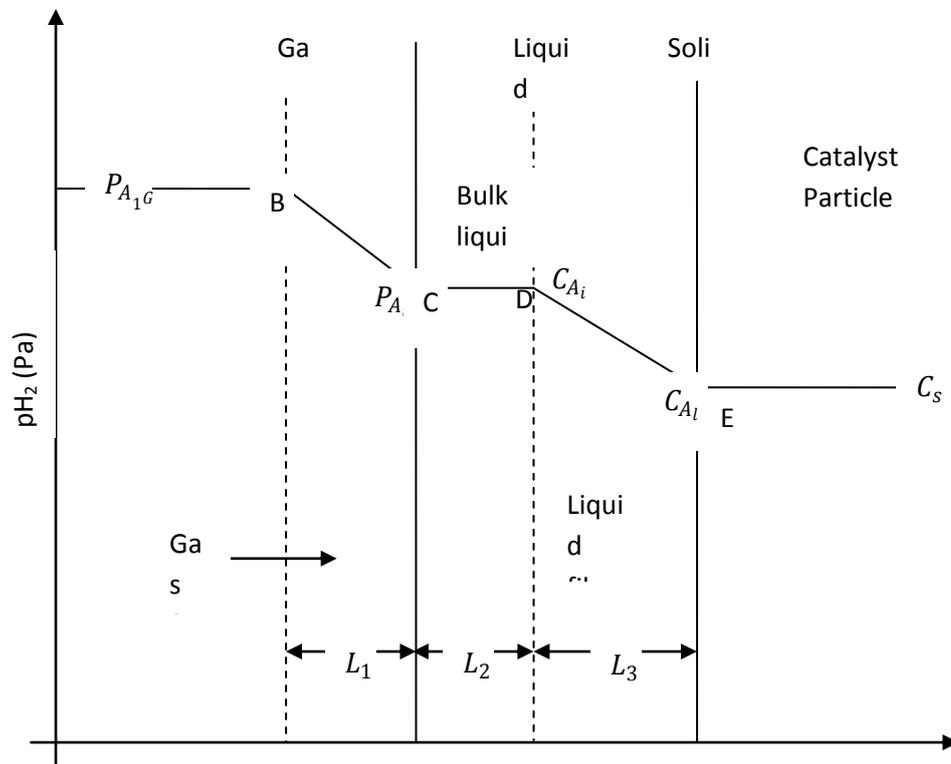

Figure1 Decreases in H_2 pressure during mass transfer in a slurry from a H_2 gas bubble through gas and liquid films bulk liquid and the liquid film surrounding the catalyst particle to a catalyst surface where H_2 reacts [Farrauto, 1997].

III. METHOD

3.1 Slurry Reactor Model Formulation

Figure 1 shows the reaction scheme of the reactor modeled as three-phase systems comprising gas, liquid and solid phase. While, maintaining the following assumptions for heterogeneous reactor models as stated below:

- Steady State process *[SSP]*
- Solids are perfectly mixed and of uniform size
- Catalyst decay lumped in the kinetic parameters determined
- Reactions occurs in the emulsion phase
- Axial diffusion i.e. transport by effective diffusion in the emulsion phase is negligible hence plug flow is assumed in the emulsion phase
- Since the gas is hydrogen and it diffuses rapidly through the gas film, the film resistance is negligible.

Hence, developing and /or writing the rate laws for the 3-phases in the kinetic scheme figure 1 gives equation (2), (3), and (4)

$$(-r_{Ag}) = K_G a_g (P_{AG} - P_{Ai}) \tag{2}$$

$$(-r_{AL}) = K_L a_L (C_{Ai} - C_{AL}) = \frac{K_L a_L}{H_A}(P_{AL} - P_{Ai}) \tag{3}$$

$$(-r_{Ag}) = K_s a_s (C_{As} - C_{Ai}) = \frac{K_s a_s}{H_A}(P_{As} - P_{Ai}) \tag{4}$$

The overall rate of reaction using Henry's law for mass transfer principle yields equation (5);

While, Henrys law is given by

$C_{H2} = P_{H2}/H_A$.

$$(-r_A)''' = \frac{P_{AG}}{\frac{1}{K_G^l a_g} + \frac{H_A}{K_L^l a_l} + \frac{H_A}{K_S^l a_s}} \tag{5}$$

Consequently, these phases mole balance of the species is stated in equation (6), (7) and (8), as follows:

$$(-r_g) = \frac{dN_{A_G}}{dt} = \frac{D_1}{RTL_1}(P_{AG} - P_{Ai}) = K_G a_g (P_{AG} - P_{A_i}) \tag{6}$$

$$(-r_L) = \frac{dN_{A_L}}{dt} = \frac{D_2}{L_2}(C_{A_i} - C_{A_l}) = K_L a_L (C_{A_i} - C_{A_L}) \tag{7}$$

$$(-r_s) = \frac{dN_{A_s}}{dt} = \frac{D_3}{L_3}(C_{A_L} - C_{A_S}) = K_S a_S (C_{A_L} - C_{A_S}) \tag{8}$$

Relating equations (6), (7), and (8) with Henry's law to get the Henry's constant of species A diffusing; the overall mass transfer coefficient is given as:

$$\frac{1}{K_G'} = \frac{1}{K_G} + \frac{H_A}{K_L} \tag{9a}$$

$$\frac{1}{K_L'} = \frac{1}{HK_G} + \frac{1}{K_L} \tag{9b}$$

$$\frac{1}{K_S'} = \frac{1}{K_L} + \frac{H}{K_S} \tag{9c}$$

Hence, overall rate of mass transfer for the hydrogenation process is derived as:

$$(-r_A''') = (-r_g) + (-r_l) + (-r_s) = \frac{P_{AG}}{H_A\left(\frac{1}{H_A K_G^l a_S} + \frac{1}{K_L^l a_L} + \frac{1}{K_S^l a_S}\right)} \tag{10}$$

Since, the plug flow-slurry reactor is operating at 125^0C (398K), a rate law obeying temperature effects and incorporating the three-phase mass transfers is proposed equation [11] [Torres, M; Sanchez, J; Dalmon, J. A; Bernauer, B; and Lieto, J, 1994]

$$\frac{d\alpha_A}{dz} = \frac{(1-\alpha_A)}{H_A\left(\frac{1}{H_A K_G^l a_S} + \frac{1}{K_L^l a_L} + \frac{1}{K_S^l a_S}\right)}\left(A_o exp^{\frac{-E}{RT}}\right) \tag{11}$$

3.2 ENERGY BALANCE
For 1 mole of feed entering the reactor, energy balance is given mathematically as,

$$\rho_A C_{P_A} A dz dT = -\rho_A C_{P_A} A v dt dT + (-\Delta H_r)(-r_A''') A dz dt - Q dt \tag{12}$$

Divide by $\rho_A C_{P_A} A dz dt$ yields;

$$\frac{dT}{dt} = -\frac{v dT}{dz} + (-\Delta H_r)(-r_A''') \tag{13}$$

Equation (3.43) can be rearranged to give

$$\frac{dT}{dt} + \frac{v dT}{dz} = (-\Delta H_r)(-r_A''') - \frac{q}{\rho_A C_{P_A}} \tag{14}$$

Since,

Adz =V and Q/Adz =q

Then, equation (14) is the model equation of energy balance of a slurry process occurring in a plug flow reactor, but reaction rate for the process is given by

$$(-r_A''') = \frac{y_{AO} P_T (1-\alpha_A)}{H_A \left(\frac{1}{H_A K_G' a_g} + \frac{1}{K_L' a_l} + \frac{1}{K_s' a_s} \right)} \tag{15}$$

At steady state process, mathematically,

$$\frac{\partial T}{\partial t} = 0 \tag{16}$$

Substituting equation (16) into (14) gives the proper energy balance equation (17) for the research.

$$v \frac{dT}{dz} = (-\Delta H_r)(-r_A''') - \frac{q}{\rho_A c_{PA}} \tag{17}$$

3.2 Solutions techniques

Equation models [11] and [17] were resolved numerically applying the right parametric controls for the research. And, correspondingly depicted in figures 1,2 3 and 4 as clear evidence of steady state plug flow- slurry reactor.

IV. DISCUSSIONS

Figures 1, 2, 3, and 4 predominantly exhibit typical trends for plug flow reactor studies from literatures. For a given reaction process in plug flow reactor arrangement the rate of reaction shows exponential pattern to a maximum and becomes steady at a point (dy_i/dz), which is the point at which the process gradually comes to an end.

The temperature also increases along the reactor length, giving rise to aniline product formation, because reaction rate is a function of temperature and concentration of the process. Also, the fractional conversion as depicted in figure 3 increases progressively to a maximum along the reactor length. The reactor size chosen for the study is relatively small and can be scaled up for large production of aniline which is major industrial chemical and high economic value.
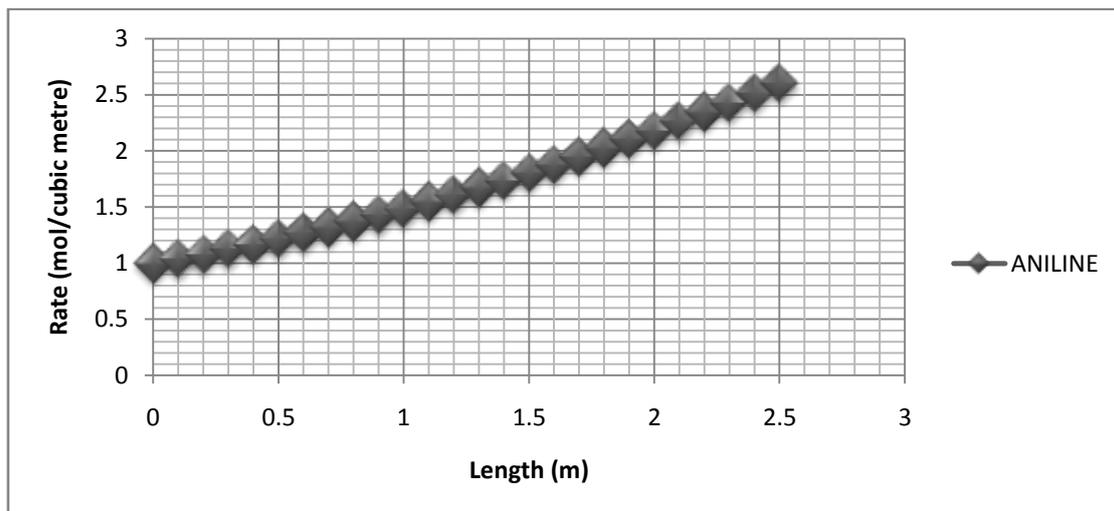

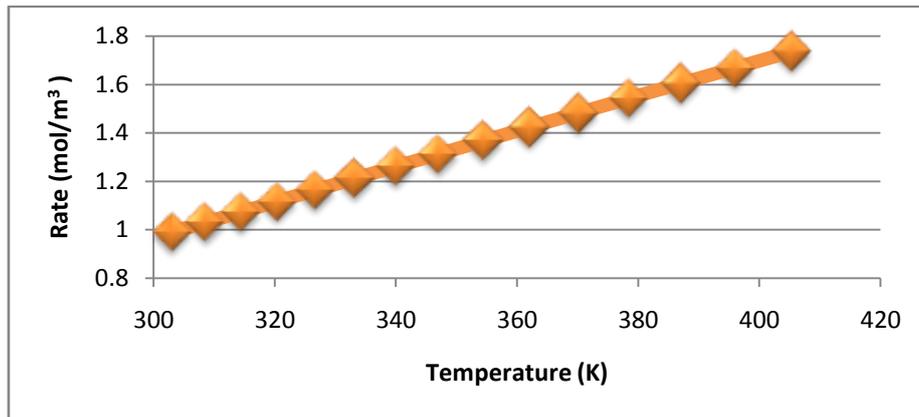**Figure 1** plot of rate against length of the reactor

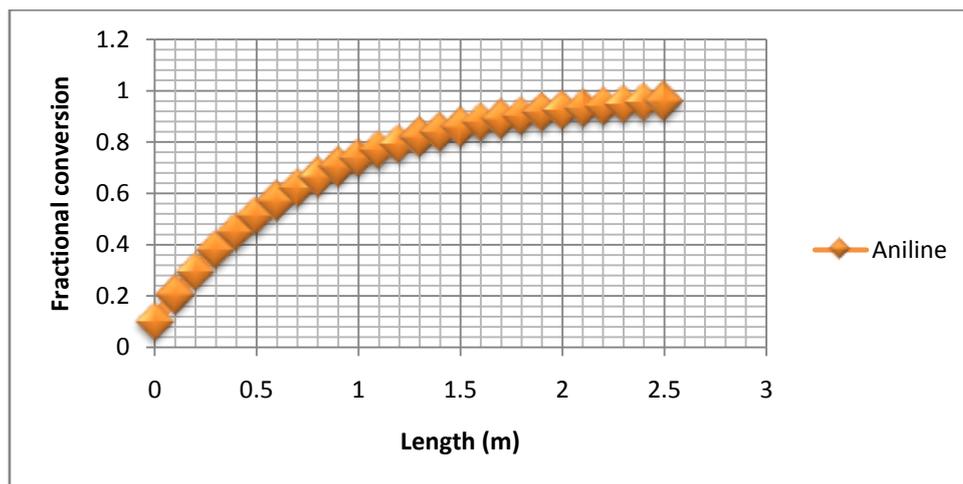**Figure 2** plot of rate against temperature

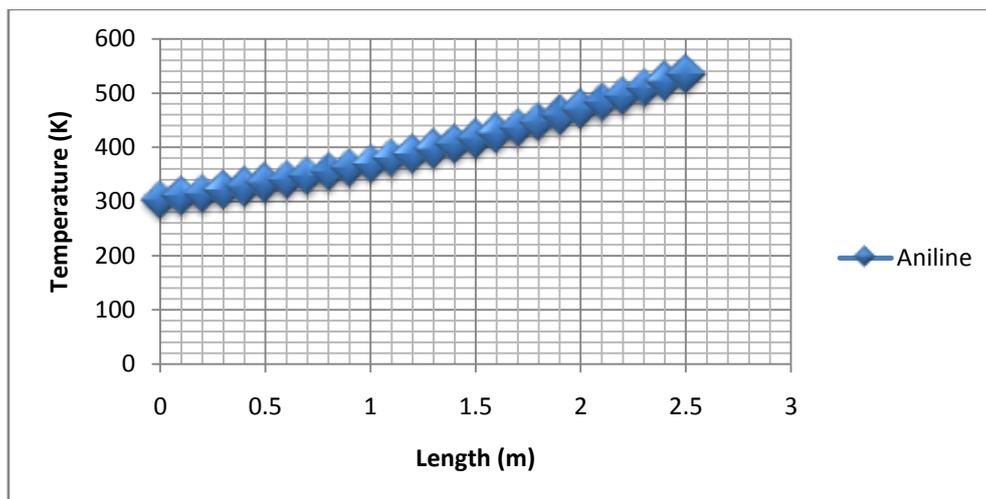**Figure 3** plot of fractional conversion against length of the reactor

Figure 4 plot of temperature against length of the reactor

V. CONCLUSION

The research utilizes the fundamental principles of material component and energy balance cum Henrys law approach to formulate the required steady state model and the 3-phase rate laws of gas, liquid and solid phases which explain the mass transfer resistance on the hydrogenation processes for simultaneous simulation of the reactor models.

NOMENCLATURE

$$D_1 \ = \ D_{AB} \ = Diffusivity \ of \ the \ gas \ phase$$

$$D_2 \ = \ D_{BC} \ = diffusivity \ of \ the \ liquid \ phase$$

$$K_G = \frac{D_{AB}}{RTL_1} = mass \ transfer \ coefficient \ of \ the \ gas$$

$$K_L = \frac{D_{BC}}{L_2} = mass \ transfer \ coefficient \ of the \ liquid$$

$$K_L \ is \ the \ mass \ transfer \ coefficient$$

LITERATURE CITED

[1]. Butt, J. B [2000]. Reaction Kinetics and Reactor Design. Second edition, Revised and Expanded. Marcel Dekker.
[2]. Fogler, H. Scott [1998]. Elements of chemical reaction engineering, fourth edition, PearsonInternational edition,
[3]. Torres, M; Sanchez, J; Dalmon, J.A; Bernauer, B; and Lieto, J [1994]. Modeling and Simulation of a Three-phase catalytic membrane reactor for nitrobenzene hydrogenation. Industrial and engineering chemistry research, 33. 2421-2425.
[4]. Octave Levenspiel,[2007]. Chemical reaction engineering, 3th edition, John Wiley & Sons (Asia).
[5]. Rylander, P. N, (1973). Catalytic hydrogenation in organic synthesis, Academic Press. NY