MODELING OF A SULFONATION REACTOR IN A DETERGENT FACTORY

Essam K. Halabia, Ahmed M. Al-Braficani, and Mohammed F. Abid
Al-Qaqa'a State Company

ABSTRACT

A mathematical model was developed of a sulfonation falling film reactor in the General Company for Vegetable Oils industry in Baghdad. This model will give the relationship between the various parts of the system and explain to the process engineer, the effects of the numerous system parameters on conversion and temperature distribution (axially and radially) through the liquid film along the reactor. The geometric and the process variables for the sulfonator are taken as input data in the calculation cycle of the model.

INTRODUCTION

The falling film reactor is commonly used to carry out fast and highly exothermic reactions between a reactive gas and a liquid, particularly when the liquid is fairly viscous.

Chlorination and sulfonation reactions have been carried out on a large scale using falling film reactors, The latter process is important in the manufacture of household and industrial detergents. In the falling film reactor, a liquid film of the organic reactant falls by gravity, completely wetting the solid wall of the column and contacting the concurrently flowing SO3 vapor which is diluted with an inert gas, generally air. The solid surface is refrigerated by externally circulating water. Due to the high surface to volume ratio of liquid in the column, efficient heat elimination takes place.

In the earlier development stages of sulfonation, batch reaction kettles were extensively used. From the history of such sulfonators it is known that there were maximum temperature restrictions during sulfonation. It was important to keep the organic liquid in the kettle under140-150 F during the sulfonation of dodecylbenzene [1].In these exper iments it was found that darkening became noticeable at 158-176 F. When a C12 alcohol was sulfnated, it was important to keep the temperature under 105 F in order to obtain acceptable product quality .

It therefore seems reasonable that the longitudinal and even radial temperature profiles in a thin film sulfonation reactor are significant variables which may have a substantial effect on the final product. The thermal history of organic liquid being sulfonated should have an effect on degradations side reactions, higher temperatures promoting more severe oxidation and charring of the material.

Johnson and Crynes[2] interpreted experimental results from a thin film SO3 -tridecylbenzene reactor in terms of a model with lumped concentration and temperature in the film cross-section. They assumed that the reaction rate is to be controlled by diffusion of SO3 to the interface and that the reaction occurred primarily at the interface without significant pentration of the reaction zone into the liquid film.By their model they could predict conversion as a function of reactor length and the axial temperature profiles for the interfacial and mean bulk gas temperature. The principal objections to their model are that no attempt was made to introduce realistic fluid mechanics to model the liquid film flow and the interfacial temperature was obtained by assuming a linear temperature profile in the film, and this assumption cannot be justified without solution of the energy equation.

Davis et al.[3] worked on the sulfonation of tridecylbenzene, and based their model on industrial data. They predicted the behavior of a falling film reactor using a two-dimensional, non-isothermal model with variable film thickness, and simplified the model by assuming the reaction to be instantanous. Their model predicts exit temperatures far better than the model of Johnson and Crynes[2]. Davis et al.[3] determined through the laminar microscopic balance equation, the heat transfer in liquid film and from this the temperatures of the process . They numerically solved this equation in integrated form to get a stable solution.

Gonzales et al.[4] formulated a model for a falling film sulfonation reactor . The model includes a turbulent diffusivity term for the liquid mass transfer, valid through the entire liquid film. They claimed that their model is applicable to a process in which any step,as liquid mass transfer, reaction rate or gas mass transfer, can affect the process rate. The mathematical model predicts conversions and interfacial temperatures as the most important variables for product yields and products quality . They constructed an experimental sulfonation of dodecylbenzene to verify their model , and the variance of the fit was 3.2 %.

It is the purpose of this paper to develop a mathematical model for the falling film sulfonation reactor which is in operation in AL-MAMOON FACTORY at the General Company for Vegetable Oils Industry. This model will give the relationship between the various parts of the system and explain to the process engineer, the effects of the numerous system parameters on conversion and temperature distributions in the reactor. Of particular interest is the prediction of the maximum temperature in the reactor and the factors which can be controlled to maintain the temperature at desirable level. The geometric and the process variables for the sulfonator are taken as input data in the calculation cycle of the model.

The Mathematical Model

Consider the falling film flow system shown in Fig.1. The mathematical model will consist of differential balance equations in the liquid phase with their corresponding boundary conditions. Through these equations, velocity, concentration and temperature profiles are obtained. The equations are for steady state operation,common in industrial and laboratory reactors.

The column is divided into N number of annular segments ,so we have N number of equations for the liquid reactant with the same number of equations for the dissolved gas.

To formulate a comprehensive model, it must include the effects of hydrodynamics, mass transfer, kinetics, and heat transfer.

Principal Assumptions. The liquid phase was modelled under the following assumptions: (i) The overall liquid-phase reaction between dissolved SO3 and Alkylbenzene is second order , first order in SO3 and first order in Alkylbenzene [4] . (ii) Liquid reactant and liquid product are assumed to be nonvolatile at working Temperature. (iii) The film thickness is small compared to the column radius. (iv) The liquid film is symmetric with respect to the reactor axis. (v) The liquid phase flows in a laminar flow, and the gas phase flows cocurrently in a turbulent flow. (vi) The solubility of the reactant gas in the liquid reactant is ideal according to Raoults law .

Hydrodynamics. The liquid shear and velocity profiles are obtained from Navier Stockes equation, which for steady one dimensional flow and constant axial pressure gradient reduces to:

$$\frac{d^2U_y}{dx^2} = -\frac{\phi}{\mu_L} \tag{1}$$

where , $\phi = \rho_{Lg} - \frac{\partial P}{\partial y}$

The gas phase exerts an interfacial shear Ri on the liquid film , and the velocity vanishes at the solid boundary, so we can write the boundary conditions as :

$$\left.\begin{aligned} &\text{On } x=\delta\ , \quad \frac{dU_y}{dx} = \frac{R_i}{\mu_L} \\ &\text{On } x=0\ , \quad U_y = 0 \end{aligned}\right\} \tag{2}$$

Integrating equation (1) twice, and applying boundary conditions, to obtain:

$$U_y = \frac{\phi x^2}{2\mu_L} + \left(\frac{R_i}{\mu_L} + \frac{\phi\delta}{\mu_L}\right)x \tag{3}$$

Equation (3) describes the velocity profile in the liquid film, and the equation which describes the shear profile through the liquid film is:

$$R = \phi(\delta - x) + R_i \qquad (4)$$

where, $R_i = f_i \rho_G U_G^2$, as interpreted by Hanratty and Engen[5] and by Cohen and Hanratty[6].

The film thickness is obtained from the volumetric flow rate per unit length of wetted perimeter, (QL) which is related to the velocity distribution by :

$$Q_L = \int_0^\delta U_y(x).dx \qquad (5)$$

$$Q_L = \frac{R_i \delta^2}{2\mu_L} + \frac{\phi \delta^3}{3\mu_L} \qquad (6)$$

Equation (6) is acubic equation in (δ) which is readily solved by means of $Q_L, R_i, \phi,$, and μ_L Interfacial friction factor (fi), due to turbulent flow of the gas,is evaluated using Blasius equation [12].

$$f_i = 0.04 R_{eG}^{-0.25} \qquad (7)$$

Mass Transfer. For mass transfer, the general case will be considered, for which the gasous solute diffuses in the liquid film and then reaction occured, so the process of diffusion and chemical reaction can still be represented by an extension of the film theory by a method due to Hatta [7]. There is thus a zone of reaction between solute A and liquid reactant B,which moves away from the gas-liquid interface taking up some position towards the bulk of the liquid. The final position of this reaction zone will be such that the rate of diffusion of A from the gas-liquid interface is equal the rate of diffusion of B from the main body of the liquid.

According to Fig.2, for any element of the liquid of dimensions $(\delta_x * \delta_y * 1)$ to be in equilibirum, the amount of A carried in the y direction by bulk flow, plus the amount of diffusing in x direction, must be sufficient to supply the chemical reaction proceeding within the element. Expressing this fact symbolically :

Input rate - Output rate+Consumption rate = 0

$$U_y.\frac{\partial C_A}{\partial y} = \frac{\partial}{\partial x}\left(D_A.\frac{\partial C_A}{\partial x}\right) + r_A \qquad (8)$$

Similarly for liquid reactant B, the differential balance equation is :

$$U_y.\frac{\partial C_B}{\partial y} = \frac{\partial}{\partial x}\left(D_B.\frac{\partial C_B}{\partial x}\right) + r_B \qquad (9)$$

The boundary conditions required to integrate equations (8) and (9) are:

(a) On $X = 0$; $\frac{\partial C_B}{\partial x} = 0$, $\frac{\partial C_A}{\partial x} = 0$

(b) On $X = \delta$; $\frac{\partial C_B}{\partial x} = 0$, $N_A = K_G\left(C_A - C_A^{IG}\right)$

(c) On $Y = 0$; $C_B = C_B^0$, $C_A = 0$

The condition (a) indicates that the components can not pass the solid wall of the tube. The condition (b) indicates that B is not volatile (assumption no.ii) and it can not cross the interface and that A crosses the interface at a rate depending on mass transfer coff. Of A.

Mann and Moyes[8] suggested the use of a theoretical ideal solubility which determined from an application of Raults law at the interface as follows :

$$C_A^{IG} = \frac{\text{vapor pressure of solute}}{\text{total system pressure}}.C_A^{IL} \qquad (10)$$

Mann and Moyes[8] introduced a set of curves showing an exponential relation between saturation solubility of SO3 in dodcylbenzene and interface temperature.Each curve was for certain mole fraction of SO3 in the gas phase .

$$C_A^{IL} = Ze^{-G(T_S - T_r)} \qquad (11)$$

where Z , G are constants depend on mole fraction of So3 in gas phase and evaluated by curve fitting method.

Vapor pressure of So3 is related to interface temperature by Antion equation [9] Gas side mass transfer coefficient is estimated using McReady and Hanratty equation [10].

$$K_G = P.U^*.(Sc_G)^{-0.070} \tag{12}$$

where P is a correction term determined by correlation with experimental results. Using the definition of Siu-Ming Yih et al.[11] for friction velocity, equation(12) can be written as:

$$K_G = P.\sqrt{f_i}.U_G.(Sc_G)^{-0.070} \tag{13}$$

Heat Transfer. Referring to Fig.2, apply a heat balance through a liquid element of dimensions $(\delta_x * \delta_y * 1)$ to obtain : Heat input (by convection+by conduction) - Heat Output (by convection+by conduction) +Heat generated = 0

$$U_y.\frac{\partial}{\partial y}(\rho_L C_{PL} T) = -\frac{\partial}{\partial x}\left(-K_L.\frac{\partial T}{\partial x}\right) - \Delta H_R.r_A \tag{14}$$

The boundary conditions required to integrate equation (14) are as follows :

(a) On x=0; $-K_L \frac{\partial T}{\partial x} = U_L.(T_{X=0} - T_R)$

(b) On x= δ ; $-K_L \frac{\partial T}{\partial x} = h_G.(T_G - T_{X=\delta})$

(c) On y=0 : $T = T^0$

Condition (a) relates the temperature of the liquid film to the temperatures of the refrigeration water. Condition (b) is the heat transfer from the liquid to the gas.

Gas-side heat transfer coefficient is determined using the statement of Bird et al.[12] who stated that the solutions of many mass transfer problems at low mass transfer rate can be obtained by analogy with corresponding problems in heat transfer. Based on this principle Mcready and Hanratty[10] introduced an equation for the gas-side heat transfer coefficient :

$$h_G = P\sqrt{f_i}.U_G.(P_{rG})^{-0.0704}.\rho_G.C_{PG} \tag{15}$$

Heat transfer coefficient (h) for heat transfer from liquid film to cooling water is calculated using the empirical correlation of Davis and David[13]. Johnson and Crynes[2] stated that this equation correlates purely convective heat transfer within an average absolute error of 6-17% over a wide range of tube sizes, flow rates, pressures, and heat fluxes. The equation is based on steam-water and air-water data and generally corresponds to the annular or mist-annular flow conditions :

$$h_L = \frac{K_L}{d}.(0.06)\left(\frac{\rho_L}{\rho_G}\right)^{0.28}.\left(\frac{d.G_t.X}{\mu_L}\right)^{0.87}.\left(\frac{Cp\mu}{K}\right)_L^{0.4} \tag{16}$$

Overall heat transfer coefficient between cooling water and liquid film based on inside area of tube wall , is estimated using the general formula :

$$\frac{1}{U_L} = \frac{1.A_i}{h_W.A_0} + \frac{1.A_i}{h_m.A_v} + \frac{1}{h_L} \tag{17}$$

Reaction Rate. The reaction of SO3 (i.e, A component) with Alkylbenzene (i.e, B component) in liquid phase is an elementry second order. The rate expression is expressed by:

$$-r_A = K.C_A.C_B \tag{18}$$

Nielsen and Villadsen[14] expressed the behavior of the reaction rate constant by Arrhenaous equation :

$$K = K_0.\exp\left[-\frac{E}{R_g}\left(\frac{1}{T} - \frac{1}{T_r}\right)\right] \tag{19}$$

Solution of the Mathematical Model

Equations (8), (9), and (14) are two dimensional second order partial differential equations which include : C =f(x,y), C=g(x,y), and T=s(x,y), where f, g, and s are functions of two independent variables (i.e, x and y) through the liquid film. The above equations cannot be solved analytically, so this is done numerically.

A comperhensive mass and energy balance is performed on the first annular section and on the outputs . These calculations are used as inputs for the second segment. Mass and energy balances are then per formed on the second segment and so on down the reactor. Velocity profiles, film thickness, and physical properties of the materials are estimated for the first segment before applying the balances, but are adjusted for the next segment according to the output temperatures and mass flow rates from each previous segment. This method of calculation allows the determination of concentrations and temperatures in the liquid film for the entire length of the reactor.

In order to obtain velocity profiles through equation (3), the shear stress at the gas-liquid interface (Ri), has to be determined. This value is related to the friction factor, fi, and the value of (fi) can be determined by means of equation (7). The film thickness, , is calculated through equation (6) by iteration .

Concentration profiles are obtained by means of the implicit finitedifference multigrid method developed by Wesseling[15]. This method implies the resolution of N equations (N being number of the annular segments) for SO3 component and another system with the same number of equations for the Alkylbenzene component. The systems are solved by matrix calculs .

Base Case and Different Operating Conditions

The geometric and operating conditions for the falling film reactor in the sulfonation unit of Al-Mamoon Factory are as shown in Table 1.

Table 1. Dimensions and Operating Conditions of Sulfonator/AL-MAMOON FACTORY

1.Reactor Dimensions :
  Number of tubes= 37
  Inside diameter of tube=25 mm
  Wall thickness = 1.5 mm
  Reactor length = 6000 mm
2.Flow Rates :
  Production rate= 1500 kg/hr of 100% active matter.
  Mole fraction of SO3-air mixture= 0.07
3.Temperatures :
  SO3/air inlet temperature = 50-55 0C
  Organic inlet temperature = 30-40 0C
  Product outlet temperature = 45-55 0C
  Cooling water inlet temperature=25-30 0C
4.Reactor Pressure :
  1.2 bar abs.
5.Physical and Chemical Properties of Materials :
  From literatures.

To use the model as a tool for selection of the best operating condition which give the maximum yield of acceptable product specifications, many assumed conditions are tabulated in Table 2, as input data to the model and examples of outputs are shown for Runs 4,5, and 6. Run 5 represents the operating conditions of the sulfonator in AL-MAMOON FACTORY.

Tale (2) Different Plant Operating Conditions

Run no.	CSO 3GO	QGX 100	QLX 1000 0	Y1	TO	TG	TR
1	2.718	1.1	1.35	0.06	318	323	305
2	3.2	1.114	1.35	0.07	318	323	305
3	3.61	1.126	1.35	0.08	318	323	305
4	2.71	1.299	1.35	0.06	318	323	305
5	3.2	1.114	1.35	0.07	318	323	305
6	3.61	0.975	1.35	0.08	318	323	305
7	3.2	1.114	1.366	0.07	318	323	305
8	3.2	1.114	1.3	0.07	318	323	305
9	3.2	1.114	1.24	0.07	318	323	305
10	2.71	1.299	1.35	0.06	318	323	300
11	3.2	1.114	1.35	0.07	318	323	300
12	3.61	0.975	1.35	0.08	318	323	300
13	3.2	1.114	1.35	0.07	318	310	305
14	2.71	1.299	1.35	0.06	318	310	305
15	3.61	0.975	1.35	0.08	318	310	305
16	3.2	1.114	1.35	0.07	318	310	305
17	2.71	1.299	1.35	0.06	328	323	305
18	3.61	0.975	1.35	0.08	328	323	305
19	3.2	1.114	1.35	0.07	318	323	293
20	3.2	1.114	1.35	0.07	308	323	305
21	3.2	1.114	1.35	0.07	318	323	305

RESULTS AND DISCUSSION

The results of the mathematical model which were applied on the conditions of the base case (i.e, Run 5) can be graphically seen in Figures 3 - 10.

In Figures (3) and (4), the effect of SO3 composition in the gas phase on conversion and on gas-liquid interfacial temperature is shown respectively. The model predicts a better SO3 conversion (i.e, 0.9545) with a lower interfacial temperature (i.e, Ts=385K) when the mol %SO3 in gas=6%. While increasing the mol percent of SO3 in the gas, results in increasing interfacial temperature and this will promote corrosion in tubes and affects badly the quality of sulfonic acids (i.e, products charring).

To explain this behavior, it is of importance to note that when SO3 mol fraction is decreased, the increase in gas flow rate causes a thinning of the film and a decrease in the liquid-phase resistance to mass transfer. However, this thinning is not enough to explain the increase in conversion. Our model takes into account the influence of the gas shear stress on the liquid mass transfer resistance. This shear induces turbulence in the liquid phase, decreasing its resistance to mass transfer.

Figures (5) and (6) show that the inlet gas temperature is proportional to both SO3 conversion and interfacial temperature, so an optimization should be carried out to compensate these effects, since a higher gas-liquid interfacial temperature is not desirable while the goal is to increase conversion to obtain a higher product quality .

The different operating conditions of Runs (5,14, and 21) are used as input data to the model, which predicts the following results :

Run no.	Gass Temp.K	Interface Temp.K	SO_3 conversion
5	323	394	0.9459
14	310	378	0.928
21	333	406	0.958

From the results above an optimum inlet gas temperature (= 323) is suggested to use.

Figure (7) showed the prediction of the model to Alkyl benzene radial concentration profile at the entrance of the reactor, and Figure (8) showed the radial temperature profile. Both figures indicate that sulfonation reaction is fast and occurred almost at the layer adjacent to the gas-liquid interface. Figure (9) indicates that thickness of the liquid film is proportional to the formation of the viscous sulfonic acid in liquid phase.

Figure (10) indicates that velocity profiles of the liquid film are inversely proportional to the rate formation of the viscous sulphonic acid phase .

CONCLUSIONS

a) The effect of change in the air flow rate is shown in Figures (3) and (4) increasing the air flow rate decreases the peak liquid temperature. An increased non reactive gas flow has three principal effects :

1. The reaction rate is reduced due to a decrease in SO3 concentration in the gas stream. The decrease in the driving force for mass transfer is greater than the increase in the mass transfer coefficient associated with the higher gas Reynolds number.
2. The liquid film is thinned, thereby increasing the rate of heat transfer to the wall.
3. The gas phase serves as a thermal sink, and the thermal capacity of the gas phase is increased by increasing the flow of unreactive gas.

There is a limit to the advantages of increasing the gas flow rate, for a higher gas flow rate large amplitude waves occur at the interface and the wave crests can break off, leading to entrainment of droplets in the gas core. Once droplets are entrained the heat of reaction is not readily transferred from the droplets and undesirable charring and by-product formation can occur.

b) A Change in the liquid flow rate requires a change in SO3 flow rate if the stoichometric ratio is to be maintained constant. The greater the liquid flow rate increases the film thickness, which increases interfacial temperature, and the increased SO3 concentration in the gas stream increases the mass transfer rate and related rate of chemical reaction, thereby increasing the interfacial heat generation. The result is that an increase in liquid throughput increases the peak temperature of the liquid film. Thus anything that enhances transport of heat through the liquid film will reduce the peak interfacial temperature .

c) Since peak temperature occures within a short distance from the inlet, it is desirable to promote turbulence in that region to improve heat transfer to the cooled wall. An altrnate method of reducing the peak temperature would be to reduce the mass transfer to the liquid film either by dilution of the reactant gas or by redistribution of it by suitable means. It is unlikely that turbulence promotors will have much effect in the downstram part of the falling film reactor because of the substantial increase in viscosity that occures as sulfonic acid forms.

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NOMENCLATURE

Ai = inside wall area of the tube, m2

Ao = outside wall area of the tube, m2

Av = average wall area of the tube, m2

C = concentration, mol / m3

CSO3go = initial concentration of SO3 in gas phase, mol /m3

Cp = heat capacity, J /kg. K

D = diffusivity, m2 /sec

E = activation energy. J /mol SO3

f = friction factor, dimensionless

g = gravitational accelaration, m /sec2

H = heat of reaction, J /mol SO3

hw = cooling water heat transfer coefficient, J / m2 .sec.K

hm = heat transfer coefficient for tube wall, J / m2 .sec.K

k = reaction rate constant, m3 /mol.sec

k = liquid thermal conductivity, J /m.sec.K

ko = reaction rate constant at reference temperature, m3 /mol.sec

P = system pressure, N / m2

Q = volumetric flow rate, m3 /sec

r = rate of reaction, mol /sec

T = liquid film temperature, K

Tr = reference temperature (= 298K)

Ts = gas-liquid interface temperature, K

u = velocity, m /sec

u* = friction velocity, m /sec

U = overall heat transfer coefficient, J / m2 .sec.K

x = radial coordinate, m

y = axial coordinate, m

Dimensionless groups

Pr = Prandtle number

Re = Reynolds number

Sc = Schmidt number

Subscripts and Superscripts

A = solute (i.e, SO3)

B = liquid reactant

G = gas phase

i = interface

IG = at gas interface

IL = at liquid interface

o = initial

Greek Symbols

μ Viscosity
ρ Density, kg/m^3
δ Film thickness, m

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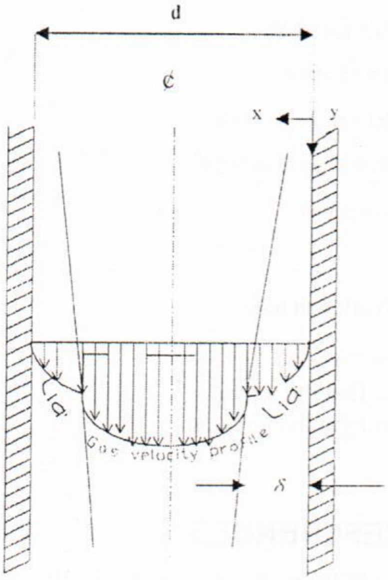

Fig. (1) The falling film reactor

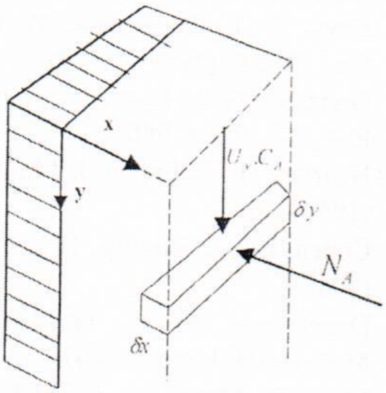

Fig. (2) Mathematical analysis of a falling film

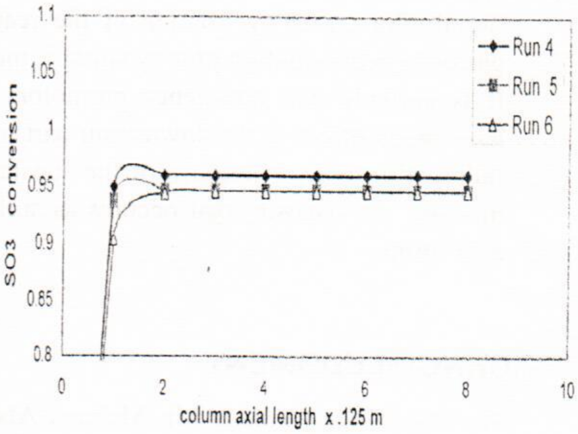

Fig. (3) Effect of gas composition on SO_3 conversion

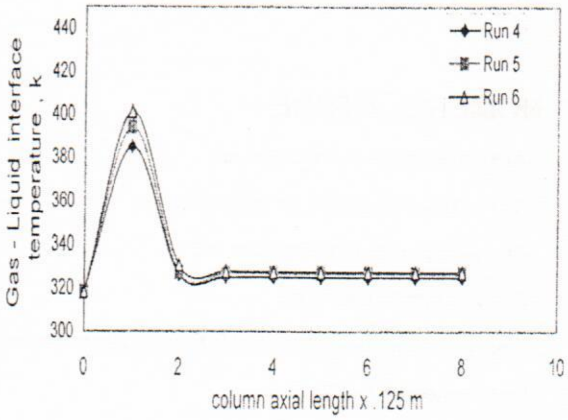

Fig. (4) Effect of SO_3 content in gas on interfacial temperature

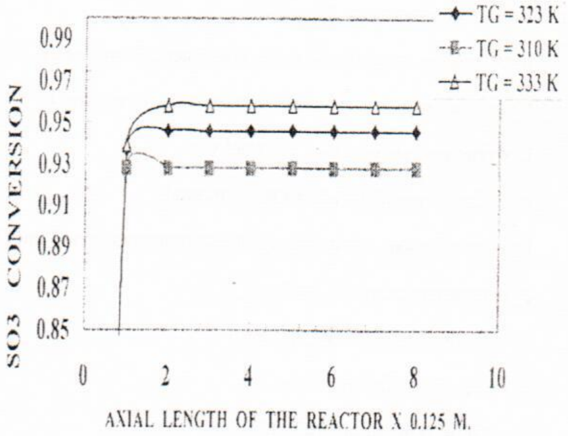

Fig. (5) Effect of inlet gas temperature on SO_3 conversion

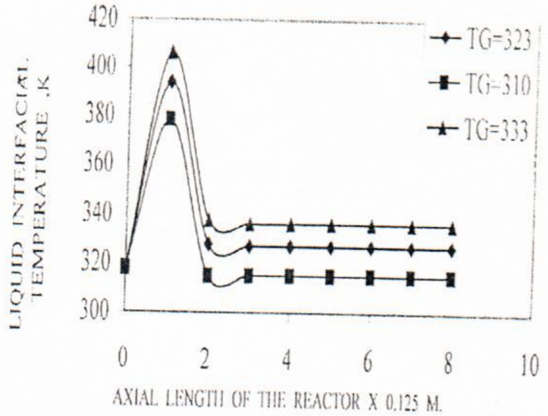

Fig. (6) Effect of inlet gas temperature on gas-liquid interface temperature

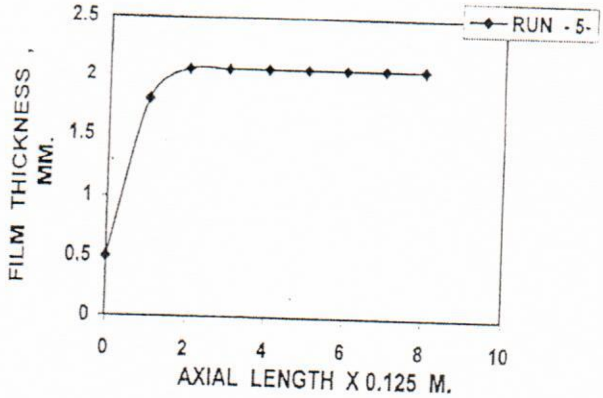

Fig. (9) Film thickness along the length of the reactor

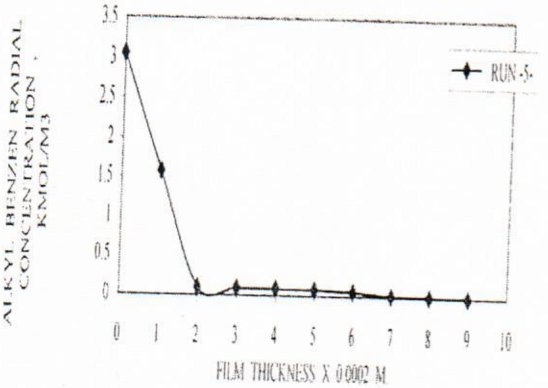

Fig. (7) Alkayl benzene radial concentration profile at entrance zone of the reactor

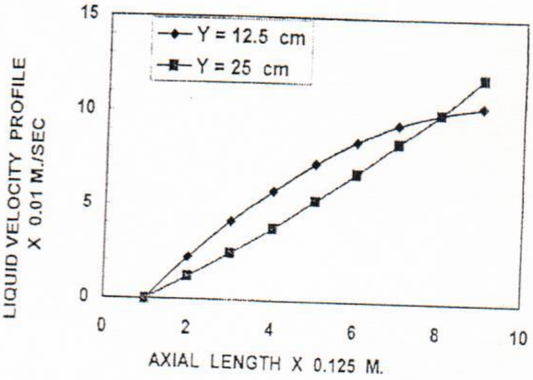

Fig. (10) Radial velocity profiles at different distances from the top of the reactor

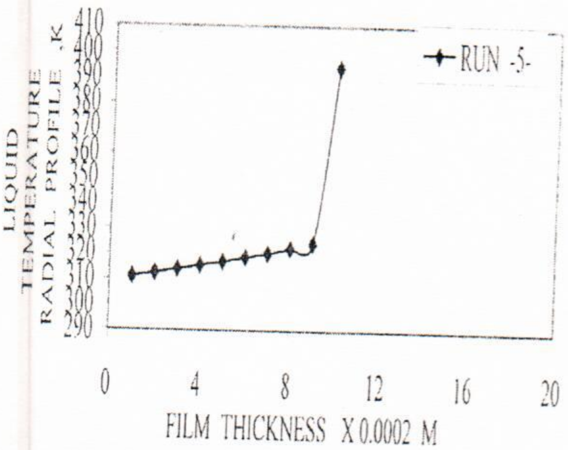

Fig. (8) Liquid temperature radial profile at (Y=12.5 cm) from the top of the reactor