

Enhancement Factor Simulation of H₂S Absorption by Fe₂(SO₄)₃ Aqueous

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Abstract- The study aims to compute the enhancement factor (E) of the absorption of H₂S by aqueous Fe₂(SO₄)₃ solution with second order irreversible chemical reaction at isothermal condition. The study was conducted theoretically simulation program. The value of E was computed based on the derivation of the basic equation of film model absorption, and then the non linear film theory equations are solved numerically using orthogonal collocation method under MATLAB program.

Mass transfer film thickness is assumed to be equal. The value of E Independent various parameters such as dimensionless Hatta Number, concentration of solvent, and liquid flow rate was studied.

The value of Hatta Number was varied for fast reaction regime. However, under fast reaction regime, increasing these parameters will increase the value of Enhancement factor. This means that the absorption phenomena is more controlled by reaction and diffusion process rather than gas solubility.

Keywords: gas absorption, modeling, enhancement factor

I. INTRODUCTION

Hydrogen sulfide is being produced by many industrial activities such as petroleum refining, natural gas and petrochemical plants, viscose rayon manufacturing craft, pulp manufacturing, food processing, aerobic and anaerobic wastewater treatments and many other industries [1]. Sour gas contains hydrogen sulfide gas and ammonia. The existence of hydrogen sulfide in sour gas is very disturbing, besides it smells bad, on combustion it will evolve (SO₂) gas which pollutes environment, in global, it will cause acid rain. So that, it needs to be eliminated from sour gas.

For well-known reasons, the reactive absorption of a gas in liquid is normally preferred over physical absorption A.L. Kohl et al. [2]. In the reactive absorption of a gas in a liquid, the contribution of the chemical reaction to the enhancement of the mass transfer rate is traditionally quantified by a term called enhancement factor (E). This parameter needs to be quantified accurately for a good design of the gas-liquid contactor.

In gas absorption in which gas-liquid mass transfer is accompanied by a chemical reaction in the liquid phase the gas absorption rate may be enhanced significantly. Generally, the chemical reaction enhances the rate of absorption because it depletes the diffusing in the region of the interface producing a steeper concentration gradient, for describing this effect the enhancement factor concept is applied, in which the enhancement factor, E, is defined as: the ratio of the specific rate of gas absorption in a reactive liquid to the specific rate of absorption under identical conditions in a non-reactive liquid (physical mass transfer). Due to the importance of this enhancement factor for design purposes, several theoretical models have been developed to calculate this effect.

While a large number of mass transfer models is available in literature to describe the absorption process in gas-liquid systems with a well-defined liquid bulk K.R. Westerterp et al. [2], only three mass transfer models based on the film, penetration and surface renewal theories respectively are widely used to predict the contribution of the chemical reaction in enhancing the mass transfer rate (enhancement factor). Although for a wide range of operating conditions, the film model gives similar enhancement factors as those of the other two models, it is physically unrealistic and should therefore only be chosen because of its ease of use.

The penetration and surface renewal models involve unsteady-state diffusion with chemical reaction. As analytical solutions for the above mass transfer models are available for only certain asymptotic conditions, numerical solutions are generally required. Numerical solution of the mass transfer models is usually laborious and complex, necessitating the development of approximate solutions for calculating the enhancement factors based on one of the above mentioned mass transfer models. D.W.van Krevelen et al [2] developed an approximate solution for the enhancement factor based on the film theory. Yeramian et al. [2], Hikita and Asai [2] proposed approximate solutions based on Higbie's penetration theory. Onda et al. [2] and DeCoursey [2] have provided approximate solutions based on Danckwert's surface renewal theory. It should be noted that the above-cited references for the approximate solutions to various mass transfer theories are only indicative, as considerably more information is available in literature. Generally, the film model is regarded as the most simplified one, therefore, physically most unrealistic model.

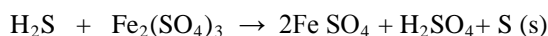
To solve a full numerical scheme using the above theories a number of mass balance are needed to describe the system. These are typically formulated as non-linear partial differential equations. Even with the current technological advances, solving a full numerical scheme is still computationally heavy. One way to reduce the complexity of a mass transfer model is to introduce the

enhancement factor, which is defined as the ratio of mass transfer from chemical absorption compared to physical absorption. It is therefore a relative factor which indicates the improvements of a reactive solvent compared to a physical non-reactive solvent. The enhancement factor is preferred in process simulations since it reduces the computational load. Several enhancement factor approximations were developed during the last century. One of the pioneering works is the simplified approach introduced by van Krevelen and Hofstijzer (1948). It describes the mass transfer rate of a reactive system in the pseudo-first order regime. It describes the mass transfer rate of a reactive system in the pseudo-first order regime. Later, an algebraic method for a second-order reversible reaction was presented by Onda et al. (1970). Since then, various approximate models were derived for well-defined reaction regimes and reaction kinetics [3]

A Hatta number \sqrt{M} and the instantaneous enhancement factor E_i are used in the calculations. The Hatta number is a relative parameter which compares the rate of reaction in a liquid film to the rate of diffusion. Thus a large Hatta value implies a much higher reaction rate compared to diffusion. Hence the reaction takes place mostly in the film. The instantaneous enhancement factor shows the intensification of a transfer phenomenon by an instantaneous and irreversible reaction. It corresponds to the asymptotic maximum limit of mass transfer enhancement. The approximate film model adjusts the instantaneous enhancement factor of the film to account for diffusivity differences of the species in the liquid film. It was concluded that the approximate film theory developed by Han and Rochelle (1982) compares well to the surface renewal model and it is also equivalent to the penetration theory. The traditional two-film model on the other hand differs to the surface renewal model especially at high Hatta numbers and large differences in diffusivity [3]

It is clear from the previous work on gas absorption with chemical reaction that the literature on isothermal gas absorption with irreversible chemical reaction is still inadequate. And the aim of present study is to analyze the absorption of gas accompanied by irreversible reaction in isothermal condition.

In this study, the chemical absorption of hydrogen sulfide into aqueous ferric sulfate has been studied on a sieve trays column has not done yet. In this process an aqueous $Fe_2(SO_4)_3$ solution is used as an absorbent. H_2S is absorbed and oxidized to elemental sulfur [4]. At the same time, Fe^{3+} is reduced to Fe^{2+} according to



II. MATERIALS AND METHODS

This study was carried out by developing mathematical model and simulation program to estimate enhancement factor for gas absorption accompanied by irreversible chemical reaction in isothermal condition based on film mass transfer model. (See Fig.1).

Several models have been proposed to describe these phenomena. Attention will be focussed only on the simple two-film model. In the two-film model (Fig. 1) a stagnant film is assumed at both sides of the interface and all resistance to mass transport is localized in these two films. This means that concentration gradients will only develop in these films [5]. It is further assumed that no resistance to transport occurs at the interface itself, so that the interface concentration of the gaseous component in the solution is related to the interfacial partial pressure by Henry's law:

$$p_{Ai} = H C_{Ai}$$

(1)

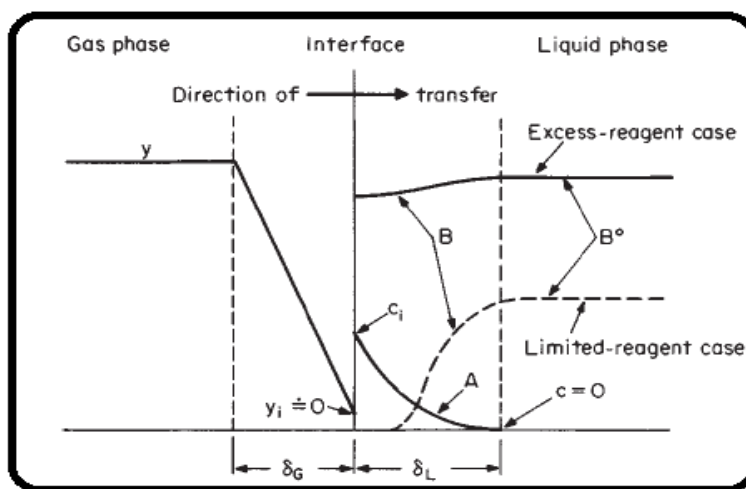
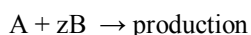


Figure. 1: Gas phase and liquid phase solute concentration profiles for second-order reaction

If a reaction



(2)

is carried out, the following continuity equations in the liquid film for both reactants hold :

$$D_A \frac{d^2 C_A}{dx^2} = r \qquad r = k C_A^n C_B^n \qquad (3)$$

$$D_B \frac{d^2 C_B}{dx^2} = zr$$

with boundary conditions

$$(4) \quad C_A = C_{Ai} \quad \text{and} \quad dC_B/dy = 0 \quad \text{at} \quad x = 0$$

$$C_A = 0 \quad \text{and} \quad C_B = C_{Bo} \quad \text{at} \quad x = \delta$$

For not too rapid reactions, the depletion will be moderate and the B profile will remain rather flat. With increasing rate, the depletion will become more severe and pronounced B profiles will develop. The limiting case of the instantaneous regime is reached when B becomes fully depleted at the interface[5]. The set of equations for a second order reaction with z=1 reads:

$$D_A \frac{d^2 C_A}{dx^2} = k C_A C_B \qquad (5)$$

$$D_B \frac{d^2 C_B}{dx^2} = k C_A C_B$$

and appropriate boundary conditions as given in relations (4). There is no analytical solution for Eqs (5), and a rigorous analytic expression for the enhancement factor cannot be given. However the enhancement factor can be obtained from numerical integration of the set of Eqs. (5). This is facilitated by reshaping these equations into dimensionless form. Introducing the dimensionless variables

$$A = \frac{C_A}{C_{Ai}} \qquad B = \frac{C_B}{C_{Bo}} \qquad X = \frac{x}{\delta} = \frac{k_1 x}{D_A}$$

$$dA = \frac{dC_A}{C_{Ai}} \qquad dB = \frac{dC_B}{C_{Bo}} \qquad dX = \frac{dx}{\delta} = \frac{k_1 dx}{D_A} \qquad (6)$$

$$M = \frac{k_2 C_{Bo} D_A}{k_L^2} \qquad E_i = 1 + \frac{D_B C_{Bo}}{D_A C_{Ai}}$$

the general Eqs. (5) are transformed into

$$\frac{d^2 A}{dX^2} - MAB = 0$$

$$\frac{d^2 B}{dX^2} - \frac{MAB}{E_i - 1} = 0 \qquad (7)$$

The set of equations is now integrated numerically for a series of values for the two parameters E_i and M and the enhancement factor evaluated as well. The isothermal enhancement factor can be predicted in equation (8), where the value of can be estimated using orthogonal collocation method. [6]. The enhancement factor for the isothermal case is defined, similarly as

$$E = \frac{\bar{R}}{k_L C_{Ai}} = \frac{-D_A [dC_A/dx]_{x=0}}{k_L C_{Ai}} \qquad (8)$$

The enhancement factor which computed by approach adopted from Van Krevelen and Hoftijzer (1948) [6] and given by the equation:

$$E = \frac{\sqrt{M \frac{E_i - E}{E_i - 1}}}{\tan h \sqrt{M \frac{E_i - E}{E_i - 1}}} \qquad (9)$$

Numerical Solution (Interface Modeling)

The exit improvement to be introduced into the collocation method is to choose orthogonal polynomials for trial function. For simplicity in deriving the derivative matrices we can also write the series as [7]

$$y(x_j) = \sum_{j=1}^{N+2} d_i x_j^{i-1}$$

(10)

Taking the first and second derivatives of Eq. 10 we evaluate them at the collocation points. We take the collocation points as the N roots : these roots are between 0 and 1 ($x_1 = 0$ and $x_{N+2} = 1$). The location of the n internal collocation points (x_2 to x_{N+1}) are determined from the roots of the polynomial $P_n(x) = 0$, this points is described as following. [7]

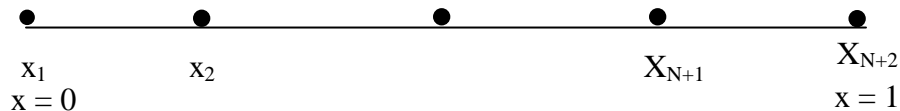


Figure. 2. Collocation Points Position.

The derivatives of Eq, 10 at the $N+2$ collocation points are

$$\frac{dy}{dx}(x_j) = \sum_{j=1}^{N+2} d_i(i-1)x_j^{i-2} \tag{11}$$

$$\frac{d^2y}{dx^2}(x_j) = \sum_{j=1}^{N+2} d_i(i-2)(i-2)x_j^{i-3} \tag{12}$$

The equations above could be written in matrix notation Q , C and D . Matrices Q , C and D are matrices of size $(N+2) \times (N+2)$. Eq. (10) may be presented in matrix notation as

$$y = Q.d \tag{13}$$

where d is the matrices of coefficient and

$$Q_{ji} = x_j^{i-1} \begin{matrix} i=1,2,\dots,N+2 \\ j=1,2,\dots,N+2 \end{matrix} \tag{14}$$

Solving Eq (10) for d we find

$$d = Q^{-1}.y$$

from the derivative of y in Eq (11) which in the matrix form become

$$\frac{dy}{dx} = Cd = CQ^{-1}y = Ay \tag{15}$$

where

$$C_{ji} = (i-1)x_j^{i-2} \tag{16}$$

For the derivative of y in Eq. (12) can be written in matrix form [7]

$$\frac{dy}{dx} = CQ^{-1}y = Ay \tag{17}$$

where

$$\frac{d^2y}{dx^2} = DQ^{-1}y = By \tag{18}$$

$$D_{ji} = (i-1)(i-2)x_j^{i-3} \tag{19}$$

With orthogonal collocation method, the collocation equation made an A_i , B_i , explicit to be solved by successive approximation method .[7]

$$\frac{d^2y}{dx^2} = \sum_{j=1}^{n+2} D_{ij}y_j; \frac{dy}{dx} = \sum_{j=1}^{n+2} C_{ij}y_j \tag{20}$$

For component A

$$A_i = \frac{\sum_{j=1}^{N+2} D_{ij}A_j - D_{ii}A_i}{(MA_i - D_{ii})} \tag{21}$$

For component B

$$B_i = \frac{\sum_{j=1}^{N+2} D_{ij}B_j - D_{ii}B_i}{\frac{MA_i - D_{ii}}{S}}$$

The system of non linear differential equations was solved using orthogonal collocation method and collocated equations described as non linear algebraic equations was solved using orthogonal collocation method.

Sherwood and Holloway (1940) in Danckwerts (1970) give the following expression for k_L and a [6]

$$k_L = 0.42 \left(\frac{g\mu}{\rho} \right)^{\frac{1}{3}} \left(\frac{D_{AB}\rho}{\mu_L} \right)^{\frac{1}{2}} \quad (22)$$

$$a = 0.38 \left(\frac{u}{u_t} \right)^{0.775} \left(\frac{u\rho}{nd\mu_L} \right)^{0.125} \left(\frac{g\rho}{d\sigma} \right)^{\frac{1}{3}} \quad (24)$$

Here u is the velocity of rise of the bubbles in the froth (taken to be 26.5cm/s under most conditions), n the number of holes per unit area of plate .

For sieve trays, Chan and Fair (1983) give the following expression for gas-phase mass-transfer coefficient $k_G a$ [9].

$$k_G a = \frac{316D_G^{1/2}(1030f + 867f^2)}{h_L^{1/2}} \quad (25)$$

Where : f = approach to flood, fractional

The interfacial Concentration of H_2S gas dissolved at interface estimated from solubility data following Henry's law and by considering gas side resistance that is,

$$C_{Ai} = \frac{k_G P_A + E.k_L C_A^0}{E.k_L + k_G H_e} \quad (26)$$

Ferric sulfate solution is used for H_2S absorption the reaction rate can be expressed as [8]

$$r = k C_{H_2S} C_{Fe^{3+}}$$

(27)

By assuming that the kinetic constant varies with temperature according to an Arrhenius function, the activation energy can be calculated. Therefore the reaction rate constant values were obtained as a function of temperature [8]

$$\log k = 9.3855 - \frac{2636.6}{T} \quad (28)$$

IV. RESULT AND DISCUSSION

In this study were assumed steady state and isothermal condition and this study of simulation comprises sieve trays column 70 cm in diameter filled with sieve trays 50 cm spacing to the height of 450 cm. Simulation the absorption of H_2S from sour gas.

This study presents a summary of the important features of the effect of chemical reaction on the absorption process expressed in the terms of enhancement factor. Figure.1 and Fig.2 shows enhancement factor (E) versus Hatta number \sqrt{M} plot with E_i as parameter for absorption of H_2S in $Fe_2(SO_4)_3$ solution of finite depth accompanied by an irreversible second order reaction in the sieve tray column. Simulation conditions : H_2S inlet mole fraction was $y_{Ain} = 0.28875$, $G = 751144.763 \text{ cm}^3/\text{s}$, $L = 10000 \text{ cm}^3/\text{s}$, $C_{(Fe_2(SO_4)_3)}$ was 0.002 mol/cm^3 , temperatures 30°C .and pressure = 1 atm

E is the enhancement factor, the factor by which the of absorption is increased by the reaction. E_i is the enhancement factor corresponding to instantaneous reaction.

Figure.1 shows numerical simulation results for the enhancement factor E as a function of Hatta number \sqrt{M} according to the film theory, calculated according to Eq. 8 with E_i parameter. For a given value of E_i an increase in \sqrt{M} brings about an increase in E until a limiting value is approached where $E = E_i$. The value of $E_i = 50$ shows the highest E value compared to the value $E_i = 4$ and $E_i = 20$. Increasing the value of E_i will decrease the amount of gas A absorbed and value of E will increase proportionally. The similarity between this figure and the familiar van Krevelen Hoftijzer plot for isothermal absorption of H_2S is apparent; one can find a remarkable similarity between Fig .1 and the traditional E versus \sqrt{M} plots. For a given E_i , the enhancement factor tends to reach an asymptotic value which is determined by the instantaneous reaction regime. Increasing the value of E_i will increase the amount of H_2S absorbed and value of E will increase proportionally.

With the same value of parameter used in Figure.1, E is plotted as a function of \sqrt{M} with the value of $E_i = 6.6$ in Figure.2. In this figure shows the compares between the numerical simulation data of the film model and Krevelen and Hoftijzer equation (adapted as per Eq.9) for enhancement is given for the same asymptotic enhancement factor. The curve of E vs \sqrt{M} shows that for low values of \sqrt{M} the absorption takes place in the slow reaction regime, and therefore is E nearly equal to 1, while for the higher values of \sqrt{M} the transition to the fast regime takes places

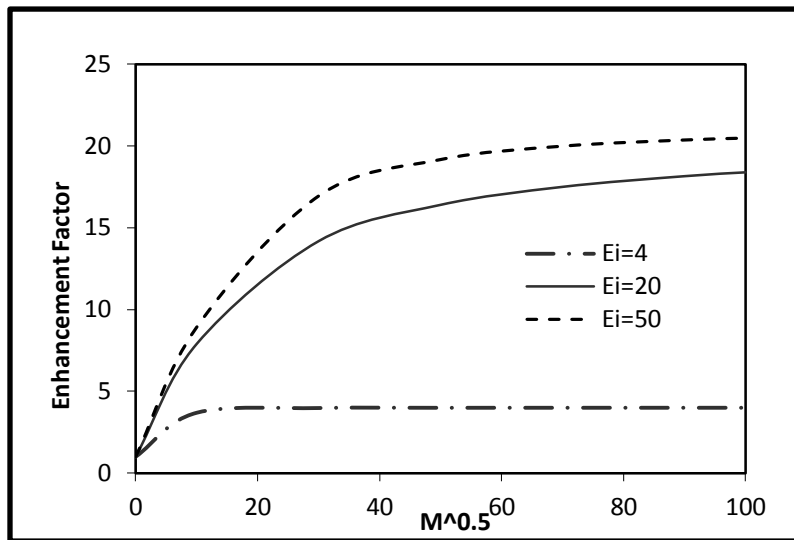


Figure. 1: Variation of the Enhancement Factor with Hatta Number for different values of E_i

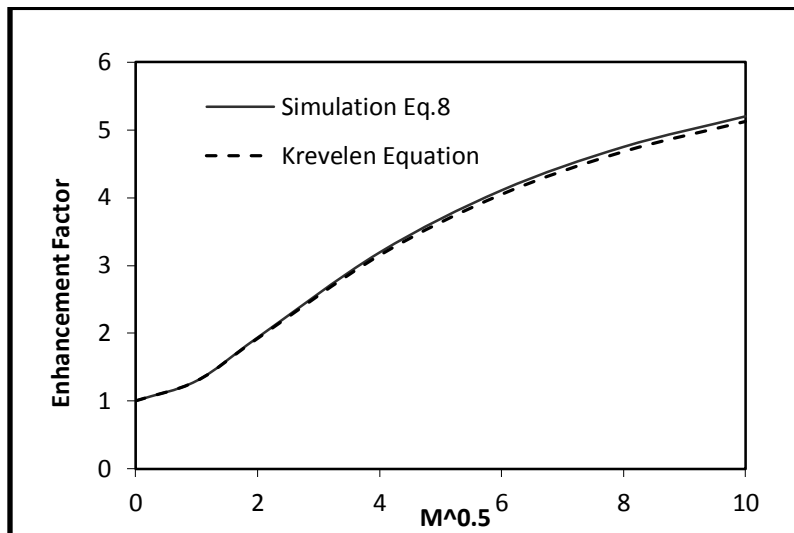


Figure.2: Relationship between simulation data and Krevelen and Hoftijer equation for Enhancement factors $E_i = 6.6$

Figure.3 shows with the same value of parameter used in Figure.1 with different concentrations of $Fe_2(SO_4)_3$ (1, 3, and 4mol/cm^3). The variation of the enhancement factor at different $C_{Fe_2(SO_4)_3}$ is simulated in Figure.3 the result shows the effect of the concentrations of $Fe_2(SO_4)_3$ on the enhancement factor. The enhancement factor increases with increased concentration of $Fe_2(SO_4)_3$ because with increasing $C_{Fe_2(SO_4)_3}$ increasing chemical reaction rate, i.e. increasing Hatta number, enhancement of mass transfer occurs resulting in an increased concentration. They are better known when the solution behaves more like pure H_2O . A decrease in the $Fe_2(SO_4)_3$ concentration will decrease the amount of H_2S removed from the sour gas and this could affect the statistical results; the difference of removal from one run to another could be so small that there would not be much difference between results,

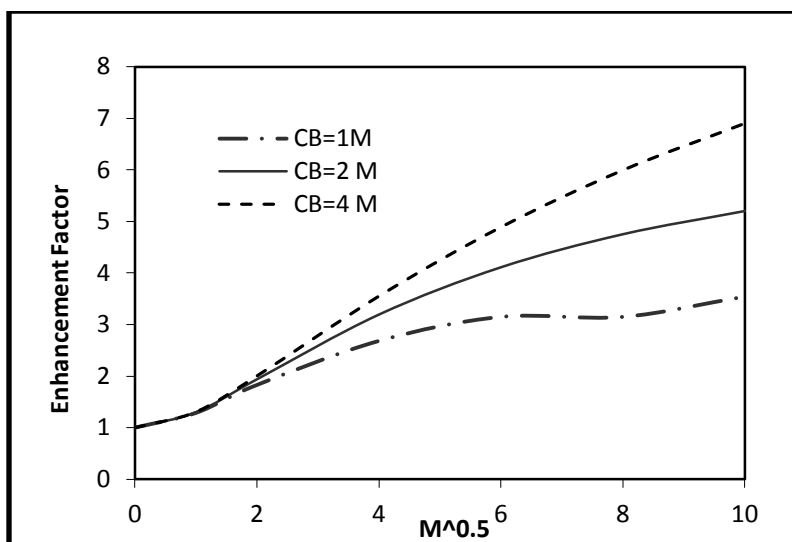


Fig.3: Effect of $C_{Fe_2(SO_4)_3}$ on Enhancement factors as function of \sqrt{M}

V. CONCLUSION

In this paper, a description of mathematical modeling and simulating for the isothermal gas absorption with chemical reaction in the sieve trays with the sample calculation of H_2S with $Fe_2(SO_4)_3$ solution was studied by means of numerical simulations. In this contribution, it was shown that approximate solutions for the enhancement factor, developed originally for mass transfer with chemical reaction. A fundamental description of isothermal mass transfer accompanied by irreversible chemical reaction has been presented, isothermal enhancement factor is dependent on the parameter E_i , and also on the concentration of solvent. The present work develops a film method for enhancement factor calculation. The model also is compared with the van Krevelen model. The numerical model used for the comparison is based on the two-film theory.

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