Optimum Operating Conditions for Direct Oxidation of H_2S in a Fluidized Bed Reactor

Fahimeh Golestani, Mohammad Kazemeini, Moslem Fattahi and Ali Amjadian

Abstract—In this research a mathematical model for direct oxidization of hydrogen sulfide into elemental sulfur in a fluidized bed reactor with external circulation was developed. As the catalyst is deactivated in the fluidized bed, it might be placed in a reduction tank in order to remove sulfur through heating above its dew point. The reactor model demonstrated via MATLAB software. It was shown that variations of H_2S conversion as well as; products formed were reasonable in comparison with corresponding results of a fixed bed reactor. Through analyzing results of this model, it became possible to propose the main optimized operating conditions for the process considered. These conditions included; the temperature range of 100-130ºC and utilizing the catalyst as much as possible providing the highest bed density respect to dimensions of bed, economical aspects that the bed ever remained in fluidized mode. A high active and stable catalyst under the optimum conditions exhibited 100% conversion in a fluidized bed reactor.

Keywords—Direct oxidization, Fluidized bed, H_2S, Mathematical modeling, Optimum conditions.

I. INTRODUCTION

THE international restrictions concerning the release of gases containing sulfur compounds into the atmosphere are becoming more and more drastic during recent decades. In this way, it is of interest to find more efficient methods for removing H_2S and especially SO_2 (*i.e.*; SO_x) to limit their emissions. A large amount of hydrogen sulfide (H_2S) is released from crude oil, natural gas refineries and metal smelting process in steel industries. The coal liquefaction process is also considered to be a major source of H_2S emissions [1-3]. Hydrogen sulfide generated by these processes must be recovered before releasing the gases into the atmosphere, due to the high toxicity of the H_2S. The general trend is to selectively transform H_2S into elemental sulfur by the well known equilibrated Claus process [4]. Because of thermodynamic limitations, the maximum

efficiency of Claus process cannot be greater than 98%. This means that, for a conventional sulphur plant, the SO_2 emissions may amount up to many thousands of tons per year released into the atmosphere. These limitations led to the development of new processes to deal with the Claus tail-gas, in order to remove as much as possible the H_2S concentration in the off gas before releasing it to the atmosphere [1]. All these processes to deal with the Claus tail-gas are based upon either oxidation of H_2S by oxygen or H_2S absorption/recycling technologies. These processes are based upon catalysts supported on different oxide supports such as α-alumina (α-Al_2O_3), TiO_2, SiO_2 and to a lesser extent activated charcoal. However, most of the oxide supports used; were rather sensitive to the problem of sulfating during the reaction in the presence of steam, sulfur, SO_2 and oxygen. In recent researches it was observed that SiC based catalyst seemed to be a promising candidate due to its chemical inertness [1-5]. On the other hand, all processes dealing with catalytic oxidation of H_2S into elemental sulfur were tested in fixed bed reactors and experimental investigations in fluidized bed reactors yet to be realized. Since fluidized bed reactors exhibited elevated conversion factor and selectivity towards the product, it was recommended to study direct catalytic oxidization of H_2S in a fluidized bed reactor; however certain difficulties encountered especially during extending bench data to industrial scale.The aim of this work was to develop a mathematical model for the catalytic oxidation of H_2S in a fluidized bed reactor on a NiS_2/SiC catalyst. Since no experimental data reported for this reaction in fluidized beds, at first results including the variations of H_2S conversion was compared with those of a fixed bed. However, it was hoped that achieving suitable results involving this reaction in fluidized bed reactors will be realized via more extended investigations utilizing an experimental setup. Next, through analyzing results of the model, parameters influencing this process were determined. Ultimately, studying effects of these parameters, procedures proposed to reach optimum operating conditions for this process.

F. Golestani is with the Department of Chemical and Petroleum Engineering, Sharif University of Technology, Azadi Avenue, P.O. Box 11365-9465, Tehran, Iran (e-mail: fg1186@gmail.com).

M. Kazemeini is with the Department of Chemical and Petroleum Engineering, Sharif University of Technology, Azadi Avenue, P.O. Box 11365-9465, Tehran, Iran (corresponding author to provide phone: +98-21-6616-5425; fax: +98-21-6602-2853; e-mail: kazemini@sharif.edu).

M. Fattahi is with the Department of Chemical and Petroleum Engineering, Sharif University of Technology, Azadi Avenue, P.O. Box 11365-9465, Tehran, Iran (e-mail: moslemfattahi@che.sharif.edu).

A. Amjadian is with the Department of Chemical Engineering, Tarbiat Modares University, Tehran, Iran (e-mail: aliamjadian14@gmail.com)

II. FLUIDIZATION

Fluidization described the condition when a gas passed up through a bed of solid particles became suspended. Fluidization occurred when superficial velocity of the gas lied in between the minimum fluidization and terminal velocity. If the gas velocity was set to less than the minimum fluidization

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velocity the reactor behaved as a fixed bed however, if this quantity exceeded terminal velocity of the largest particle, the overall bed along with gas started to move. The aforementioned velocities were functions of density and diameter of solid particles. This type of reactor possessed particular specifications, some of which were noted below:

- The pressure drop across the bed equaled to the weight of the bed per unit area of cross section and was independent of gas velocity.
- Solid particles might have moved through pipes analogous to liquids.
- Mixing solid particles improved mass and heat transfer limitations imposed upon this system.

In recent years fluidized bed reactors have been looked upon positively in industrial applications due to such specifications. However, the complex hydrodynamic behavior of the fluidized bed led to a risk and expensive expansion of bench into industrial scale. Hence applications of this technology in industrial scale might yet to be realized through extending of computational facilities [6-10].

III. MATHEMATICAL MODEL OF THE REACTOR

The fluidized bed proposed for the catalytic reaction considered in this research was a cylinder with external circulation connected to a reduction tank. As such, the problem of deactivation of the catalyst due to sulfur deposition might be overcome when it is transferred into reduction tank to be regenerated. This is foreseen through removing sulfur by heating up the catalyst at above sulfur's dew point temperature. Then the reduced catalyst returned to the reactor. It is noteworthy that, results obtained in this model indicated that for catalysts with high storage capacity of sulfur such as; NiS_2/SiC, the amount of produced sulfur may not cause deactivation of the catalyst. It seemed essential to develop a mathematical model of this fluidized bed to better understand the reactor behavior, hence optimize it. The model presented here is based upon the work carried out by Rubio *et al.* on 2004 [11]. This model might be directly solved under steady state. In the present work the bubble size was monitored as a function of reactor height. Horio and Nonaka relation was employed for calculation of bubble diameter [12]. The dynamic model of the fluid employed assumed three individual regions inside the bed including the bubble, wake and emulsion. As bubbles reached the fluidized bed; the overall solids in the wake transferred into the emulsion phase. In addition, mass transfer between wake and emulsion phases has been taken into account in this work. Hence, mixing of solids occurred by bubbles in the fluidized bed. It is assumed that concentration of any gaseous component in bubble and wake phases would be the same (*i.e.;* the gas mixed completely in both of these phases). Furthermore, it is assumed that concentration of gas in the cloud around the bubble is the same as that in the emulsion phase. In this model in addition to solid transfer, gas transfer between bubble and emulsion phases was considered. Other simplifying assumptions applied to this model included;

- Isothermal bed: This is a usual assumption in fluidized bed reactors. In fact in experimental works carried out by other researches, it was found that there are practically no temperature gradients in the bed [5]. This is expected because the solid is vigorously agitated by the fluid passing through the bed mixing the solids. Therefore energy balance equations are not needed to be solved in this model.
- Gas velocity and porosity in emulsion phase considered to be the same as those under the condition of minimum fluidization velocity.
- Non-catalytic reactions in gas phase are neglected.

In fact, the model employed for the gas stream is a theoretical three-phase model. The gas in emulsion phase is assumed to move up with a velocity equal to minimum fluidization velocity and remained gas in the bubble phase passed up. The gas within bubbles, based upon Davidson and Harison model accounted for, to diffuse continuously and moderately into emulsion phase with recirculation. The bubble during the pass upward carried some solids called wake. Equations applied for estimation of bubble velocity, gas transfer coefficient between bubble and emulsion, solid transfer coefficient between wake and emulsion and other parameters in the model [11] were listed in Table-1. Parameter f_w (volumetric percent of wake in bubble) was set equal to 0.1 according to data of fluidized bed published in literature [5]. Excessive dispersion of experimental data for this parameter rendered its precise prediction difficult. However parametric studies showed that; change of f_w in the range of 0.05 to 0.15 caused negligible variations (*i.e.*; lower than 1%) in conversion predicted through this model [11].

TABLE I
EQUATIONS USED IN A DYNAMIC MODEL OF THE FLUID [13, 14]

$u_B = u_0 - u_{mf} + u_{br}$		
$u_{br} = \begin{cases} 0.711\,(gd_b)^{1/2} & \dfrac{d_b}{D_t} < 0.125 \\ [0.711\,(gd_b)^{1/2}]1.2\exp\left(-1.49\dfrac{d_b}{D_t}\right) & 0.125 < \dfrac{d_b}{D_t} < 6 \end{cases}$		Bubble rising velocity
$K_{bc} = 4.5\left(\dfrac{u_{mf}}{d_b}\right) + 5.85\left(\dfrac{D^{1/2}g^{1/4}}{d_b^{5/4}}\right)$		Gas interchange between bubble and emulsion phases
$K_{ce} = 6.77\left(\dfrac{D\,\varepsilon_{mf}\,u_{br}}{d_b^3}\right)^{1/2}$		
$K_{we} = \begin{cases} \dfrac{0.075\,(u_0 - u_{mf})}{u_{mf}\,d_b} & \dfrac{u_0}{u_{mf}} \le 3 \\ \dfrac{0.15}{d_b} & \dfrac{u_0}{u_{mf}} > 3 \end{cases}$		Solid interchange between wake and emulsion phases
$\alpha = \dfrac{u_0 - (1 - \alpha - \alpha f_w)u_{mf}}{u_B} \approx \dfrac{u_0 - u_{mf}}{u_B}$		Percentage volume of bubbles in bed

IV. MASS BALANCES

The reactor model contained four gaseous components including; hydrogen sulfide, oxygen, steam and helium. Mass balance equations comprise of a system of partial differential equations which may convert to a system of ordinary differential equations assuming steady state. Mass balances for solid should affect flow of solid stream up along with bubble sizes versus height. This is due to the bubble size hence, bubble velocities varied with increased height.

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Therefore following equations are applied to gaseous components:

a) In bubble and wake phases:

$$\frac{\partial[(\alpha + \alpha f_w \varepsilon_{mf})AC_{i,B}]}{\partial t}$$
$$= -\frac{\partial[A(\alpha + \alpha f_w \varepsilon_{mf})u_B C_{i,B}]}{\partial z} + (\lambda_1 C_{i,B} + \lambda_2 C_{i,e})\frac{\partial[(\alpha + \alpha f_w \varepsilon_{mf})Au_B]}{\partial z} \qquad (1)$$
$$- K_{Be}A(\alpha + \alpha f_w \varepsilon_{mf})(C_{i,B} - C_{i,e}) + r_{i,B}\rho\frac{(1-\varepsilon_{mf})f_w}{(1+f_w \varepsilon_{mf})}A(\alpha + \alpha f_w \varepsilon_{mf})$$

b) In emulsion phase:

$$\frac{\partial[[1-(\alpha + \alpha f_w)]AC_{i,e}]}{\partial t}$$
$$= -\frac{\partial[A[1-(\alpha + \alpha f_w)]u_{mf}C_{i,e}]}{\partial z} - (\lambda_1 C_{i,B} + \lambda_2 C_{i,e})\frac{\partial[(\alpha + \alpha f_w \varepsilon_{mf})Au_B]}{\partial z} \qquad (2)$$
$$- K_{Be}A[1-(\alpha + \alpha f_w)](C_{i,e} - C_{i,B}) + r_{i,e}\rho(1-\varepsilon_{mf})[1-(\alpha + \alpha f_w)]A$$

The following equations are applied to elemental solid sulfur:

a) In wake phase

$$\frac{A f_w \rho \,\partial(\alpha C_{sw})}{\partial t} = -\frac{A f_w \rho \,\partial(\alpha u_B C_{sw})}{\partial z} + (\lambda_1 C_{sw} + \lambda_2 C_{se})\frac{A f_w \,\partial(\alpha u_B)}{\partial z} - K_{we}A f_w \alpha\rho(C_{sw} - C_{se}) \qquad (3)$$
$$+ r_{sw}A f_w \alpha\rho$$

b) In emulsion phase:

$$\frac{A \rho \,\partial[[1-(\alpha + \alpha f_w)]C_{se}]}{\partial t}$$
$$= -\frac{A \rho \,\partial[[1-(\alpha + \alpha f_w)]u_{se}C_{se}]}{\partial z} - (\lambda_1 C_{sw} + \lambda_2 C_{se})\frac{A f_w \,\partial(\alpha u_B)}{\partial z} \qquad (4)$$
$$- K_{we}A[1-(\alpha + \alpha f_w)]\rho(C_{se} - C_{sw}) + r_{se}[1-(\alpha + \alpha f_w)]A\rho$$

Also be noted the following boundary conditions was applied [5]:

$$\lambda_1 = 0 \quad \lambda_2 = 1 \quad for \quad \frac{\partial(\alpha u_B)}{\partial z} \geq 0 \qquad (5)$$

$$\lambda_1 = 1 \quad \lambda_2 = 0 \quad for \quad \frac{\partial(\alpha u_B)}{\partial z} < 0 \qquad (6)$$

V. RESULTS AND DISCUSSION

In order to determine the results of the model, experimental data obtained from direct oxidization of H_2S in a fixed bed was substituted into the model. These data are listed in Table-2:

TABLE II
EXPERIMENTAL DATA FROM A FIXED BED REACTOR [15]

Temperature (ºC)	60
Internal reactor diameter (m)	0.03
Bed height (m)	0.6
Catalyst particle diameter (μm)	400
Catalyst amount (kg)	0.0052

It is reminded that in general; the range of operational conditions in fluidized beds is different from those of fixed beds. Generally the catalyst pellets used in fluidized bed may have a lower diameter than those utilized in a fixed bed. Furthermore, the operating temperature in fluidized bed is often greater than that of a fixed bed. In addition, the amount of catalyst used and the reactor dimensions must allow establishment of fluidized mode in practice. Finally the variation of quantities across the bed when applying data of fixed bed is reasonable and expected. Nonetheless, the conversion in a fluidized bed is observed to be considerably lower than the corresponding value in a fixed bed. In other words, in a fixed bed reactor with the same inlet data as a fluidized one, 100% H_2S conversion in some cases is achievable [15]. This contradiction arises from inlet data of fluidized bed which uses the corresponding amounts of fixed bed. (Figures-1 and -2)
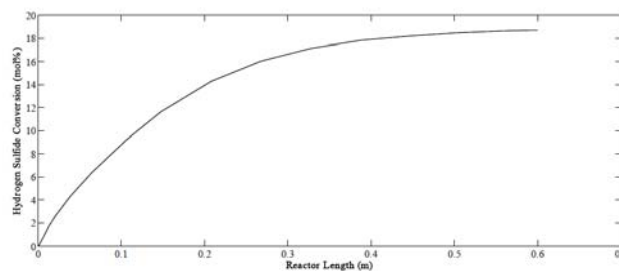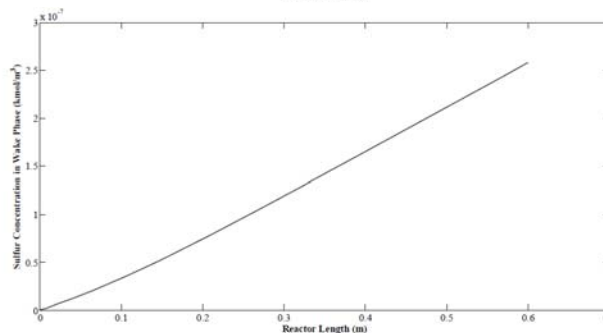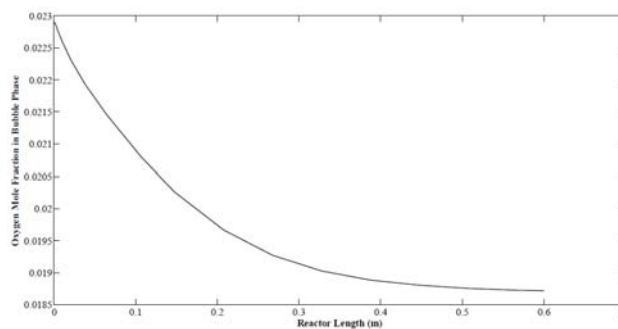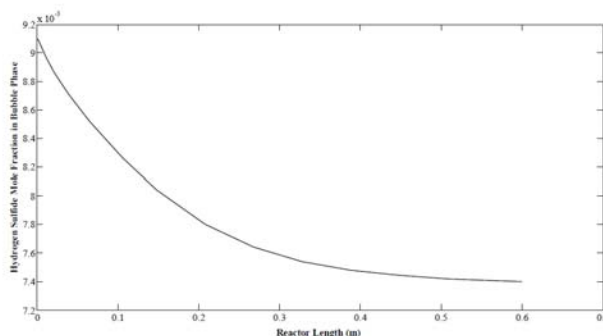

Fig. 1 Hydrogen Sulfide profile vs. the reactor bed

Fig. 2 Concentration variation profile of hydrogen sulfide, oxygen and elemental sulfur across the reactor length

In order to better understand the system considered, the conversion behavior as a function of parameters including temperature, the amount of used catalyst in bed, reactor dimensions, particle diameters and bed porosity under conditions of minimum fluidized velocity and reaction activation energy were investigated. Figure-3 showed H_2S conversion profile in terms of changes of these parameters. It is seen that the model predicted increase in hydrogen sulfide conversion under conditions of: i) increase in operational temperature, ii) increase in the amount of used catalyst in bed, iii) increase in height and decrease in bed diameter, iv)

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increase in particles diameter (up to 8×10^{-4}m above which the model diverges), v) increase in catalytic bed porosity and vi) decrease in reaction activation energy. These results were not only logical but also rather expected. It is essential to note that the exactness of applied kinetics for catalytic reaction was very important. In other words, it was observed that a little change in reaction activation energy, led to considerable change in conversion percentage. Amongst aforementioned considered parameters, temperature and the amount of utilized catalyst through the bed (*i.e.*; fluidized bed density) were key ones concerning fluidized beds. Hence simultaneous change of these two parameters while keeping others constant, could have determined their true effects. Figure- 4 indicated H_2S conversion profile versus these two parameters, utilizing experimental data for fixed beds up to applicable amounts to fluidized beds. The amount of used catalyst in fluidized bed in this figure was indicated in the R_{ob} form with kg unit. As observed in this figure, change of these two parameters in some cases led to 100% conversion.
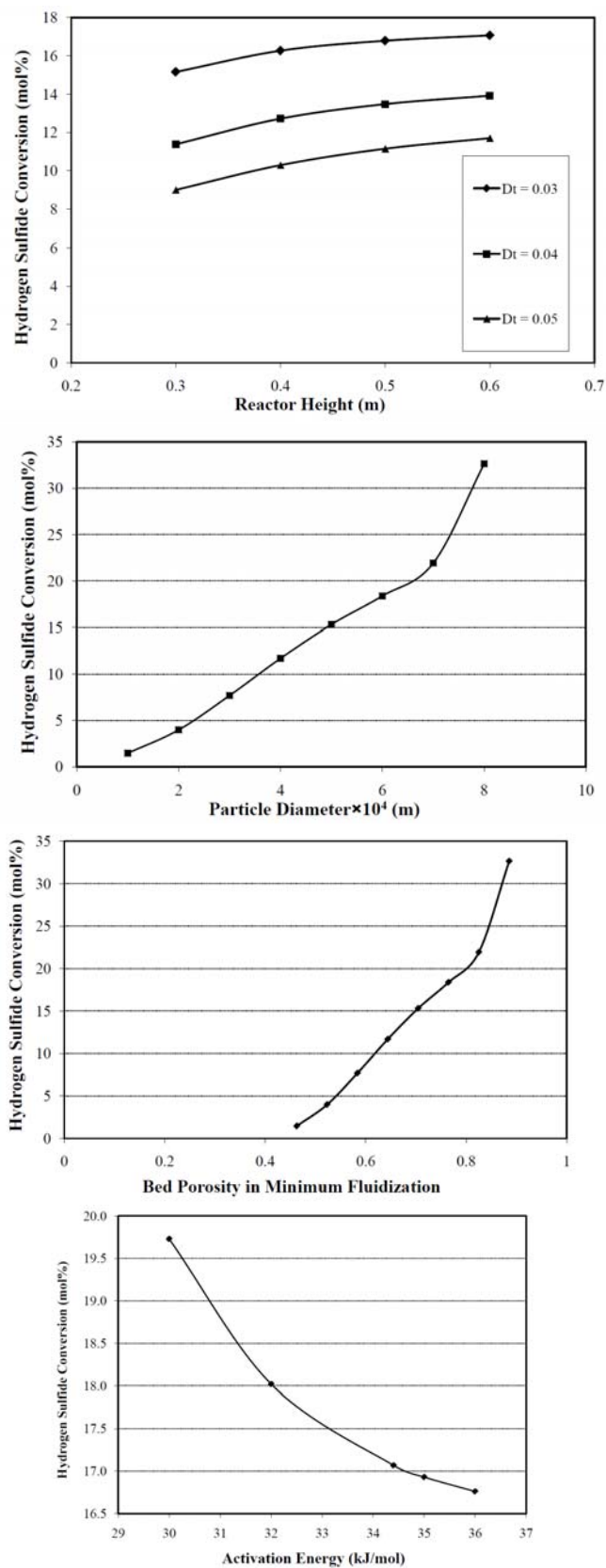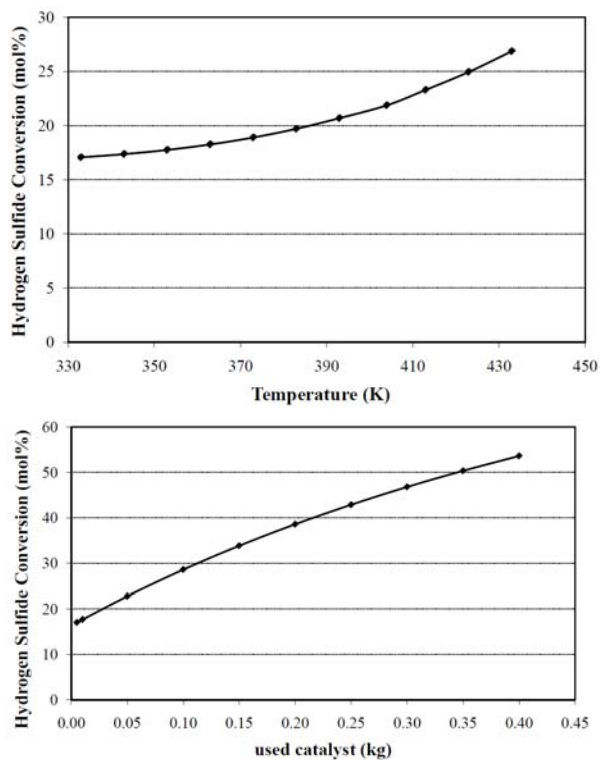
Fig. 3 hydrogen sulfide conversion in terms of temperature, the amount of used catalyst, reactor dimensions, particles diameter, catalytic bed porosity and reaction activation energy
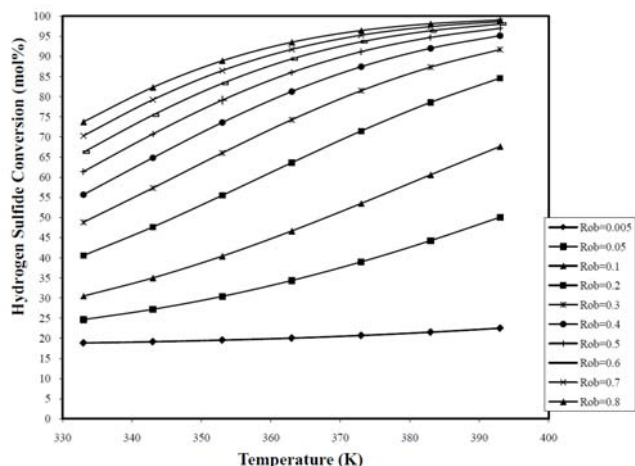
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Fig. 4 Variations in H_2S conversion with temperature and amount of used catalyst (kg/m^3) in a fluidized bed reactor

VI. Conclusions

Fluidized bed technology has its relative advantages in comparison with a fixed bed however, the complex hydrodynamic behavior of the fluidized bed led to a risk and expensive extension of experimental bench into industrial scale. The developed model presented here confirmed theoretically that this technology could be used for direct oxidization of H_2S in tail-gas of the Claus process. Results of this simulation indicated the optimum conditions for the process considered were at temperatures above those of fixed bed (*e.g.*; between 100-130ºC) and utilizing enough catalyst providing the highest bed density so that under operation the bed ever remained fluidized with reasonable economical costs. Furthermore, a high active and stable catalyst such as silicon carbide-supported nickel sulfide-based was utilized. Under the aforementioned optimum conditions, 100% conversion obtained in a fluidized bed reactor. In addition, deactivation of the catalyst seemed unlikely due to low concentrations of sulfur in the feed. In addition, if the catalyst deactivated, it might have been recovered via external circulation.The next step of this research currently undertaken in these authors laboratory is experimentally performing this process in a fluidized bed reactor to obtain appropriate data to model the process more accurately. This work will be followed with extension of data from the bench into industrial scale trying to assemble an effective mean to achieve environmental standards in oil and gas industries and optimization of other parameters like activation energy, fluidization velocity and porosity of bed.

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