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Modelling Pressure Drop to Calculate Conversion of Silicon and Methyl Chloride in a Fluidized bed Reactor

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Abstract

Three experiments were curried out at different reaction temperatures [250, 300, 330 °C], for the reaction of silicon with methyl chloride in a fluidized bed reactor, in order to evaluate a new predicted model that calculate both conversions of reacted solid (silicon) and reacted gas (methyl chloride) as function of pressure drop along the bed.

The reacted gas velocity was selected to be above the minimum fluidization velocity [velocity selected 2.6 cm/s, minimum fluidization velocity 1.8 cm/s] for the solid particles (size used 130 µm). A digital pressure drop measuring device was used at three points of the reactor (before and after the distributor and finally 50 cm above the distributor), to determine the pressure drop along the column, also an online GC was connected to the outlet reacted gas to analyze the product.

A comparison between the conversions of methyl chloride and silicon calculated from pressure drop data and that detected by the online GC, show a proper agreement with less than 5 % absolute average error.

Two equations [16, 18], derived analytically, were equation [8, 18] used to calculate the conversion of silicon and methyl chloride as function of pressure drop, equation [16] used to calculate the conversion of silicon as function of conversion of methyl chloride.

Key word; fluidized bed reactor, pressure drop, reactor modelling

النمذجة الرياضية لتخلخل الظغط داخل مفاعل الطبقة المتميعة لحساب نسبة التحول لكل من السلكون والمثيل كلورايد

الخلاصة

تم اجراء ثلاثة تجارب في ظروف درجات حرارة تفاعل مختلفة تتراوح بين (٢٥٠, ٣٠٠, ٣٣٠ درجة مئوية) لتفاعل السلكون وغاز المثيل كلورايد في مفاعل الطبقة المتميعة وذلك لتقييم موديل رياضي جديد لحساب نسبة التحول لكل من المادة الصلبة المتفاعلة (السلكون) والغاز المتفاعل(المثيل كلورايد) وذلك كدالة لتخلخل الظغط في المفاعل.

تم اختيار سرعة الغاز المتفاعل اعلى من القيمة الصغرى لسرعة التميع (السرعة المختارة ٢,٦سم/ثا, القيمة الصغرى لسرعة التميع هي ١,٨ سم/ثا) نسبة لحجم الدقائق المستعملة ١٣٠ مايكرومتر, تم استخدام جهاز رقمي لقياس تخلخل الظغط داخل المفاعل وذلك في ثلاثة نقاط , قبل وبعد موزع الغاز وثالث على ارتفاع ٥٠ سم فوق موزع الغاز كذلك تم ربط جي سي بشكل مباشر مع نواتج التفاعل وذلك لحساب نسبة التحول.

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تم اجراء مقارنة بين نسبة تحول الغاز المتفاعل (المثيل كلورايد) و المادة الصلبة المتفاعلة (السلكون) المحسوبة كدالة لتخلخل الظغط والتي تم الحصول عليها من جهاز ال جي سي , وقد اعطت نتائج جيدة مع نسبة ضئيلة للخطا . المعادلتان (١٦،١٨) هما معادلتان جديدتان تم استنتاجهما من خلال تحليل رياضي بحت , تم استخدام المعادلتان (٨،١٨) لحساب نسبة تحول المثيل كلورايد والسلكون كدالة لتخلخل الضغط في المفاعل, والمعادلة (١٦) لحساب نسبة تحول السلكون كدالة لنسبة تحول المثيل كلورايد .

Nomenclatures

Symbol	Definition	***Units***
b	Reaction stoichiometry	
C_A	Reactant concentration (kgmol/m^3)	
$C_{A\,i}$	Initial reactant concentration	*(kgmol/m^3)*
C_{Ad}	Reactant concentration in the dense phase (emulsion phase)	*(kgmol/m^3)*
D	Column diameter	*(m)*
d_p	Particle diameter	*(m)*
d_{pi}	variable particle diameter	*(m)*
d_{po}	Initial particle diameter	*(m)*
g	Gravity acceleration	*(m/s^2)*
H_{mf}	Bed high at minimum fluidization velocity	*(m)*
K_d	Deactivation rate constant	*(1/s)*
k	Reaction rate constant	*(1/s)*
K	Reaction number	*(-----)*
M_s,M_{so}	Weight of bed , initial weight of bed	*(kg)*
mw_s	Molecular weight of solid particle	*(kg/kgmol)*
M_p	Weight of single particle	*(Kg)*
U_{mf}	Minimum fluidization velocity	*(m/s)*
U	Superficial gas velocity	*(m/s)*
X_A	Fluid (gas) conversion	*(---)*
X_s	particle (silicon) conversion	*(---)*
t	time	*s*
Greek Lets.		
$\in$	Voidage of the bed	*(---)*
$\in_{mf}$	Voidage at minimum fluidization	*(---)*
ΔP_{fb}	Pressure drop across bed	*(mbar)*
β	Ratio of gas flow via bubble phase to total gas flow	*(---)*
ρ_s, ρ_p	Particle density	*(kg/m^3)*

Introduction

The organohalosilanes compounds are important raw materials for industry for use in many commercial products which enter our life. The first production of these compounds was carried out by Rochow at 1940 , the direct process reaction is shown in equation below [Bablin 2002] , the reaction is carried out commercially in a fluidized bed reactor using copper as catalyst and some promoters to increase the production of Dimethyl-dichlorosilanes (Di) .

$$Si + CH3Cl \xrightarrow[\substack{Cu\ (0.5 - 5\ \%)\\ Zn\ (100 - 5000\ ppm)\\ Sn\ (5 - 100\ ppm)\\ Al\ (500 - 4000\ ppm)}]{280 - 350\ ^{o}C}$$

$(CH3)_2SiCl_2$ (Di , 70 - 90 %) +
$CH3SiCl_3$ (Tri , 4 -12 %)+
$(CH3)_3SiCl$ (Mono , 1 - 5 %)+
$CH3HSiCl_2$ (MH , 0.5 - 5 %)+

The temperature of the reaction is between 280 – 350 ^{o}C , the reaction produces many products with high selectivity for Di (70 - 90 %) by using suitable promoters. Dimethyl-dichlorosilane is the aim of the reaction which is the raw material for silicon polymers.

The direct process is the main process for the production of organosilane. This reaction has been uncovered and most of the parameters that effect the reaction have been known and published, such as: reaction temperature, reaction rate constant, catalyst, promoters [Floquest et.al.,1994], [Lewis et.al.,2002], [Ward et. al.2001], [Lewin, 2001], [Aramata et. al., 2002] and the mechanism and kinetics of the reaction [Rethwish and Wessel, 1996], [Han and et. al., 2000], [Ward et. Al.,2000], [Bablin et. al.,2002]. There are many models that show the behaviour of the fluidized bed reactor such as Werthers, Orcutt, and Kunii and Levenspiel [Ergun 1999],[Fogler H. Scott. 1997], [Geldart D., 1986], [Kunii Daizo and Levenspiel Octave, 1969], these models don't include the pressure drop to calculate the conversion of the reacted gas.

In the present model the pressure drop is the main parameter, it is used to predict the conversion of both the reacted solid and gas (silicon and methyl chloride). By this model the parameters of the fluidized bed reactor can be predicted directly during the reaction through a pressure drop measuring devise connected to the reactor and this will give a quick estimation for the conversion of the reacted materials during the process with time. The model can be used to estimate the time for changing the reacted solid: for example when to add more solid to the reactor, decrease the reacted gas velocity as the reacted solid shrinking etc.

The aim of the present study is to show the ability of using the pressure drop along the fluidized bed reactor to estimate the conversion of both reacted solid and gas. The pressure drop can be registered by a simple pressure drop device which is much simpler than using the GC.

Theory

In the fluidized bed reactor, the solid particles are held in a state of suspension by upward flowing gas. The pressure drop ($P_1 - P_2$) of the fluid passing through a fluidized bed is equal to the total apparent weight of the suspension per unit cross-section area of the bed, i.e. the static pressure of the entire bed;

$$\Delta P_{fb} = P_1 - P_2 = \frac{M_s.g}{A} + \frac{M_f.g}{A} \qquad (1)$$

For solid-gas fluidization:

$$M_s = \frac{p.D^2.\Delta P}{4.g} \qquad (2)$$

On the other hand the total apparent weight of the suspension is equal to the weight of one particle multiplied by the number of particles, (for spherical particle and equal weight);

$$M_s = n.M_p = n.V_p.r_p = n.r_p.\frac{p}{6}(d_{pi})^3 \qquad (3)$$

Combining equation (2) and (3), gives the variation in particle diameter as;

$$d_{pi} = \left[\frac{3.\Delta P.D^2}{2.n.r_p.g}\right]^{1/3} \qquad (4)$$

Assuming the number of particles is constant (the only change due to reaction is in particle diameter);

$$n = \frac{M_{so}}{M_p} = \frac{6.M_{so}}{p.r_p.(d_{po})^3} \qquad (5)$$

Substituting equation (5) in (4), gives the variation in particle diameter as function of pressure drop;

$$d_{pi} = \left[\frac{p.(d_{po})^3.\Delta P.D^2}{4.g.M_{so}}\right]^{1/3} \qquad (6)$$

The conversion of solid particles in the fluidized bed reactor is represented by the equation below [levenspeal 1996];

$$X_s = 1 - \left(\frac{d_{pi}}{d_{po}}\right)^3 \qquad (7)$$

Substituting equation (6) in (7), gives the conversion of the solid reacted in terms of pressure drop in the reactor;

$$\boxed{X_s = 1 - \left[\frac{p.D^2.\Delta p}{4.g.M_{so}}\right]} \qquad (8)$$

The conversion of the reacted gas, concentration of the gas in the dense phase and the reaction rate constant in a fluidized bed reactor as presented by Orcutt model [Levenspeil 1996]; ,[Ihsan Hamawand et.al. 2005]; gives

$$X_A = \frac{K_1(1 - b.e^{-x})}{1 - b.e^{-x} + K_1} \qquad (9)$$

$$C_{Ad} = \frac{C_{Ai}(1 - b.e^{-x})}{1 - b.e^{-x} + K_1} \qquad (10)$$

$$K_1 = \frac{k_1.H_{mf}.(1 - \in_{mf}).e^{-k_d.t}}{U} \qquad (11)$$

Multiplying equation (10) by K_1;

$$\frac{C_{Ad}.K_1}{C_{Ai}} = \frac{K_1(1 - b.e^{-x})}{1 - b.e^{-x} + K_1} = X_A \qquad (12)$$

The particle diameter variation with time is given as,[Ihsan Hamawand et.al. 2005];

$$\frac{d_{pi}}{d_{po}} = \exp\left[\frac{-b.k_1.mw_s.C_{Ad}.t}{3.r_s}\right] \quad (13)$$

Multiplying the exponential in equation (13) by $\left(\frac{K_1.C_{Ai}}{C_{Ai}.K_1}\right)$ gives;

$$\frac{d_{pi}}{d_{po}} = \exp\left[\frac{-b.k_1.mw_s.t.C_{Ai}}{3.r_s.K_1}\frac{C_{Ad}.K_1}{C_{Ai}}\right] \quad (14)$$

Substituting equation (12) in (14) gives;

$$\frac{d_{pi}}{d_{po}} = \exp\left[\frac{-b.k_1.mw_s.t.C_{Ai}X_A}{3.r_s.K_1}\right] \quad (15)$$

Substituting equations (7) and (11) in (15) gives;

$$X_s = 1-(\exp\left[\frac{-b.C_{Ai}.mw_s.t.X_A.U}{3.r_s.H_{mf}.(1-\in_{mf}).e^{-K_d t}}\right])^3 \quad (16)$$

Equation (16) can be used to calculate the conversion of the reacted solid as function of the conversion of the reacted gas.

Substituting equation (8) in (16) gives;

$$1-\left[\frac{p.D^2.\Delta p}{4.g.M_{so}}\right] = 1-(\exp\left[\frac{-b.C_{Ai}.mw_s.t.X_A.U}{3.r_s.H_{mf}.(1-\in_{mf}).e^{-K_d t}}\right])^3 \quad (17)$$

Conversion of the reacted gas can be calculated as function of pressure drop as;

$$X_A = \frac{r_s.H_{mf}(1-\in_{mf}).e^{-K_d t}}{b.C_{Ai}.mw_s.U.t}\ln\left[\frac{4.g.M_{so}}{p.D^2.\Delta P}\right] \quad (18)$$

Thus equations (8) and (18) gives the conversion of the reacted solid and gas in the fluidized bed reactor as function of pressure drop in the bed.

Experimental Section

A stainless steel column with (5cm) inner diameter and (50cm) height was used as the reactor and it was equipped with an electrical heater rod (1.5m long rod that was turned around the column). The outlet from the reactor column was connected to a cyclone to collect the fine particles to be recycled to bed. Effluent from the reactor is filtered through a filter to collect any particle that cyclone did not catch before gases enter the GC, as shown in figure (1).

Three thermocouples were used to detect temperatures in three sites and one was connected to the controller to control the temperature in the reactor.

A digital-pressure measuring device was used to measure pressure along the column in three points (before and after the distributor and finally 50 cm above the distributor), with range between zero to 9999mbar.

Gas chromatography was used to analyze the reacted gas and the products on-line directly, (Gaw-Mac Spectra' by Gaw-Mac instrument Co. LTD., Ireland with integration type 'Varian 4290', U.S.A).

A typical run began by preparing an amount of pulverized silicon with CuCl catalyst (10% Cu based on silicon) and pouring it inside the column from the top. Temperature controller setting was: on 250, 300, 330 ^{o}C, and the heater began to work slowly because it was connected to

voltage variac which was set on 60% so that the temperature rose slowly.This avoided temperature rise above the set point. The reactor temperature did not rise more than ±5 ^{o}C after reaching the set point.

An inert gas (nitrogen) was supplied to the reactor at a small flow rate after it flowed through a 2m long pipe inside the furnace to preheat the gas to (150 ^{o}C). After 15min the flow of nitrogen was stopped and methyl chloride (MeCl) was allowed to enter the pre-heater and then to the reactor. The tube that carried the product was split into two lines, one going to the condenser and the other to the GC. A hydrodynamic experiment was carried out in a glass column to find both H_{mf} and $\in_{mf}$. Every 20min the product was injected into the GC (online) to be analyzed.

Results and Discussions

The parameters used as inputs to the model equations [8, 16, 18] were: dp_o= 160 – 100 μm, ρ_s = 2.32 gm/cm^3, Mso = 350 gm, U= 2.6 cm/s, H_{mf} = 14.2 cm, Mws = 28 gm/gmol, U_{mf} = 1.7 cm/s, D = 5 cm, b = 0.5 , P = 1 atm , $\in_{mf} = 0.45$.

$C_{Ai} = y_{Ao} * P / R* (T + 273)$, R= 82.06 cm3.atm / gmol.K

$Y_{Ao} = 0.667$.

Figures (2, 3, 4, 5, 6, 7, 8, 9), are plots of the data of conversion of silicon and methyl chloride resulting from the experiments and those predicted from equations for different reaction.

Figure (2) shows the experimental pressure drop along the bed with time, as the contact mass (silicon) consumed with time due to reaction with methyl chloride. The volume of the contact mass decreases with time and this lead to a decrease in the weight of the bed, as a result the pressure drop along the bed decreased.

This decrease in the volume of the reacted solid (silicon) with time led to a decrease in the surface area of the particles which is responsible for the decrease in the reacted gas (methyl chloride) conversion with time as it shown in figure (3).

Plotting the experimental conversion of methyl chloride with pressure drop along the bed in figure (4) shows the decrease in conversion of methyl chloride with the decrease in the pressure drop along the bed due to consumption of the contact mass with time. But for the temperature 250 ^{o}C there is a sharp decrease in the conversion of methyl chloride because the temperature is not satisfying the reaction.

Figure (5), is a comparison between the experimental pressure drop registered by the digital pressure drop device and the theoretical pressure drop predicted by equation (18) as function of the experimental conversion of methyl chloride. It is clear from the figure that there is good agreement between the two results (0.16, 5, 6 % absolute average error for the three temperature respectively).

There is also good agreement was found for the comparison between the experimental conversion of methyl chloride and the predicted conversion by equation (18) as plotted in figure (6), (67, 13, 18 % absolute average error for the three temperature respectively), only for 250 ^{o}C there is high error because of

the sharp decrease in the reacted gas conversion were the temperature is not enough to carry out the reaction leading to disagree between the two conversion, the results give the conclusion that equation (18) can be used as a modeling equation to predict the conversion of the reacted gas with low level of error.

Equation (8) is used to predict data for the conversion of reacted solid (Silicon) as function of the pressure drop along the bed, as plotted in Fig.(7) where it is clear from the figure that the decrease in the conversion of silicon correspond to decrease in the pressure drop (experimental), it is possible that the decrease in the volume of the particles is responsible for the observed results. Figure (8) is a comparison between the predicted conversion of silicon from equation (8) by using the experimental and theoretical pressure drop data (theoretical pressure drop has been predicted from equation (18) as function of the experimental reacted gas conversion). The figure shows a good agreement between the two predicted solid conversion because of the high agreement between the experimental and theoretical pressure drop (4.6, 4.0, 4.4 % absolute average error for the three temperature respectively). Also in figure (9), is comparisons between the solid conversions predicted by equations (8) and (16) were it is function to pressure drop along the bed in the first equation and function of reacted gas conversion in the second. There is a good agreement for two reactions temperatures between the two predicted solid conversion processes (67, 3.8, 3.1 % absolute average error for the three temperature respectively). Also only at 250^{o}C the same error predicted. It is concluded that there is a good interaction between these equations, the good agreement between the experimental data and the data predicted by these equations give these equation a good potential to represent the real reaction.

Conclusion

For the three experiments carried out at three different temperatures of reaction, a good agreement between the experimental results for the conversion of methyl chloride and that predicted from equation (18) gives a support that these equations have a good potential to represent the gas solid reaction in a fluidized bed reactor. Placing a digital pressure drop device connected to the reactor can give a view about different parameters that affect the performance of the fluidized bed reactor, such as; time for replacing or changing the contact mass, activity and decay in the catalyst.

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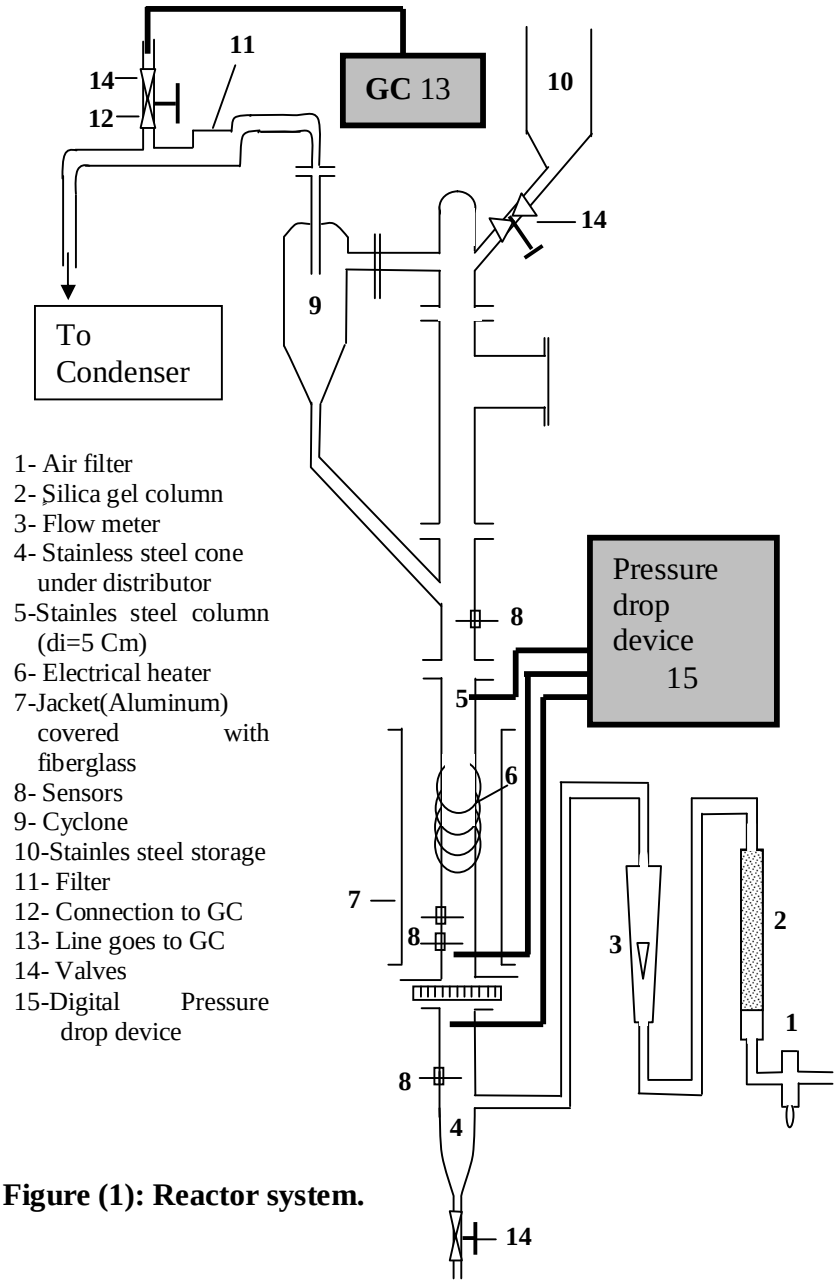

Figure (1): Reactor system.

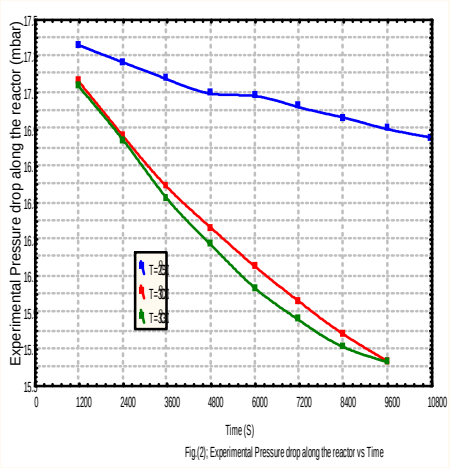

Fig.(2); Experimental Pressure drop along the reactor vs Time

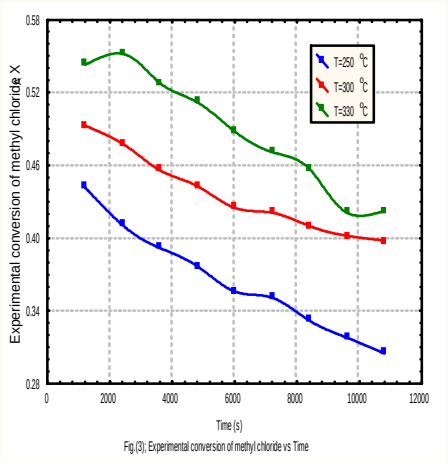

Fig.(3); Experimental conversion of methyl chloride vs Time

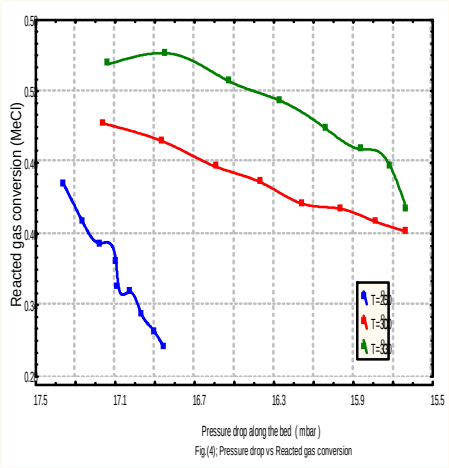

Fig.(4); Pressure drop vs Reacted gas conversion

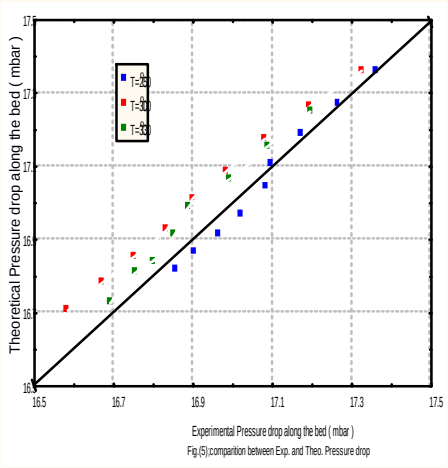

Fig.(5);comparition between Exp. and Theo. Pressure drop

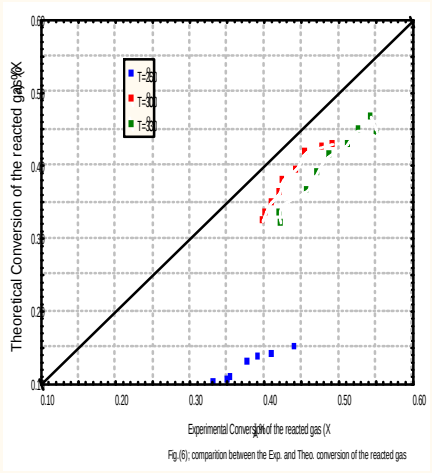

Fig.(6); comparition between the Exp. and Theo. conversion of the reacted gas

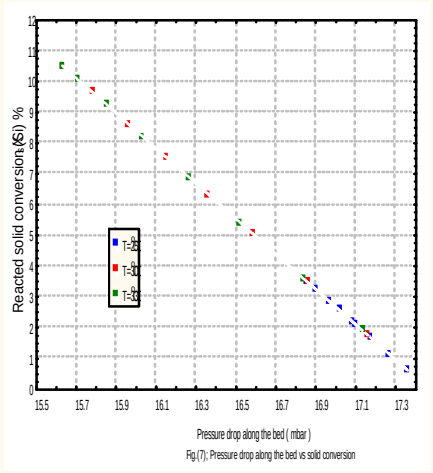

Fig.(7); Pressure drop along the bed vs solid conversion

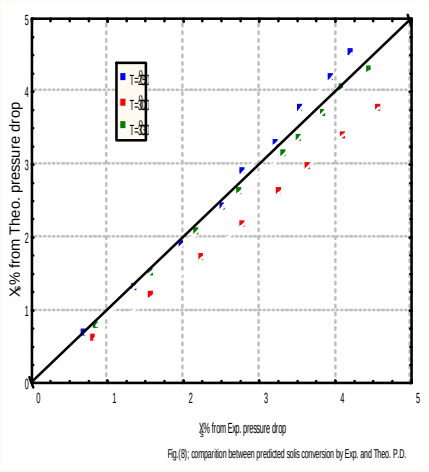

Fig.(8); comparition between predicted soils conversion by Exp. and Theo. P.D.

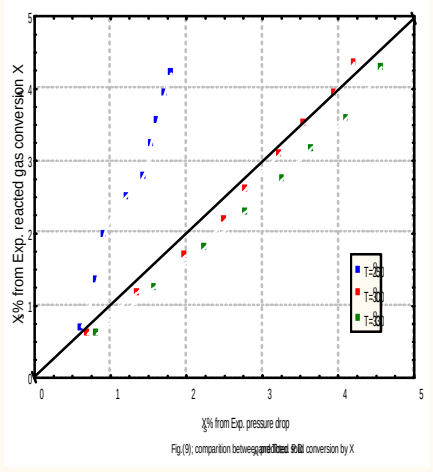

Fig.(9); comparition between predicted solid conversion by X