MATHEMATICAL MODELS FOR DIRECT REACTION OF METHYL CHLORIDE WITH *SILICON IN FLUIDIZED BED REACTOR*

Ihsan Baker / Chem. Eng. Dept.
Thamer Jasim / Chem. Eng. Dept.
University of Technology
Mouyed G. Jalhoom / Iben Seena Comp.

ABSTRACT

Methyl chlorosilanes are important raw materials for the production of polyalkylsiloxanes, the basic ingredient of silicone oils and silicone rubbers. One of the main methods for the commercial production of methyl chlorosilanes, known as direct process, involves a reaction between elemental silicon (Si) and methyl chloride (MeCl). The principal product is dimethyldichlorosilane, which is used to form the polydimethylsiloxanes.

The aim of this work is to predict a mathematical models in which it shows the behavior of the reaction. We predict four models, these models take in consideration the reaction kinetic the physical, chemical, and design equation of fluidized bed reactor.

The equations shows the conversion of MeCl as function of temperature and time, conversion of silicone as function of time, particle diameter as function of time. We have compared the result from these models with practical result from international papers, and it shows good agreement.

KEYWORDS

Fluidized bed reactor, direct reaction, mathematical model.

Acknowledgement

I* would like to thank ***Dr. Larry N. Le***wis for providing me by papers and advice.

NOTATION

a_b	Interfacial bubble area per unit bubble volume, (cm^{-1})
Ao	Orifice area (cm^2)
At	Column diameter (cm^2)
C_{Ab}	Concentration of MeCl in bubble phase, ($gmol/cm^3$)
C_{Ad}	Concentration of MeCl in the dense phase, ($gmol/cm^3$)
deq	Diameter of equivalent volume sphere = bubble diameter (cm)
deo, deq_o	Initial equivalent bubble size, (cm)
dem, deq_m	Maximum equivalent bubble size attainable by coalescence (cm)
d_v	Diameter of sphere having the same volume as the particle (cm)
dp	Particle diameter (cm)
di	Diffusivity of reacted gas (cm^2/s)
D	Column diameter (cm)
F_{Ao}	Molar flow rate of MeCl (gmol/hr)
H	Bed height, (cm)
H_{mf}	Bed height at minimum fluidization (cm)
K	Reaction rate constant, (gmol MeCl/gm Si, hr)
K_A	Adsorption equilibrium constant for MeCl, (atm^{-1})
K_B	Desorption equilibrium constant for Silane, (atm^{-1})
K_q	Bubble to dense phase mass transfer coefficient (cm/s)

MB, M_{si}	Molecular weight of Si (gmol/gm)
Me	Viscosity of reacted gas (gm.cm/s)
P_A	Partial pressure of MeCl (atm)
P_B	Partial pressure of dimethy/dichloro silane (atm)
Q	Volumetric flow rate (gmol/hr)
rp	Density of solid particle (gm/cm^3)
rg	Density of the gas (gm/cm^3)
T	Temp of the bed (C^o)
Y ,T_o	Temp of MeCl inlet (C^o)
U	Superficial gas velocity (cm/s)
Umf	Minimum fluidization velocity (cm/s)
ua	Rise velocity of a bubble in a bubbling bed (cm/s)
W	Weight of solid (cotact mass) (gm)
X , Xm	Conversion of MeCl
Xsi	Conversion of Si
ρ_{si} , ρ_p	Density of Si (gm/cm3)
β	Ratio of gas flow via bubble phase to total gas flow
$\in_b$	Fraction of bed occupied by bubble
Z	Distance above distributor (Variable with bed height)(cm)

INTRODUCTION

When on May 10, 1940, in the research laboratory of the General Electric Company in Schenectady, Ny, Rochow carried out an experiment in which he passed gaseous methyl chloride through a crushed 50% Cu-Si mixture (previously activated with gaseous HCl) in a tube furnace at 370°C and obtained as products a mixture of methylchlorosilanes (among them $(CH_3)_2\ SiCl_2$, our interest product).[1]

Rochow's direct process is still the only economical route to methylchlorosilanes. The direct process is shown in Eq.(1)

$$
\begin{aligned}
Si + MeCl \xrightarrow[Cu]{280-350\,C^{o}} \; & Me_2\,SiCl_2 && \text{(Di , 70-90\%.....(1)} \\
& + Me\,SiCl_3 && \text{(Tri , 4-12\%)} \\
& + Me_3\,SiCl && \text{(Mono , 1-5\%)} \\
& + \text{Others} && \text{(low traces)}
\end{aligned}
$$

The direct process is carried out commercially in fluidized-bed reactors using powdered silicon at approximately 300 C°. Rochow's great discovery was copper catalysis. The reaction are essentially inert without it.

A huge amount of research has been done to find promoters that will result in higher selectivities to Di.[2] The most work done by chemist scientist in which they study the mechanism of the reaction.

Ward, Ritzer, Carroll, and Flock [3], study the effect of trace elements on product distribution and rate. Fluidized and stirred bed reactors were used. A catalyst system consisting of copper, zinc, and tin was discovered which yield 90% dimethyldichlorosilane with nearly complete silicon utilization.

Lewis and Ward [2] used a contact mass of CuCl with silicon and study the effect of added zinc and phosphorus to the reaction, they found that, at Cu/Zn ratios > 30, phosphorus addition resulted in an increase in selectivity for Di, phosphorus appeared to cause an increase in formation of the eta phase (Cu_3Si).

Many patents are present in this field, study the effect of promoters on the selectivity for Di.

Aramata, Fujioka and Yuyama [4] invent a mixture of catalyst, copper or copper compound catalyst and an activated aluminum, aluminum alloy or aluminum carbide promoter. The reaction is carried out at temp. 250-400 C^o in stirred tank or fluidized bed reactor, the invention shortens the time required for activation in the Rochow reaction and increase the selectivity for desirable diorganodihalosilanes.

Aramata, Fujimoto and Saito [5], add 50-10,000 ppm of bronze phosphide to the contact mass (Metallic silicon and copper catalyst), the invention is successful in efficiently producing organoholosilanes in a high sty (space time yield) and low T/D.

In this work we try to find the design data for fluidized bed reactor by using models in which it shows the behavior of the reactor and the reaction.

THEORY

1- Model (1) Kinetic Model

For high production of Di. We assume that there is only Di in the product, so the reaction equation of silicon with methyl chloride is:

$$2CH_3Cl + Si \xrightarrow[Cu]{300\,C^o} (CH_3)_2\,SiCl_2 + Others \qquad .....(2)$$

$$A + \frac{1}{2}\,Si \longrightarrow \frac{1}{2}B + C \qquad ..... \qquad .... \; .....(3)$$

Steps in a catalytic reaction

1- Adsorption of methyl chloride on the surface of copper

$$A_{(g)} + S \qquad A.S \Longrightarrow \qquad r_{AD} = K_A\left(P_A\,C_V - \frac{C_{A.S}}{\kappa_A}\right) \; .....(4)$$

2- Reaction of MeCl with silicon on the surface of catalyst (Cu)

$$A.S + Si + S \Longrightarrow B.S + C + S \; r_S = K_S\left(C_{A.S}\,P_{Si}\,C_V - \frac{C_{B.S}\,P_C\,C_V}{\kappa_S}\right)$$

.....(5)

3- Desorption of Di (product) from the surface of Cu

$$B.S \Longrightarrow B + S \qquad r_D = K_D\left(C_{B.S} - \frac{P_B\,C_V}{\kappa_D}\right) \qquad .....(6)$$

most of the catalytic reaction is surface reaction limiting then

$$\frac{r_{AD}}{K_A} = 0 \,,\; \frac{r_D}{K_D} = 0 \,,\; C_{AS} = \kappa_A\,P_A\,C_V \,,\; C_{B.S} = \frac{P_B\,C_V}{\kappa_D} = \kappa_B\,P_B\,C_V$$

$$r_S = K_S\left(\kappa_A\,P_A\,C_V\,P_{Si}\,C_V - \frac{\kappa_B\,P_B\,C_V\,P\,C_V}{\kappa_S}\right) \quad ..... \qquad .....(7)$$

$$C_V = \frac{C_t}{\left(1+\kappa_A\, P_A + \kappa_B\, P_B\right)} \qquad \ldots\ldots \qquad \ldots\ldots \quad \ldots\ldots(8)$$

$$r_S = \frac{K_S\, C_t^2 \left(\kappa_A\, P_A\, P_{Si} - \dfrac{\kappa_B\, P_B\, P_C}{\kappa_S}\right)}{\left[1+\kappa_A\, P_A + \kappa_B\, P_B\right]^2} \qquad \ldots\ldots\ldots(9)$$

For irreversible reaction, let $K = K_S\, C_t^2\, P_{Si}$

$$-r_A' = r_S = \frac{K\,\kappa_A\, P_A}{\left[1+\kappa_A\, P_A + \kappa_B\, P_B\right]^2} = \frac{gmol\ MeCl\ reacted}{gm\ solid\ (Si + Cu).hr} \qquad \ldots\ldots(10)$$

We can assume the design equation of fluidized bed same as CSTR. Then:

$$W = \frac{F_{Ao}\, X}{-r_A'} \qquad \ldots\ldots(11)$$

From the stochiametry

$$\delta = -1\ ,\ Y_{Ao} = 0.667\ ,\ \in = -0.667\ ,\ P_{Ao} = 0.667\, P_t\ ,\ \theta_B = 0\ ,\ \upsilon_i = 0.5$$

$$P_A = P_{Ao}\,\frac{\left(1-X\right)}{\left(1+\in X\right)}\,\frac{T_o}{T} \qquad\qquad P_B = P_{Ao}\,\frac{\left(\theta_B + \upsilon_i\, X\right)}{\left(1+\in X\right)}\,\frac{T_o}{T}$$

$$\boxed{X = \frac{K\,\kappa_A\, 0.667\, P_t\, \dfrac{T_o}{T}\, \dfrac{\left(1-X\right)}{\left(1-0.667\,X\right)}\left(W / F_{Ao}\right)}{\left[1+\kappa_A\, 0.667\,\dfrac{\left(1-X\right)}{\left(1-0.667\,X\right)}\,\dfrac{T_o}{T}\, P_t + \kappa_B\, 0.667\,\dfrac{0.5\,X}{\left(1-0.667\,X\right)}\,\dfrac{T_o}{T}\, P_t\right]^2} \qquad \ldots\ldots(12)}$$

From literature, reference (6).

T C°	$K\ \frac{gmal}{gm.hr}$	$\kappa_A\ \frac{1}{atm}$	$\kappa_B\ \frac{1}{atm}$
280	0.24	0.0076	0.53
300	0.6	0.0068	0.4
320	1.17	0.0057	0.28

The reaction rate take the exponential form, then assume

$$K, \kappa_A, \kappa_B = a\ e^{-b/T}$$

By statistical program (specified regression) we find:

$$K = 45473.71\, e^{-3380.35/T} \quad .....(13)$$

$$K_A = 0.00083\ e^{622.693/T} \quad .....(14)$$

$$K_B = 0.004003\ e^{1370.53/T} \quad .....(15)$$

$$F_{Ao} = \upsilon_o\ \frac{P_t\ Y_{Ao}}{R\ T_o} = 0.00812 * Q\ \frac{P_t}{(T_o + 273)} \quad .....(16)$$

2- FLUIDIZED BED MODEL (ORCUT MODEL)

Two phase model

With the assumption that there are no particles in the bubble phase. The change in molar flux of species A at any high in the bubble phase must be accounted for by interphase transfer:

Change in molar flux = transfer from bubble to dense phase

$$\beta\ U\ \ dC_{Ab} = K_q\left(C_{Ad} - C_{Ab}\right) a_b \in_b dZ \quad .....(17)$$

$\beta = \frac{U - U_{mf}}{U}$ = fraction of gas which flows through the bubble phase at any high

$$\int_{C_{Ain}}^{C_{Ab}} \frac{d\,C_{Ab}}{C_{Ad}-C_{Ab}} = \frac{K_q\, a_b \in_b}{\beta\, U} \int_o^z d\,Z \qquad .....(18)$$

at $Z=0 \qquad C_{Ab}=C_{Ain}$

$$C_{Ab} = C_{Ad} + \left(C_{Ain} - C_{Ad}\right) e^{-\frac{K_q\, a_b \in_b\, z}{U\ \beta}} \qquad .....(19)$$

A mole balance over the entire dense phase yield:

Transfer by convection + transfer by diffusion = reacted

$$(1-\beta)U\,(C_{Ain}-C_{Ad}) + \int_o^H K_q\,(C_{Ab}-C_{Ad})\, a_b \in_b d\,z = (1-\in_b)(1-\in_{mf})H\,K_n\, C_{Ad}^n$$

..........(20)

For first order reaction $n=1.0$, $H_{mf}=(1-\in_b)\,H$, $K_1'=K_1\dfrac{H_{mf}\,(1-\in_{mf})}{U}$

$$C_{Ain} - \left[\beta\left(C_{Ab}\right)_{Z=H} + (1-\beta)\,C_{Ad}\right] = K_1'\,C_{Ad} \qquad .....(21)$$

Sub eq.(19) in eq.(21) then

$$C_{Ad} = \frac{C_{Ain}\left(1-\beta\, e^{-x}\right)}{1-\beta\, e^{-x} + K_1'} \qquad .....(22)$$

The final exit concentration is:

$$C_{Aout} = C_{Ain} - C_{Areacted} \qquad .....(23)$$

$$= C_{Ain} - K_1' C_{Ad}$$

Compare with eq.(21)

Then

$$C_{Aout} = \beta\,\left[C_{Ab}\right]_{Z=H} + (1-\beta)\,C_{Ad} \qquad .....(24)$$

sub in eq.(21)

$$C_{Ain} - C_{Aout} = K_1' \; C_{Ad} \qquad \text{.....(25)}$$

$$C_{Ad} = \frac{C_{Ain} - C_{Aout}}{K_1'} \qquad \text{.....(26)}$$

eq.(26) = eq.(22)

$$1 - \frac{C_{Aout}}{C_{Ain}} = \frac{K_1' \left(1 - \beta \; e^{-x}\right)}{1 - \beta \; e^{-x} + K_1'} \qquad \text{.....(27)}$$

$$\boxed{X_A = \frac{K_1'\left(1 - \beta \; e^{-x}\right)}{1 - \beta \; e^{-x} + K_1'} = 1 - \frac{1 - \beta \; e^{-x} + \beta \; K_1' \; e^{-x}}{1 - \beta \; e^{-x} + K_1'} \qquad \text{.....(28)}}$$

To find the rate of reaction for first order:

$$-r_A' = K_1 \, C_{Ao} \frac{(1-x)}{(1-0.667x)} \frac{T_o}{T} = \frac{K \, \kappa_A \, 0.667 \, P_t \dfrac{T_o}{T} \dfrac{(1-x)}{(1-0.667x)} \rho_{Si}}{\Bigg[1 + \kappa_A \, 0.667 \dfrac{(1-x)}{(1-0.667x)} \dfrac{T_o}{T} P_t + \kappa_B 0.667 \dfrac{0.5x}{(1-0.667x)} \dfrac{T_o}{T} P_t} \qquad \text{.....(29)}$$

$$K_1 = \frac{K \; \kappa_A \; R \; T_o \; \rho_{Si}}{\left[1 + \kappa_A \; 0.667 \dfrac{(1-x)}{(1-0.667\,x)} \dfrac{T_o}{T} \; P_t + \kappa_B \, 0.667 \; \dfrac{0.5\,x}{(1-0.667\,x)} \dfrac{T_o}{T} \; P \right]^2} \qquad \text{.....(30)}$$

$$K_1' = \frac{K_1 \; H_{mf} \left(1 - \in_{mf}\right)}{U} \qquad \text{.....(31)}$$

$$X = \frac{K_q \; a_b \; \in_b \; H}{\beta \, U} \qquad \text{.....(32)}$$

$$\beta = \frac{U - U_{mf}}{U} \qquad \text{.....(33)}$$

$$K_q = 0.75\, U_{mf} + \frac{0.975\, g^{0.25}\, di^{0.5}}{deq^{0.25}} \qquad \text{.....(34)}$$

$$A_o = \frac{\pi}{4} d_{or}^2 \qquad a_b = \frac{6}{deq} \qquad \in_b = \frac{H - H_{mf}}{H} = \frac{U - U_{mf}}{u_A} \qquad \text{.....(35)}$$

$$u_A = 0.71\, (deq * g)^{0.5} + (U - U_{mf}) \qquad \text{.....(36)}$$

$$H = \frac{W}{(1 - \in)\,(A * \rho_P)} \qquad \text{.....(37)}$$

$$A_r = \frac{\rho_P * d_V^3 * (\rho_P - \rho_g)\, g}{\mu^2} \qquad \text{.....(38)}$$

$$d_V = 1.13 dp \qquad \text{.....(39)}$$

$$deq = dem - (dem - deo)\, e^{-0.3 Z / D} \qquad \text{.....(40)}$$

$$dem = 0.374 \left(\pi D^2 * (U - U_{mf})\right)^{0.4} \qquad \text{.....(41)}$$

$$deo = 1.38 \left(Q_o^{0.4}\right)\left(g^{-0.2}\right) \qquad \text{.....(42)}$$

$$Q_o = A_o\, (U - U_{mf}) \qquad \text{.....(43)}$$

$$H_{mf} = H\,(1 - \in_b) \qquad \text{.....(44)}$$

$$\text{if } dp \langle = 0.01 \qquad U_{mf} = \frac{(\rho_P - \rho_g)^{0.934}\, g^{0.934}\, dp^{1.8}}{1111 * \mu^{0.87}\, \rho_G^{0.066}} \qquad \text{.....(45)}$$

$$dp \rangle\ 0.01 \quad U_{mf} = \left(\frac{\mu}{\rho_g\, d_V}\right)\left((1135.7 + 0.408\, Ar)^{0.5} - 33.7\right) \qquad \text{.....(46)}$$

3- Model (3) Particle Diameter

$$-dN_{Si} = -b\,dN_A = -\left(\frac{\rho_{Si}}{M_{Si}}\right)dV = -\left(\frac{\rho_{Si}}{M_{Si}}\right)d\left(\frac{4}{3}\pi r^3\right) \qquad .....(47)$$

$$= -4\pi\,\frac{\rho_{Si}}{M_{Si}}\,r^2\,dr \qquad .....(48)$$

$$-\frac{1}{V}\,\frac{d\,N_{Si}}{dt} = b\,K_1\,C_{Ad} \qquad .....(49)$$

$$-\frac{1}{\frac{4}{3}\pi r^3}\,4\pi\left(\frac{\rho_{Si}}{M_{Si}}\right)r^2\,\frac{dr}{dt} = b\,K_1\;C_{Ad} \qquad .....(50)$$

$$-\int_R^r \frac{dr}{r} = \frac{b\,K_1\,C_{Ad}\,M_{Si}}{3\,\rho_{Si}}\;d\;t \qquad .....(51)$$

$$dp_i = dp\;e^{-\frac{b\,K_1\,C_{Ad}\,M_{Si}\,t}{3\;\rho_{Si}}} \qquad .....(52)$$

$$C_{Ad} = \frac{C_{Ai}\left(1-\beta\,e^{-x}\right)}{1-\beta\,e^{-x}+K_1'} \qquad .....(53)$$

4- Model (4) Conversion of Silicon

$$1\text{-}\;\; X_{Si} = \frac{Volume\;of\;\;unreacted\;\;core}{Total\;\;volume\;\;of\;\;particle} = \frac{\frac{4}{3}\pi\,r^3}{\frac{4}{3}\pi\,R^3} = \left(\frac{r}{R}\right)^3 \qquad ..(54)$$

$$X_{Si} = 1-\left(\frac{r}{R}\right)^3 \qquad .....(55)$$

$$X_{Si}=1-\left(\frac{dp_i}{dp}\right)^3 \qquad .....(56)$$

or

$$X_{Si}=1-e^{-\frac{b\,K_1\,C_{Ad}\,M_{Si}\,t}{\rho_{Si}}} \qquad .....(57)$$

Computer Programs

Four programs were presented by Quick Basic to predict the data from above models.

1st program, kinetic model was used to evaluate the conversion of MeCl as function of Temp., using trial and error method because the conversion variable (X) was impossible to separate.

2nd program, same us in one, conversion of MeCl was evaluate as function of Temp., by using model two.

3rd program, used model three with two to predict the particle diameter as function of time, also different particle diameter mean different U_{mf} (minimum fluidization velocity), in which give different ratio of gas flow via bubble phase to total gas flow $\beta(\beta = U - U_{mf}/U)$, so this can be used to show the conversion of MeCl as function of time.

4th program, model four with three and two where used to show the conversion of Si and MeCl as function of time.

RESULTS AND DISCUSSION

1- Data obtained from model one and two for different weight of contact mass (silicon/ capper) and molar flow rate, these data compared with observed data [6] as shown in table (1).

These data were presented in Fig. (1) and Fig. (2), they show a good agreement between the observed and predicted data, also it show the increase of MeCl conversion with increase of Temp., this result from increase in reaction rate constant.

2- Fig. (3) and Fig. (4), for different weight of silicon and different velocity of MeCl gas, the two models are showing accelent agreement with each other, also it shows increase in conversion of MeCl with increasing weight of contact mass (increase in height) this due to increase in contact time between MeCl and Si, and decrease in conversion of MeCl with increasing velocity of MeCl, this is due to decrease in contact time.

3- Fig. (5), shows the decrease of particle diameter (dp) with time, this is due to consumption of silicon due to reaction with MeCl.

4- Fig. (6), shows decrease of MeCl conversion and increase of silicon conversion with time, because with time the total consumption of Si will increase and this mean decrease in dp or decrease in weight of contact mass, this will lead to decrease the contact time for MeCl with Si, this mean decrease MeCl conversion.

5- **Z** , (distance above the distributor) , it is very important factor in the second model, it icrease with increasing weight of contact mass and increasing velocity , it mean it is a function of high of the bed .

REFERENCES

1- American Chemical Society, "Cover essay", Organometallics 2001, 20, 4978-4992.
2- Lewis Larry N. and Ward William J., Ind. Eng. Chem. Res. 2002, 41, 397-402.
3- Ward W.J., Ritzer A., Carroll K.M., and Flock J.W., Journal of catalysis 100, 240-249, 1986.
4- Aramata Mikio, Fujioka Kazutoshi and Yu Yama Masahiro, Patent No: US 6,339,167 B2, Jan. 15, 2002.
5- Aramata Mikio, Tutsuya, Masahiro, Tetsuya and Hajime, Patent No: US 6,288, 258 B1, Sep. 11, 2001.
6- Voorhoeve R.J.H., "Organohalosilanes Precursorsors to Silicons", Elsevier publishing company, Amsterdam, 1967.
7- Geldart D., "Gas Fluidization Technology", John Wiley & Sons, USA, 1986.
8- Levenspiel Octave, "Chemical Reaction Engineering", Third edition, John Wiley & Sons, USA, 1999.

Table (1) observed and predicted data for conversion of MeCl as function of Temp

$W = 66.5$ gm , $F_{Ao} = 6.435$ gmol/hr

T	$X_{observed}$	$X_{model\text{-}1}$	$Y_{model\text{-}2}$
303	0.0043	0.01	0.009
323	0.0075	0.01	0.016
343	0.0264	0.03	0.026

$W = 53.5$ gm , $F_{Ao} = 4$ gml/hr

289	0.007	0.01	0.013
310	0.018	0.02	0.025
334	0.04	0.04	0.042
359	0.084	0.08	0.081

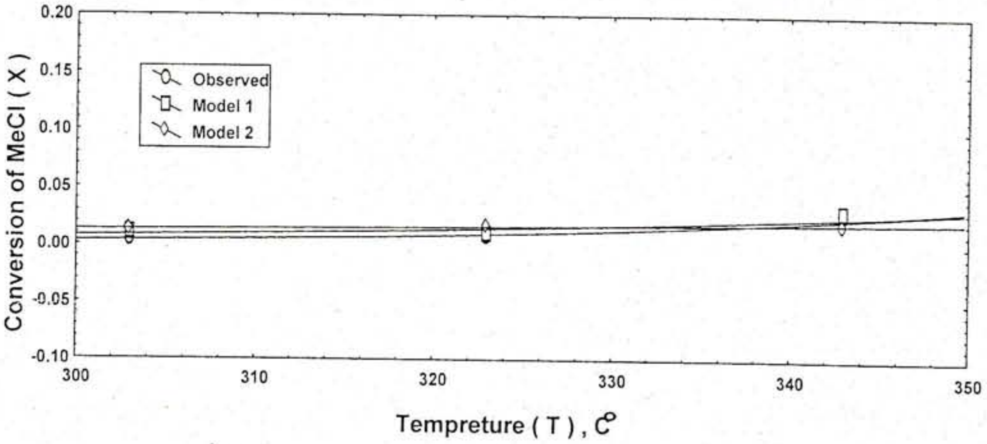

Figure (1) Conversion MeCl (X) Vs. Temperature (T) comparison between observed and predicted data W=66.5 gm, FA°= 6.435 gmol/hr

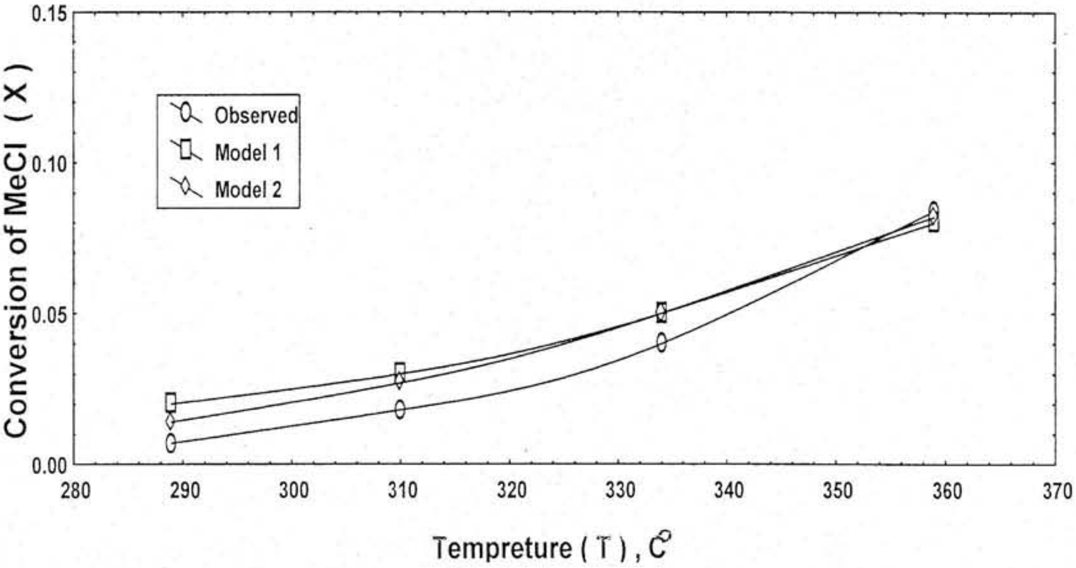

Figure (2) Conversion of MeCl (X) Vs. Temperature (T) comparison between observed and predicted data W=53.5 gm, FA°= 4 gmol/hr

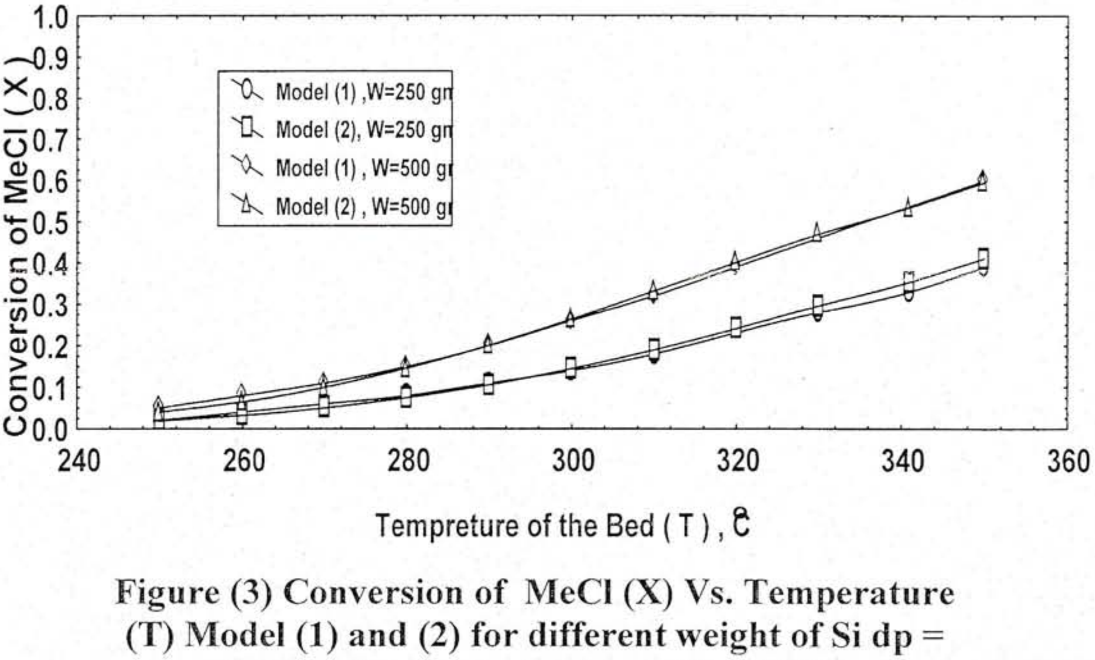

Figure (3) Conversion of MeCl (X) Vs. Temperature (T) Model (1) and (2) for different weight of Si dp = 0.1 cm, U=4 cm/s, D= 5 cm, T0= 300°C

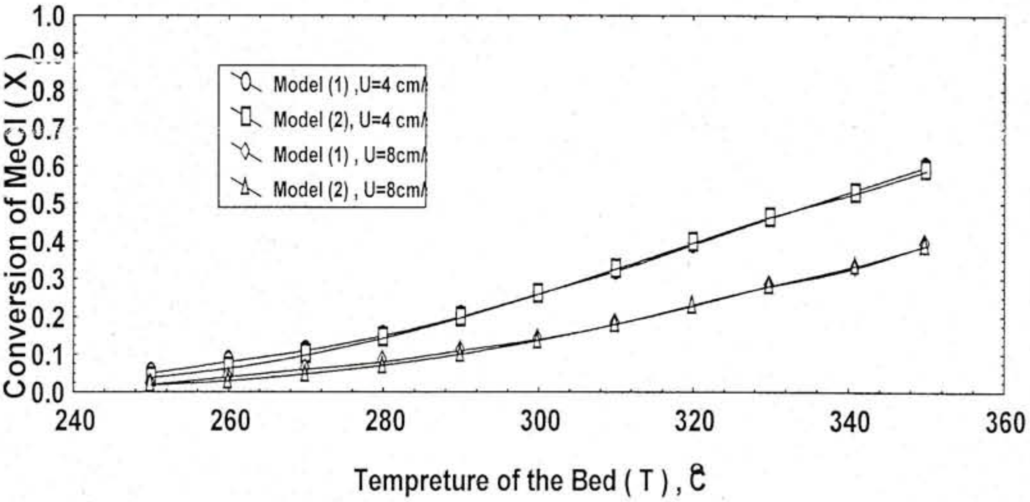

Figure (4) Conversion of MeCl (X) Vs. Temperature (T) Model (1) and (2) for different velocity of MeCl dp = 0.1 cm, W= 500gm , D= 5 cm, T_0= 300°C

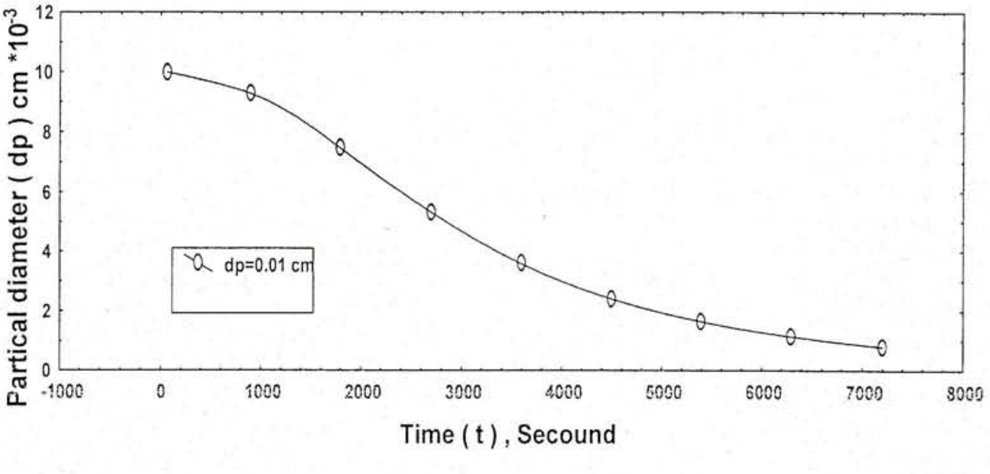

Figure (5) Partial diameter (dp) Vs. Time(t) Model (3), dp = 0.01 cm, U= 4 cm/s, H= 27.44 cm , D= 5 cm, T,T_0= 350, 300°C

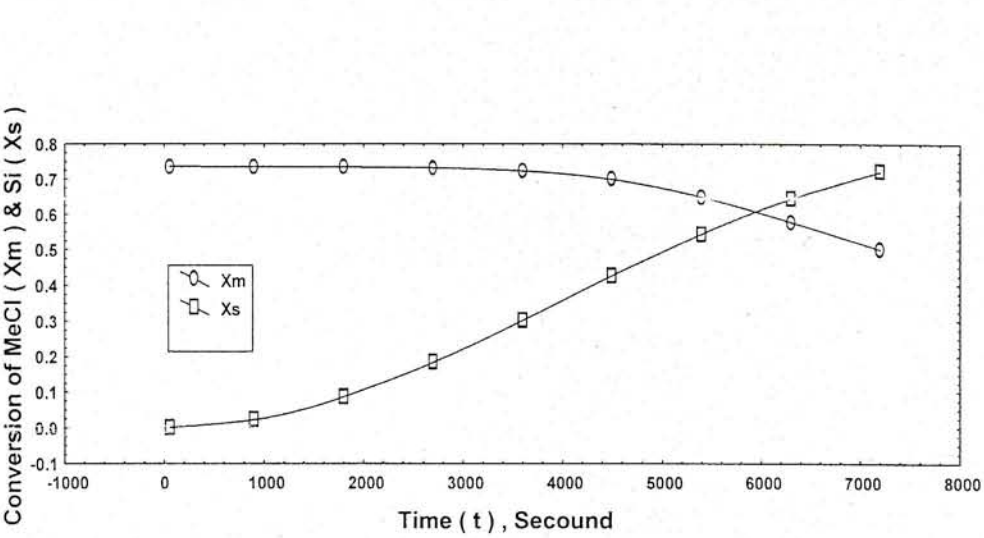

Figure (6)Conversion of MeCl and Si Vs. Time(t) Model (4), dp = 0.01 cm, U= 2 cm/s, H= 27.44 cm , D= 5 cm, T,T_0= 350, 300°C

Program - 1

```
                        Pt = ?
W = ?
                        U = ?
                    Q = U * At * 3600
y = ?
FA = (.0081282 * Q * pt) / (y + 273)
PRINT "U= "; TAB (5) ; U; TAB (15); "Cm / s"
PRINT "Q= "; TAB (5) ; Q; TAB (15); "Cm^3 /hr"
PRINT "pt= "; TAB (5) ; pt; TAB (15); "atm"
PRINT "W= "; TAB (5) ; w; TAB (15); "gm"
PRINT "To= "; TAB (5) ; y; TAB (15); "C"
PRINT "FAo= "; TAB (5) ; FA; TAB (15); "gmol / hr"
PRINT "TAB (4); "X"; TAB (17); "T"; TAB (32);"V"
PRINT "TAB (3); "------"; TAB (16); "-----"; TAB (31);"-----"
FOR T = 250 TO 350 STEP 5
FOR X = 0.0 TO 1 STEP. 01
K = 45473.71 * EXP (-3380.357/ T)
KA = .00083 * EXP (622.693 / T)
KB = .004003 * EXP (1370.53 / T)
A = INT (X * 1000 + .5) / 1000
B = KA * .667 * pt (y / T) * (1 – X) / (1 - .667 * X)
                                                  C = K * B
D = 1 + B
E = KB * .667 * .5 * X * pt * (y / T) / ( 1 - .667 * X)
F = C * (w / FA) / (D + E) ^ 2
R = INT (F * 1000 + .5) / 1000
G = R – A
V = INT (G * 1000 + .5) / 1000
IF V < .01 AND V > = 0 THEN PRINT A, T, V
NEXT X
NEXT T
```

Program - 2

```
                              Pt = ?
y = ?
x = ?
R = 82.06
dp = ?
rp = 2.32
rg = .001073
Me = .000215
Z = ?
W = ?
∈ = ?
H = w / ((At * rp) * (1 – E))
D = ?
g = 980
U = ?
$\in_{mf}$ = ?
di = ?
Ao = ?
dv = 1.13 * dp
          Ar = rg * dv ^ 3 * (rp – rg) * g / Me ^ 2
IF dp <= .01 THEN Umf = ((rp – rg) ^ .934 * g ^ . 934 * dp ^
1.8) / (1111 * Me^ .87 * rg ^ .066)
IF dp > .01 THEN Umf = (Me / rg * dv) * ((1135.7+.0408*Ar)^
.5– 33.7)
β = (U – Umf) / U
$d_{em}$ = .374 * (3.14 * (D ^ 2) * (U – Umf)) ^.4
Qo = Ao * (U – Umf)
$d_{eo}$ = 1.38 * (Qo ^ .4) * (g ^ -.2)
$d_e$ = dem – (dem – deo) * EXP (-.3 * Z / D)
     Kq = .75 * Umf + .975 * g ^ .25 * di ^ .5 / de ^ .25
$a_b$ = 6 / de
$u_a$ = .71 * (g * de) ^ .5 + (U – Umf)
$\in_b$ = (U – Umf) / ua
XC = Kq * ab * $\in_b$ * H / (β * U)
```

```
Hmf = H * (1 – ∈b)
PRINT "Pt="; TAB (5); pt; TAB (15); "atm"
PRINT "To="; TAB (5); y; TAB (15); "C"
PRINT "X="; TAB (5); X; TAB (15); "---"
PRINT "R="; TAB (5); R; TAB (15); "cm^3/atm gmol k"
PRINT "z="; TAB (5); z; TAB (15); "cm"
PRINT "H="; TAB (5); H; TAB (15); "cm"
PRINT "∈="; TAB (5); E; TAB (15); "---"
PRINT "W="; TAB (5); W; TAB (15); "gm"
PRINT "Hmf="; TAB (5); Hmf; TAB (15); "cm"
PRINT "dp="; TAB (5); dp; TAB (15); "cm"
PRINT "D="; TAB (5); D; TAB (15); "cm"
PRINT "g="; TAB (5); g; TAB (15); "cm/s^2"
PRINT "U="; TAB (5); U; TAB (15); "cm/s"
PRINT "Umf="; TAB (5); Umf; TAB (15); "cm/s"
PRINT "∈mf="; TAB (5); Emf; TAB (15); "----"
PRINT "di="; TAB (5); di; TAB (15); "cm^2/s"
PRINT "Ao="; TAB (5); Ao; TAB (15); "cm^2"
PRINT ;TAB (4); "T"; TAB (17); "X"
FOR T = 250 TO 350 STEP 10
K = 45473.71 * EXP (-3380.357 / T)
KA = .00083 * EXP (622.693 / T)
KB = .004003 * EXP (1370.53 / T)
A = (K / 3600) * KA * R * 2.34 * (y + 273)
B1 = 1 + .667 * KA * (y / T) * pt * ((1 – X) / (1 - .667 * X))
C = .667 * KB * .5 * X * pt * (y / T) / (1 - .667 * X)
K1 = A / (B1 + C) ^ 2 Kd = K1 * Hmf * (1 – ∈mf) / U
J = 1 – β * EXP (-XC) + β * Kd * EXP (-XC)
L = 1 – β * EXP (-XC) + Kd
X1 = INT ((1 – (J / L )) * 1000 + .5) / 1000
PRINT T, X1, Umf
NEXT T
```

Program -3

```
Pt = ?
Y = ?
T = ?
                              R = 82.06
dp = ?
rp = 2.32
rg = .001073
Me = .000215
MB = 28
Z = ?
W = ?
∈ = ?
H = w / ((At * rp) * (1 – E))
D = ?
g = 980
U = ?
∈mf = ?
di = ?
Ao = ?
PRINT “pt=”; TAB (5); pt; TAB (15); “atm”
PRINT “To=”; TAB (5); y; TAB (15); “C°”
PRINT “T=”; TAB (5); T; TAB (15); “C°”
PRINT “R=”; TAB (5); R; TAB (15); “cm^3 atm/gmol k”
PRINT “z=”; TAB (5); z; TAB (15); “cm”
PRINT “H=”; TAB (5); H; TAB (15); “cm”
PRINT “MB=”; TAB (5); MB; TAB (15); “gm/gmo1”
PRINT “dp=”; TAB (5); dp; TAB (15); “cm”
PRINT “D=”; TAB (5); D; TAB (15); “cm”
PRINT “g=”; TAB (5); g; TAB (15); “cm/s^2”
PRINT “U=”; TAB (5); U; TAB (15); “cm/s”
PRINT “W=”; TAB (5); W; TAB (15); “gm”
PRINT “ ∈=”; TAB (5); E; TAB (15); “---”
PRINT “Me=”; TAB (5); Me; TAB (15); “gm.cm/s”
PRINT “ ∈mf=”; TAB (5); Emf; TAB (15); “---”
PRINT “di=”; TAB (5); di; TAB (15); “cm^2/s”
```

```
PRINT "Ao="; TAB (5); Ao; TAB (15); "cm^2"
PRINT "rp="; TAB (5); rp; TAB (15); "gm/cm^3"
PRINT "rg="; TAB (5); rg; TAB (15); "gm/cm^3"
PRINT ; TAB (4) ; "t"; TAB (17) ; "X"
CAi = .667 * pt / (R * (y + 273))
K = 45473.71 * EXP (-3380.357 / T)
KA = .00083 * EXP (622.693 / T )
KB = .004003 * EXP (1370.53 / T)
A = (K/ 3600) * KA * R * 2.34 * (y + 273)
B1 = 1 + .667 * KA * (y / T) * pt * ((1 – x) / (1 - .667 * X))
C = .667 * KB * .5 * X * pt * (y / T) / (1 - .667 * X)
K1 = A / (B1 + C) ^ 2
FOR I = 60 TO 7200 STEP 60
dv = 1.13 * dp
Ar = rg * dv ^ 3 * (rp – rg) * g / Me ^ 2
IF dp > .01 THEN Umf = (Me / rg * dv) * ((1135.7 + .0408 * Ar)
^ .5 – 33.7)
IF dp <=.01 THEN Umf=((rp–rg)^ .934*g^ .934*dp^
1.8)/(1111*Me^ .87*rg^.066)
β = (U – Umf) / U
dem = .374 * (3.14 * (D ^ 2) * (U – Umf)) ^ .4
Qo = Ao * (U – Umf)
deo = 1.38 * (Qo ^ .4) * (g ^ -.2)
de = dem – (dem – deo) * EXP (-.3 * Z / D)
Kq = .75 * Umf + .975 * g ^ .25 * di ^ .5 / de ^ .25
ab = 6 / de
ua = .71 * (g * de) ^ .5 + (U – Umf)
∈b = (U – Umf) / ua
Hmf = H * (1 – ∈b)
XC = Kq * ab * ∈b * H / (β * U)
Kd = K1 * Hmf * (1 – ∈mf) / U
S2 = K1 * MB * I *CAi * (1-β*EXP (-XC)) / (3*rp*(1–β EXP (-
XC) + Kd))
dp = dp * EXP (-S2)
J = 1 – β * EXP (-XC) + β * Kd * EXP (-XC)
```

```
L = 1 – β * EXP (-XC) + Kd
X1 = INT ((1 – (J / L)) * 1000 + 0.5) / 1000
PRINT I, X1, dp
NEXT
```

Program - 4

```
Pt = ?
Y = ?
T = ?
R = 82.06
dp = ?
dpi = ?
rp = 2.32
rg = .001073
Me = .000215
MB = 28
Z = ?
W = ?
∈ = ?
H = w / ((At * rp) * (1 – E))
D = ?
g = 980
U = ?
∈mf = ?
di = ?
Ao = ?
PRINT "pt="; TAB (5); pt; TAB (15); "atm"
PRINT "To="; TAB (5); y; TAB (15); "C°"
PRINT "T="; TAB (5); T; TAB (15); "C°"
PRINT "R="; TAB (5); R; TAB (15); "cm^3.atm/gmol k"
PRINT "z="; TAB (5); z; TAB (15); "cm"
PRINT "H="; TAB (5); H; TAB (15); "cm"
PRINT "MB="; TAB (5); MB; TAB (15); "gm/gmmo1"
PRINT "dp="; TAB (5); dp; TAB (15); "cm"
PRINT "D="; TAB (5); D; TAB (15); "cm"
```

```
PRINT “g=”; TAB (5); g; TAB (15); “cm/s^2”
PRINT “U=”; TAB (5); U; TAB (15); “cm/s”
PRINT “W=”; TAB (5); W; TAB (15); “gm”
PRINT “ ∈=”; TAB (5); E; TAB (15); “---”
PRINT “Me=”; TAB (5); Me; TAB (15); “gm.cm/s”
PRINT “ ∈mf=”; TAB (5); Emf; TAB (15); “---”
PRINT “di=”; TAB (5); di; TAB (15); “cm^2/s”
PRINT “Ao=”; TAB (5); Ao; TAB (15); “cm^2”
PRINT “rp=”; TAB (5); rp; TAB (15); “gm/cm^3”
PRINT “rg=”; TAB (5); rg; TAB (15); “gm/cm^3”
PRINT ; TAB (4) ; “t”; TAB (17) ; “Xm”; TAB (31); “Xsi”
CAi = .667 * pt / (R * (y + 273))
K = 45473.71 * EXP (-3380.357 / T)
KA = .00083 * EXP (622.693 / T)
KB = .004003 * EXP (1370.53 / T)
A = (K/ 3600) * KA * R * 2.34 * (y + 273)
B1 = 1 + .667 * KA * (y / T) * pt * ((1 – X) / (1 - .667 * X))
C = .667 * KB * .5 * X * pt * (y / T) / (1 - .667 * X)
K1 = A / (B1 + C) ^ 2
FOR I = 60 TO 7200 STEP 60
dv = 1.13 * dp
Ar = rg * dv ^ 3 * (rp – rg) * g / Me ^ 2
IF dp > .01 THEN Umf = (Me / rg*dv) * ((1135.7+.0408 * Ar) ^
.5–33.7)
IF dp <=.01 THEN Umf=((rp–rg)^ .934*g^ .934*dp^
1.8)/(1111*Me^ .87*rg^.066)
β = (U – Umf) / U
dem = .374 * (3.14 * (D ^ 2) * (U – Umf)) ^ .4
Qo = Ao * (U – Umf)
deo = 1.38 * (Qo ^ .4) * (g ^ -.2)
de = dem – (dem – deo) * EXP (-.3 * Z / D)

Kq = .75 * Umf + .975 * g ^ .25 * di ^ .5 / de ^ .25
ab = 6 / de
ua = .71 * (g * de) ^ .5 + (U – Umf)
∈b = (U – Umf) / ua
```

```
Hmf = H * (1 – ∈b)

XC = Kq * ab * ∈b * H / (β * U)

Kd = K1 * Hmf * (1 – ∈mf) / U
S2 = K1 * MB * I * CAi * (1-β * EXP (-XC))/(6*rp* (1–β*EXP
(-XC) + Kd))
dp = dp * EXP (-S2)
J = 1 – β * EXP (-XC) + β * Kd * EXP (-XC)
L = 1 – β * EXP (-XC) + Kd
X1 = INT ((1 – (J / L)) * 1000 + 0.5) / 1000
X2 = INT ((1 – (dp/dpi)) *1000 + 0.5) / 1000
PRINT i, X1, X2
NEXT
```

نماذج رياضية لتفاعل مباشر لكلوريد المثيل مع السيليكون في مفاعل الطبقة المتميعة

إحسان بكر　　د. ثامر جاسم　　مؤيد جاسم
قسم الهندسة الكيمياوية- الجامعة التكنولوجية　　شركة ابن سينا

الخلاصة

تعتبر مركبات المثيل كلوروسايلانس من المواد الأولية المهمة في انتاج البولي ألكيل سيليكونات و هي المواد الداخلة في زيوت السليكون و مطاط السليكون. و من الطرق الأساسية في الانتاج التجاري للمثيل كلوروسايلانس هي ما يعرف بالطريقة المباشرة و التي تتضمن التفاعل بين عنصر السليكون و كلوريد المثيل. إن المنتوج الأساسي هو ثنائي مثيل ثنائي كلوريد السليكون الذي يستخدم لانتاج البولي ثنائي مثيل السليكون.

إن الهدف من هذا البحث هو الحصول على موديلات رياضية توضح سلوك التفاعل. و قد تم الحصول على أربع موديلات، هذه الموديلات تأخذ بنظر الاعتبار حركية التفاعل و المعادلات الفيزيائية ، الكيميائية و التصميمية لمفاعل الطبقة المتميعة.

هذه المعادلات تمثل نسبة التحول لمثيل الكلورايد كدالة لدرجة الحرارة و الزمن. و تمت مقارنة النتائج مع مثيلتها المستحصلة من النتائج العملية لبحوث علمية سابقة و كانت على درجة جيدة من التوافق معها.

الكلمات الدالة

مفاعل الطبقة المتميعة، التفاعل المباشر، نموذج رياضي.