EXPERIMENTAL STUDY AND MATHEMATICAL MODELING OF REACTION KINETIC AND TRANSPORT MECHANISM OF U_3O_8 REDUCTION USING H_2 GAS

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Abstract

Reduction of U_3O_8 by H_2 gas is among the important steps in manufacturing coated UO_2 fuel kernels used in High Temperature Reactor (HTR). Most of previous studies in this area focus on finding operating conditions, such as temperature and reaction time, which can be used in producing high quality UO_2 kernel. The present work deals with experimental study and modeling of the transport mechanism and reaction kinetic of the U_3O_8 reduction. The reduction process was conducted in isothermal condition using a high temperature furnace namely the Opale furnace. The effects of different reduction temperature (973 K, 1073 K, and 1173 K) and reaction time on the reaction conversion were investigated. A mathematical model describing H_2 diffusion inside the kernel and the reaction kinetic were proposed and solved numerically. Effective diffusivity and reaction rate constant were determined by least square method comparing the conversion obtained from the experiment and that from the simulation. The experimental result showed most of the reaction took place at the first 60 minutes and after that the conversion increased slightly as the reaction time proceeded. Within the temperature range of 973 K and 1173 K, the effect of temperature on conversion is considerably small. It was found that the reaction rate could be approximated by the first order reaction to H_2 gas and the volume reaction model for U_3O_8 reactant consumption in which particle size was allowed to change during the course of reaction. The effect of temperature on reaction rate constant (k_s) and effective diffusivity of the initial solid (D_{e_0}) was estimated using the Arrhenius equation resulting the following equations $k_s = 422.843 exp(-\frac{4,149}{T})$, and $D_{e_0} = 1.98 \times 10^{-6} exp(-\frac{3,892}{T})$. The value of Thiele modulus was about 6 suggesting that the diffusion regime controls the overall reduction process.

Keywords: U_3O_8 reduction, Diffusion-controlled reaction, UO_2 Kernel, Effective diffusivity, Thiele Modulus.

Nomenclatures

A	Reactant A
a, b, c, d	Stoichiometric coefficient
B	Reactant B
C	Concentration, mole/m^3
D_e	Effective diffusivity, m^2/s
$F(X)$	Part of the reaction rate that depend on the conversion
$g(X)$	Function on Eq. (6)
i	Position index
j	Time index
k	First order kinetic parameter
min	minimal
r	Spatial coordinate, m
$r(c_A)$	Part of the reaction rate that depend on the concentration, mole/m^3/s
$(-r)$	Reaction rate, mole/m^3/s
ref	reference
R	Outer diameter, m
$R(C)$	Dimensionless reaction rate
s	At surface
t	Time, s
w	Weight, g
X	Conversion
z	Dimensionless coordinate

Greek Symbols

β	A constant on Eq. (5)
τ	Dimensionless time
ϕ	Thiele modulus

1. Introduction

Nuclear power plant that promising in terms of safety, reliability, availability, efficiency and highly economic competitiveness is High Temperature Reactor (HTR) type. HTR is one of the advanced power reactors which has passive and inherent safety systems. The fuel used in HTR is coated particles with a core of uranium dioxide (UO_2) kernels by 3-20 percent of enrichment. Preparation of UO_2 kernels carried out by National Nuclear Energy Agency (NNEA) - Indonesia, using a wet process (sol-gel process), followed by calcination, reduction and sintering [1].

Reduction is one of the important stages of manufacture of the UO_2 kernels, where the U_3O_8 kernels that resulted from calcinations process, will be reduced using H_2 gas at high temperature to produce UO_2 kernels. A lot of research on the this reduction process has been done, but with more emphasis on finding the optimum conditions. The kinetics and transport mechanism of the U_3O_8 reduction reaction study requires further researches with temperature and time variables [2], in order to obtain the design process parameters to support data reduction process.

This research is aimed to study the transport mechanism and the reaction rate, to formulate a mathematical model, and to determine the value of rate processes parameters of the U_3O_8 kernels reduction using H_2 as a reducing gas.

2. Experimental Procedure

From previous studies [3, 4] found that the optimum conditions of U_3O_8 reduction process at temperature range of 1023-1073 K for 180-240 minutes. It was used as basis of determining the research variables.

There are 3 sets of experiments at 3 different temperatures (973 K, 1073 K, and 1173 K) with 6 times (10 min, 20 min, 60 min, 120 min, 180 min and 240 min) of the reduction process.

The kernel samples are weighed before and after the reduction process to determine the weight loss percentage, which can then be used to calculate reaction conversion (X).
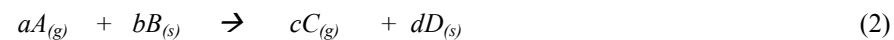
Simulation of mathematical models of this reduction process using *MATLAB* software with *ode15s* solver to solve partial differential equations, whereas to obtain the parameters process used *fminsearch* optimization.

3. Theory

The process of U_3O_8 reduction using H_2 gas is isothermal non-catalytic gas-solid reactions with the following equations :

$$H_{2(g)} \; + \; \frac{1}{2}U_3O_{8(s)} \; \rightarrow \; H_2O_{(g)} \; + \; \frac{3}{2}UO_{2(s)} \tag{1}$$
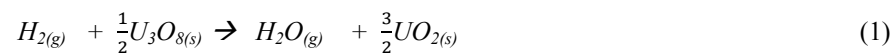
can also be written in the form :

$$aA_{(g)} \; + \; bB_{(s)} \; \rightarrow \; cC_{(g)} \; + \; dD_{(s)} \tag{2}$$

Transport processes in the reduction of U_3O_8 take place in series with the following mechanisms : mass transfer of H_2 gas to the surface of a solid U_3O_8, H_2 gas diffusion from the solid surface into the grain of U_3O_8, the chemical reaction between H_2 gas and U_3O_8 generating UO_2 and H_2O vapor, then mass transfer of H_2O vapor in the solid to the solid surface, and mass transfer of H_2O vapor from the solid surface to the gas phase. Mass transfer of gas to the solid surface generally takes place relatively quickly, and the reaction between H_2 gas and U_3O_8 solid is irreversible, so that the controlling steps are diffusion and chemical reactions simultaneously.

The assumptions used to compose the mathematical model on the reduction reaction of U_3O_8, among others: the system is isothermal, H_2 gas in the system is homogeneous, and the first order reaction of H_2 gas.

The reaction rate of this process using the assumption of first order to the concentration of H_2 gas, while the consumption of solid reactants can be represented using the volume reaction model (VRM) [5]:

$$F(X) = 1 - X \tag{3}$$

so that the reduction reaction rate becomes:

$$-br_A = -r_B = kC_A(1-X) \tag{4}$$

VRM is a model of the kinetics of solid reactant consumption that measures the reaction in all parts of the solid pellets, or in other words, the entire volume of solids participate in the reaction. This model uses the assumption that the system is at isothermal conditions and diffusion in the pellets is equimolar counter-diffusion.

The local porosity may change during the reaction, caused by the consumption of solid reactants or the difference between the volume of the solid reactant (B) and the solid product (D). In this case, the porosity of solid is changed by chemical reaction, thus causing a change in the effective diffusivity of gas. In other words, changes in the value of the effective diffusivity constant (D_e) is affected by the conversion (X). It was tried the models that D_e changes linearly with respect to X so that it can be approximated by the equations:

$$D_e = D_{e0}(1 + \beta X) \tag{5}$$
$$D_e = D_{e0}g(X) \tag{6}$$

The mathematical model proposed for the reduction process in the form of dimensionless partial differential equations which based on the gas-solid reaction model [6, 7-10] as follows:

$$\frac{\partial C}{\partial \tau} = \frac{1}{\phi_s^2}\left[\frac{2}{z}g(X)\frac{\partial C}{\partial z} + \frac{d(g(X))}{dz}\frac{\partial C}{\partial z} + g(X)\frac{\partial^2 C}{\partial z^2} - \phi_s^2 F(X)R(C)\right] \tag{7}$$

$$\frac{\partial X}{\partial \tau} = \frac{1}{2}F(X)R(C) \tag{8}$$

With the dimensionless variables as follows :

$$z = {r}/{R}, \tau = {t}/{\tau_{ref}}, C = {C_A}/{C_{As}}, \text{dan } X = 1 - {C_B}/{C_{B0}} \tag{9}$$

The value of τ_{ref} can be defined as follows:

$$\tau_{ref} = {C_{B0}}/{(br(C_{As}))} = {C_{B0}}/{(bk_sC_{As})} \tag{10}$$

whereas:

$$g(X) = 1 + \beta X; \quad F(X) = 1 - X; \quad R(C) = {r(C_A)}/{r(C_{As})} \tag{11}$$

Initial and boundary conditions in this case are:

$$\tau = 0; X = 0; C = 0 \tag{12}$$
$$z = 1; C = 1 \tag{13}$$
$$z = 0; \frac{\partial C}{\partial z} = 0 \tag{14}$$

These dimensionless partial differential equations can be elaborated by finite difference approximation as in *Appendix A*, so that can be solved by computer programme with the algorithmic as seen in *Appendix B*.

From dimensionless differential equations derived a parameter called the Thiele modulus. In the Foggler [11] mention that Thiele modulus is a measure of the ratio of "a" surface reaction rate to "a" rate of diffusion through the catalyst pellet:

$$\phi_s^2 = \frac{k_s R^2 C_{A_s}^{n-1}}{De} = \frac{k_s R C_{A_s}^n}{De[(C_{A_s}-0)/R]} = \frac{"a"\ surface\ reaction\ rate}{"a"\ diffusion\ rate} \quad (15)$$

When the Thiele modulus is large, internal diffusion usually limits the overall rate of reaction; when it is small, the surface reaction is usually rate-limiting.

In this case, Thiele modulus for a first order reaction as follows:

$$\phi_s^2 = R^2 \frac{k_s}{D_{e0}} \quad (16)$$

4. Results and Discussion

4.1. Effect of temperature and time against the mass and O/U ratio of kernels

The U_3O_8 reduction process with H_2 gas resulting in reduction of two oxygen atoms of U_3O_8 into UO_2 kernels, so it will result in a reduced kernels mass after the reduction process. Figure 1 shows the influence of temperature and time to kernels weight loss percentage. Where:

$$Weight\ loss, \% = \frac{(w_0 - w_t)}{w_0} x100\% \quad (17)$$
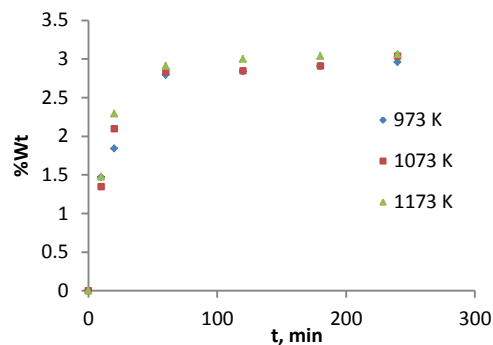

Fig. 1. The Influence of Temperature and Time to Kernels Weight Loss.

It can be seen from Fig. 1 that the weight loss percentage curves increase with time is nonlinear, in which there was a large increase of weight loss percentage in the first 60 minutes, but after that the increase is very small, even approaching a constant, ie $\approx 3\%$.

One of the important requirements of the UO_2 kernels as HTR fuel is stoichiometric O/U ratio has to be 2.00 because in this condition the UO_2 kernels have the highest thermal conductivities. In this study found that the higher the temperature and the longer time of reduction process, the smaller O/U ratio that obtained (O/U$\approx$2). The reduction process at temperature of 973-1173 K for 1-4 hours earned O/U ratio ranging from 2.10 to 2.02. This could be due to oxidation during harvesting and storing the kernels of the reduction results, because UO_2 compound is very easily oxidized. Another reason is the incomplete chemical reactions that occured during the reduction process due to the densification in the kernels (sintering). To avoid oxidation, kernels of the reduction results should be

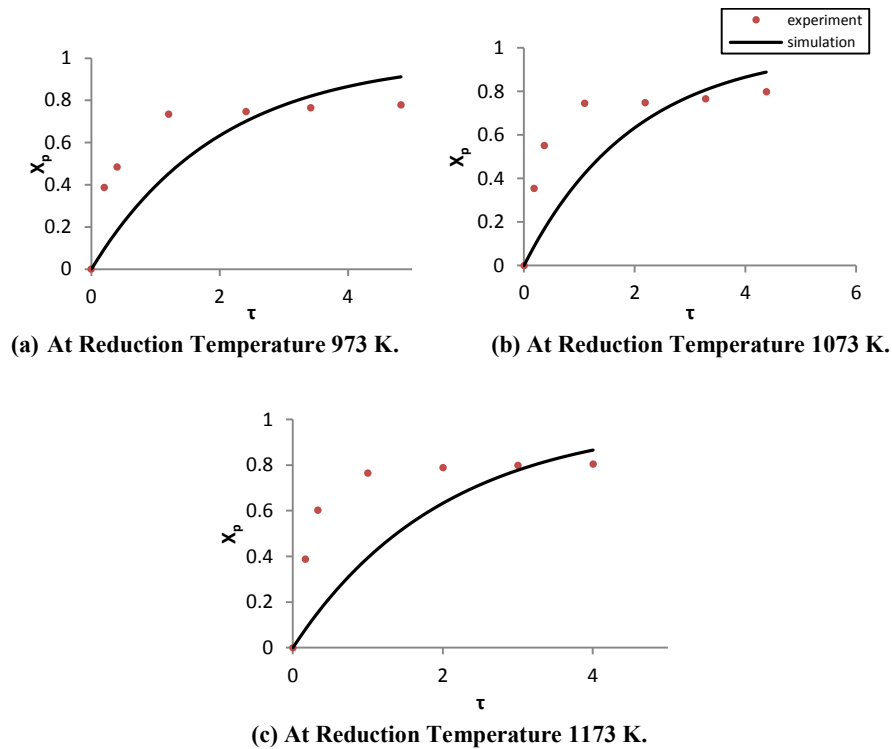stored under vaccum in exicator, before being used in the further stages of the fuel particles manufacturing.

4.2. Mathematical model

The mathematical model used in this study using two approaches, among others:

4.3. Unchanging particle size approach

Mathematical model for the reduction process using unchanging particle size approach has been done in the previous study [12]. Model simulation using *MATLAB* software generates good graphics data fitting, but one of the β parameter is negative. It means that the diffusion rate of H_2 gas getting down during the reduction reaction. It is not appropriate to unchanging particle size approach. The reduction in the number of oxygen atoms during the reduction process with unchanging particle size will increase the porosity of the material, so that the rate of diffusion will be faster or $D_e > D_{e_0}$. In other words, the β parameter value should be positive.

To obtain a positive value of β, the Lower Bound (LB) of the parameters to be optimized should be equal to zero. Optimization results with positive β can be seen in Fig. 2.

(a) At Reduction Temperature 973 K.   **(b) At Reduction Temperature 1073 K.**

(c) At Reduction Temperature 1173 K.

Fig. 2. The Average Conversion in Dimensionless Time, Assuming Unchanging Particle Size During the Reaction With Positive β.

From Fig. 2. above it can be seen that the graph of simulation results with unchanging particle size approaches and the positive value of β parameter does not closed to the experimental data, making it less appropriate to be used in the reduction process.
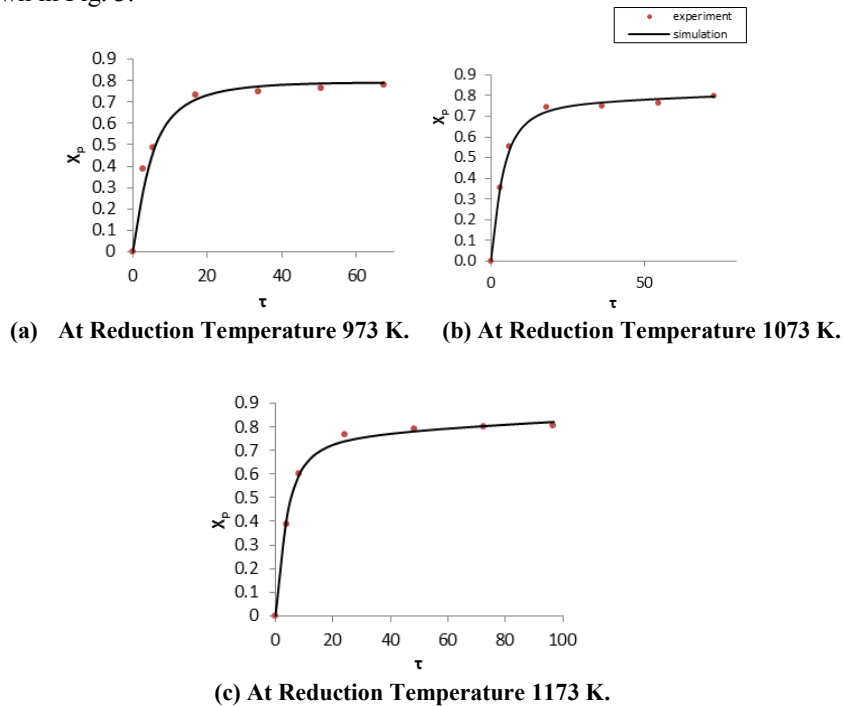
4.3.1. Changing particle size approach

During the reduction reaction, occurs the weightloss and shrinkage of kernel size. Shrinkage is due to the sintering process which makes the kernel becomes solidified. Reduced mass can be attributed to the smaller volume of the kernel. So the calculation of the conversion to the spherical shape of kernel ($V = \frac{4}{3}\pi R^3$) can be approximated by the following formula:

$$X = \frac{R_0{}^3 - R_t{}^3}{R_0{}^3 - R_{min}{}^3} \tag{18}$$

where at $X = 0 \rightarrow R_t = R_0$ and at $X = 1 \rightarrow R_t = R_{min}$. Thus obtained:

$$R_t = \left(R_0{}^3 - \left(R_0{}^3 - R_{min}{}^3\right)X\right)^{\frac{1}{3}} \tag{19}$$

The correlation equation between the conversion (X) and the radius (R) then is used as a correction of the mathematical model, which R varies during the reduction reaction or changing particle size. Simulation results obtained the graph shown in Fig. 3.

(a)   **At Reduction Temperature 973 K.**   (b) **At Reduction Temperature 1073 K.**

(c) At Reduction Temperature 1173 K.

**Fig. 3. The Average Conversion in Dimensionless
Time with the Changing Particle Size Assumption.**

In Fig. 3 graphically shows that the simulation results are quite closer to the experimental data. It showed that mathematical models with changing particle size approach can be used to describe the U_3O_8 reduction process with H_2 gas.

The higher the operating temperature, the greater the average conversion obtained. However, at any given time, the average conversion at that three temperatures close to constant. This is because the porosity of kernels become smaller due to sintering process during the reduction reaction. The smaller porosity resulting the slower diffusion of H_2 gas, thus inhibiting the reaction between the H_2 gas and U_3O_8. Thus the measured conversion was not significant increasing.

From the simulation results assuming changing particle size, obtained kernel radius (R) and the Thiele modulus (ϕ_s) shown in Table 1:

Table 1. Thiele Modulus (ϕ_s) at Various Times and Temperatures.

Reduction time (minutes)	At reduction temperature 973 K	At reduction temperature 1073 K	At reduction temperature 1173 K
0	5.9631	6.0345	6.1656
10	5.7766	5.8357	5.9206
20	5.6689	5.7276	5.8167
60	5.5485	5.6118	5.7226
120	5.5214	5.5834	5.6956
180	5.5156	5.5727	5.6810
240	5.5131	5.5652	5.6695

Table 1 shows that the value of Thiele modulus >> 1 at three temperatures. Large values of Thiele modulus indicate that the surface reaction is rapid and that the reactant is consumed very close to the external pellet surface and very little penetrates into the interior of the pellet [11]. It is called as diffusion regime or in other words diffusion limits the overall rate of reaction. While the parameter values obtained from the simulation can be seen in Table 2.

Table 2. Model Parameters Values at Various Reduction Temperatures.

Model parameters	At reduction temperature 973 K	At reduction temperature 1073 K	At reduction temperature 1173 K
k_s (1/s)	6.9695	8.3088	12.0908
D_{e_0} (m²/s)	4.24×10^{-8}	4.93×10^{-8}	6.88×10^{-8}
β	-0.9968	-0.9949	-0.9929

From the simulation results obtained that β has a negative value, which indicates that the greater the conversion, the slower the rate of diffusion. This is because the kernels porosity become smaller or kernels become more condensed leads to reduction of porosity or free space for diffusion of H_2 gas.

Parameters of the simulation results above, has a greater value as the temperature increases, but β value has relatively same at each temperature above. So it can take the average β value *(β_{av} = -0.99486)*. Furthermore, optimize parameters at each temperature with the β_{av} values. Optimization results obtained great chart data fitting with an error that is not much different from an error resulted with individual β. This indicates that the β_{av} value can be applied at any temperatures of reduction. Optimization results with β_{av} value at temperature of 973 K, 1073 K, and 1173 K generates the parameters k_s and D_{e_0} as shown in Table 3:

Table 3. Optimization Results of Model Parameters Values with β_{av}.

Model parameters	At reduction temperature 973 K	At reduction temperature 1073 K	At reduction temperature 1173 K
k_s (1/s)	6.1250	8.3078	12.7472
D_{e_0} (m^2/s)	3.74x10^{-8}	4.93x10^{-8}	7.44x10^{-8}

Like chemical reaction, diffusion is a thermally activated process and the temperature dependence of diffusion appears in the diffusivity as an Arrhenius-type equation [13].

Parameters k_s and D_{e_0} as temperature functions can be approximated by the Arrhenius equations as follows:

$$k_s = 422.843 \exp(-\frac{4,149}{T}) \tag{20}$$

$$D_{e_0} = 1.98x10^{-6} \exp\left(-\frac{3,892}{T}\right) \tag{21}$$

Parameters k_s and D_{e_0} as temperature functions and β_{av} parameter can then be used to predict the reduction process at various temperatures. For example, to obtain a high conversion at a certain temperature reduction, then the simulation using k_s and D_{e_0} as temperature function and β_{av} parameters as well, it can be predicted how long it takes the reduction process.

5. Conclusion

From research and calculations that has been carried out, it can be concluded that transport processes in the U_3O_8 reduction with H_2 gas consists of two mechanisms: diffusion and chemical reaction. Mathematical modeling of that reduction process can be approximated using the volume reaction model for solid reactant consumption, while consumption of the reactant gas can be approached using a first order reaction equation, with changing particle size approach. Kernels size shrinkage or sintering during the reduction reaction resulting in the local effective diffusivity (D_e) of H_2 gas in the U_3O_8 kernels is getting smaller, with D_e was affected by conversion (X) with equation $D_e = D_{e_0}(1 - 0.99486X)$. As for the parameters k_s and D_{e_0} at various temperatures can be approximated by the Arrhenius equation:

$$k_s = 422.843 \, exp\left(-\frac{4,149}{T}\right) \quad \text{and} \quad D_{e_0} = 1.98x10^{-6}exp(-\frac{3,892}{T}) \tag{22}$$

The kernels size is changing anytime influenced by conversion, can be approximated with the equation:

$$R_t = \left(R_0{}^3 - \left(R_0{}^3 - R_{min}{}^3\right)X\right)^{\frac{1}{3}} \tag{23}$$

Mathematical model simulation that has been done can be used as prediction to get O/U ratio of kernels that fulfil the HTR fuel specification.

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Appendix A

Solution of Partial Differential Equations

Analytical approach is difficult for solving mathematical model of unsteady state non-catalytic gas-solid reaction, i.e., reduction of U_3O_8, because there are two simultaneous and partial differential equations, so required numerically solution. Partial differential equations modified with finite difference approximation [14] so that it can easily solved by *MATLAB* programme:

$$\frac{\partial^2 C}{\partial z^2} = \frac{(C)_{i-1} - 2(C)_i + (C)_{i+1}}{(\Delta z)^2} \tag{A-1}$$

$$\frac{\partial C}{\partial z} = \frac{(C)_{i+1} - (C)_{i-1}}{2(\Delta z)} \tag{A-2}$$

$$\frac{\partial X}{\partial z} = \frac{(X)_{i+1} - (X)_{i-1}}{2(\Delta z)} \tag{A-3}$$

In this case i is the index position, wherein:

$$z_i = z_0 + \Delta z(i - 1) \tag{A-4}$$

Equation (7) turns into:

$$\frac{\partial (C)_i}{\partial \tau} = \frac{1}{\phi_s^2} \left[\left(\frac{g(X)_i}{z} \frac{[(C)_{i+1} - (C)_{i-1}]}{\Delta z} \right) + \left(\beta \frac{[(X)_{i+1} - (X)_{i-1}]}{2\Delta z} \frac{[(C)_{i+1} - (C)_{i-1}]}{2\Delta z} \right) + \left(g(X)_i \frac{[(C)_{i-1} - 2(C)_i + (C)_{i+1}]}{(\Delta z)^2} \right) - \phi_s^2 F(X)_i R(C)_i \right] \tag{A-5}$$

Equation (8) turns into:

$$\frac{\partial (X)_i}{\partial \tau} = \frac{1}{2} F(X)_i R(C)_i \tag{A-6}$$

Other equations are:

$$g(X)_i = 1 + \beta(X)_i \tag{A-7}$$

$$F(X)_i = 1 - (X)_i \tag{A-8}$$

$$R(C)_i = \frac{r(C_A)}{r(C_{As})} = (C)_i \tag{A-9}$$

Equations (A-1) – (A-9) with initial and boundary condition of Eqs. (12) – (14) can be solved using the computer programming with Matlab, generate the C and X in a variety of dimensionless positions and time ($C = f(z, \tau)$; $X = f(z, \tau)$).

After local conversion profile (X) is obtained, then the overall conversion of the solid particles (X_p) can be calculated by numerical integration [14]:
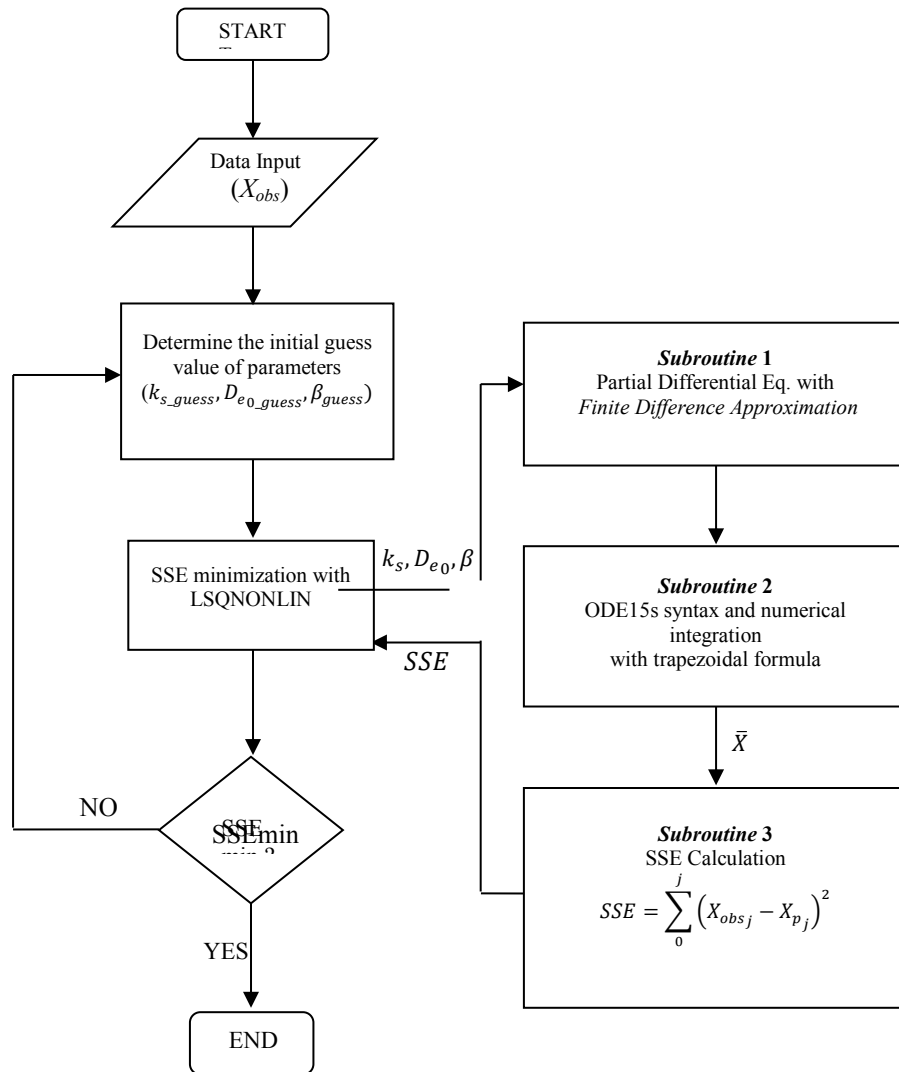
$$X_p = 3 \int_0^1 X z^2 dz \tag{A-10}$$

The parameters value in the model can be searched by fitting of mathematical model simulation results (X_p) to experimental data (X_{obs}) by using the method of minimizing the Sum of Square of the Errors (SSE) is defined as follows:

$$SSE = \sum_j^n \left(X_{obs_j} - X_{p_j} \right)^2 \tag{A-11}$$

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Appendix B
Computer Programme

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To obtain the process parameters was conducted by comparing experiment data to the observation data. The fitting process is done by minimizing the SSE. The algorithmic of the programme is shown in Fig. A-1 :

START

Data Input
(X_{obs})

Determine the initial guess
value of parameters
$(k_{s\_guess}, D_{e0\_guess}, \beta_{guess})$

Subroutine 1
Partial Differential Eq. with
Finite Difference Approximation

SSE minimization with
LSQNONLIN $\quad k_s, D_{e0}, \beta$

SSE

Subroutine 2
ODE15s syntax and numerical
integration
with trapezoidal formula

$\bar{X}$

NO $\qquad$ SSEmin

Subroutine 3
SSE Calculation
$$SSE = \sum_{0}^{j} \left(X_{obs_j} - X_{p_j} \right)^2$$

YES

END

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Fig. A-1. Algorithmic of the Computer Programme Used in this Study.

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