CHAPTER 4

MATHEMATICAL MODEL DEVELOPMENT

4.1 Mathematical Modeling and the Scientific Method

In an elementary picture of the *scientific method* (refer to Figure 4.1), we identify a "real world" and a "conceptual world." The external world is the one we call real; here we observe various phenomena and behaviors, whether natural in origin or produced by artifacts. The conceptual world is the world of the mind—where we live when we try to understand what is going on in that real, external world. The conceptual world can be viewed as having three stages: observation, modeling, and prediction.

In the *observation* part of the scientific method we measure what is happening in the real world. Here we gather empirical evidence and "facts on the ground." Observations may be direct, as when we use our senses, or indirect, in which case some measurements are taken to indicate through some other reading that an event has taken place. For example, we often know a chemical reaction has taken place only by measuring the product of that reaction.
In this elementary view of how science is done, the *modeling* part is concerned with analyzing the above observations for one of (at least) three reasons. These rationales are about developing: *models that describe* the behavior or results observed; *models that explain* why that.

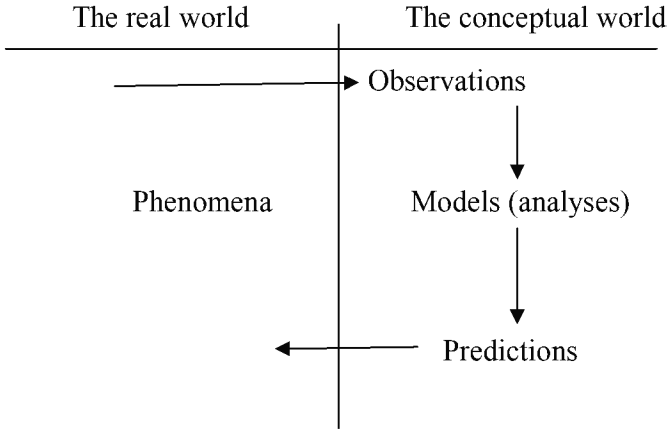

Figure 4.1: An elementary depiction of the *scientific method* that shows how our

Figure 4.1 shows how the conceptual models of the worlds are related to observations made within that real world (Dym and Ivey, 1980).

Behavior and results occurred as they did; or *models that allow us to predict* future behaviors or results that are as yet unseen or unmeasured.
In the *prediction* part of the scientific method we exercise our models to tell us what will happen in a yet-to-be-conducted experiment or in an anticipated set of events in the real

world. These predictions are then followed by observations that serve either to validate the model or to suggest reasons that the model is inadequate.

The last point clearly points to the looping; iterative structure apparent in Figure 10 It also suggests that modeling is central to all of the conceptual phases in the elementary model of the scientific method. We build models and use them to predict events that can confirm or deny the models. In addition, we can also improve our gathering of empirical data when we use a model to obtain guidance about where to look. [37]

4.2 Principles of Mathematical Modeling

Figure 4.2 depicts methodological modeling principles that are also captured in the following list of questions and answers:

• **Why?** What are we looking for? Identify the need for the model.
• **Find?** What do we want to know? List the data we are seeking.
• **Given?** What do we know? Identify the available relevant data.
• **Assume?** What can we assume? Identify the circumstances that apply.
• **How?** How should we look at this model? Identify the governing physical principles.
• **Predict?** What will our model predict? Identify the equations that will be used, the calculations that will be made, and the answers that will result.
• **Valid?** Are the predictions valid? Identify tests that can be made to *validate* the model, i.e., is it consistent with its principles and assumptions?
• **Verified?** Are the predictions good? Identify tests that can be made to *verify* the model, i.e., is it useful in terms of the initial reason it was done?
• **Improve?** Can we improve the model? Identify parameter values that are not adequately known, variables that should have been included, and/or assumptions/restrictions that could be lifted. Implement the iterative loop that we can call "model-validate-verify-improve-predict."
• **Use?** How will we exercise the model? What will we do with the model? [37]

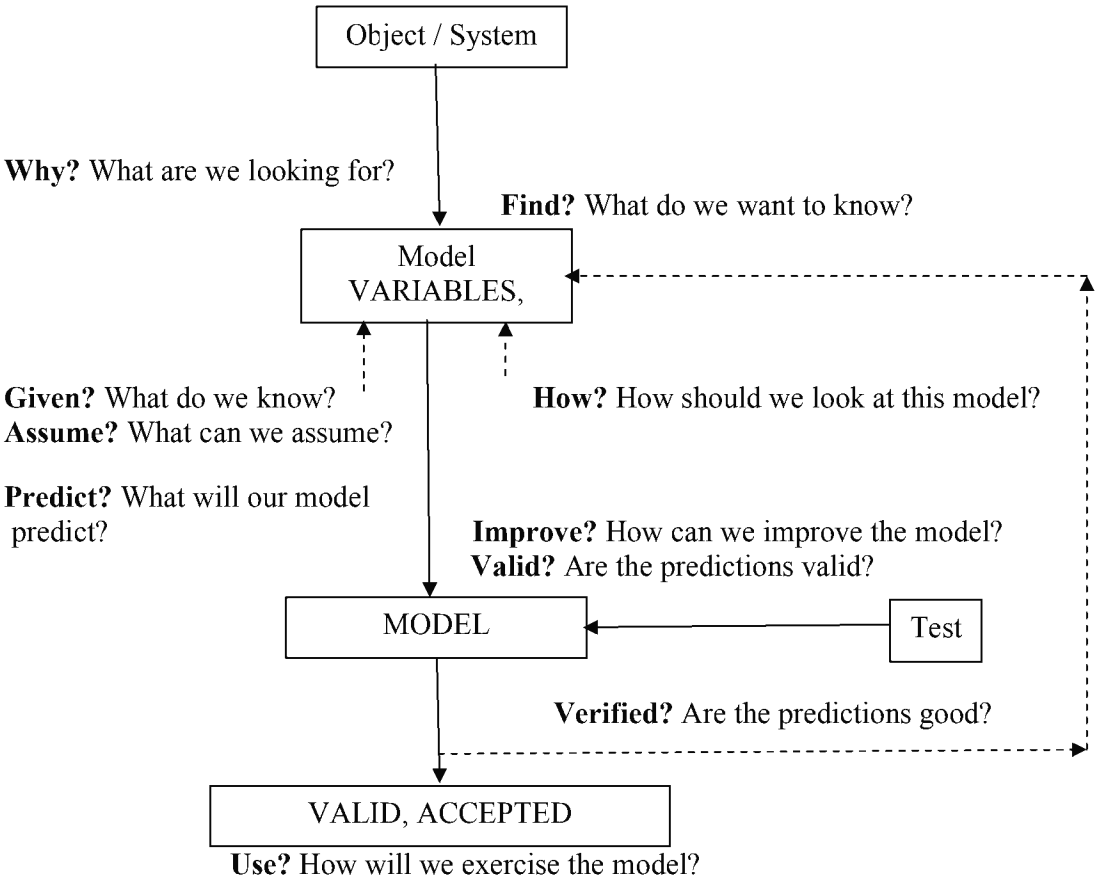

Figure 4.2 a first-order view of *mathematical modeling* that shows how the questions asked in a principled approach to building a model relate to the development of that model (inspired by Carson and Cobelli, 2001).

4.3 Uses of Mathematical Models

Without doubt, the most important result of developing a mathematical model of a chemical engineering system is the understanding that is gained of what really makes the process "tick." This insight enables you to strip away from the problem the many extraneous "confusion factors" and to get to the core of the system. You can see more clearly the cause-and-effect relationships between the variables.

Mathematical models can be useful in all phases of chemical engineering, from research and development to plant operations, and even in business and economic studies.

1. **Research and development:** determining chemical kinetic mechanisms and parameters from laboratory or pilot-plant reaction data; exploring the effects of different operating conditions for optimization and control studies; aiding in scale-up calculations.

2. Design: exploring the sizing and arrangement of processing equipment for dynamic performance; studying the interactions of various parts of the process, particularly when material recycle or heat integration is used; evaluating alternative process and control structures and strategies; simulating start-up, shutdown, and emergency situations and procedures.

3. Plant operation: troubleshooting control and processing problems; aiding in start-up and operator training; studying the effects of and the requirements for expansion (bottleneck-removal) projects; optimizing plant operation. It is usually much cheaper, safer, and faster to conduct the kinds of studies listed above on a mathematical model than experimentally on an operating unit. [38]

4.4. Mathematical Model Assumptions

The following assumptions were taken into consideration while modeling the PSA system: [21]

1. The adsorption rate was considered to be following a linear driving force (LDF) model, with single lumped mass transfer parameter.
2. The flow pattern of gas is axially dispersed plug flow model.
3. Radial temperature and concentration gradients are negligible.
4. Gas components are following ideal gas behavior.
5. Constant porosity along the bed.
6. The pressure drop along the bed is estimated by using the Ergun's equation.

The following assumptions were taken into consideration while modeling the **adiabatic adsorption system** [23,31]:

1. The gas phase behaves as an ideal gas.
2. The mass and velocity gradients are negligible in radial direction of the bed.
3. The bed is cylindrical and the axial dispersion is considered in the bulk phase.
4. The particles are cylindrical and they are packed randomly as layers with decreasing size upward into the fixed bed.
5. Pressure drop along the bed is negligible.
6. Adiabatic operation.

4.5 Basic Equations

4.5.1 Mass balance model development [14]

$$- D_L \varepsilon_b \frac{\partial^2 C}{\partial Z^2} + u_s \frac{\partial C}{\partial Z} + \frac{\partial C}{\partial t} + \frac{(1-\varepsilon_b)}{\varepsilon_b} \frac{\partial \overline{q}}{\partial t} = 0 \qquad (4.1)$$

$$\frac{1}{Pe} = \frac{0.65}{1 + 7\left[\frac{\varepsilon_b}{Re\ Sc}\right]^{0.5}} + \frac{0.67\ \varepsilon_b}{Re\ Sc} \qquad (4.2)$$

$$Pe = u_s d_p / D_L \qquad (4.3)$$

4. 5.1.1 Linear driving force model for mass transfer [15, 25]

$$\frac{\partial \overline{q}}{\partial t} = k(q^* - \overline{q}) = kK(C_i - C_i^*) \qquad (4.4)$$

$$\frac{1}{kK} = \frac{R_p}{3k_c} + \frac{R_p^2}{15 D_e} \qquad (4.5)$$

$$q^* = \frac{B_i\, q_{mi} P_i}{1 + \sum_{j=1}^{n} B_j P_j} \qquad (4.6)$$

$q_{mi} = K_1 + K_2 T$, $B_i = K_3 \exp(K_4 / T)$ (K_1:K_4 are Langmuir constant)

4.5.1.2 The correlation for effective diffusion coefficient [10, 19, 23 , 39]

$$D_{i,j} = 0.00158 \left(\frac{1}{M_{w,i}} + \frac{1}{M_{w,j}} \right)^{0.5} \frac{T^{1.5}}{P\, \upsilon_{i,j}^2\, \Omega_{Di,j}\, (\varepsilon / k_B T)} \qquad (4.7)$$

$$\Omega_{Di,J} = \frac{A}{(T^*)^B} + \frac{C}{\exp(DT^*)} + \frac{E}{\exp(FT^*)} + \frac{G}{\exp(HT^*)}$$

$$D_k = 0.97 \left(\frac{T}{M} \right)^{1/2} \qquad D_e = \left(\frac{1}{D_{i,j}} + \frac{1}{D_k} \right)^{-1}$$

$$T^* = \frac{k_B}{\nu_{AB}} T$$

4. 5.1.3 The correlation for external mass-transfer coefficient [25]

$Sh = 2.0 + 1.1\, Re^{0.6}\, Sc^{0.33}$ ---- $3 < Re < 10^4$ (4.8)

$Sh = k_c d_p / D_i$

$Re = \rho_i u_s d_p / \mu$, $Sc = \upsilon / D_i$, $\upsilon = \mu / \rho$

4.5.2 Momentum balance equation

Ergun's equation to predict pressure drop across the bed [15]

$$\frac{\partial p_{bed}}{\partial Z} = \frac{\mu 150 (1 - \varepsilon_b)^2}{d_p^2 \varepsilon_b^3} u_s - \frac{1.75 (1 - \varepsilon_b)}{d_p \varepsilon_b^3} \rho u_s^2 \qquad (4.9)$$

4.5.3 The energy balance [12,29]

$$\varepsilon_b C C_{v,g} \frac{\partial T_g}{\partial t} + u_s C C_{p,g} \frac{\partial T_g}{\partial Z} - \varepsilon_b \lambda_L \frac{\partial^2 T_g}{\partial Z^2} + (1 - \varepsilon_b) \rho_p C_s \frac{\partial T_s}{\partial t} \qquad (4.10)$$

$$-(1 - \varepsilon_b) \rho_p \sum_i (-\Delta H_i) \frac{\partial \overline{q}}{\partial t} + \frac{4 h_w}{\varepsilon_b d_{int}} (T_g - T_w) = 0$$

(4.11)

4.5.3.1 Solid phase energy balance [10,15]

$$\rho_p C_s \frac{\partial T_s}{\partial t} = \frac{6 h_f}{d_p}\left(T_g - T_s\right) + \rho_p \sum_i \left(-\Delta H_i\right) \frac{\partial \overline{q}}{\partial t}$$

5.3.2 Column wall energy balance [10&15]

$$\rho w C_{p,w} \frac{\partial T_w}{\partial t} = \alpha_w h_w \left(T_g - T_w\right) - \alpha_{wl} U \left(T_w - T_\infty\right) = 0 \qquad (4.12)$$

- Assuming the temperature of the column wall is the same as the temperature of the gas phase and solid phase (this would decrease computational time).
  Replace T_g, T_s and T_w with T

And by substituting eqn. (4.11) in (4.10) to get (4.13)

$$\varepsilon_b C_{v,g} \frac{\partial T}{\partial t} + u_s C_{p,g} \frac{\partial T}{\partial Z} - \varepsilon_b \lambda_L \frac{\partial^2 T}{\partial Z^2} + (1-\varepsilon_b) \frac{6 h_f}{d_p} T + \frac{4 h_w}{\varepsilon_b d_{\text{int}}} T = 0 \qquad (4.13)$$

Boundary conditions are: [9,2]

Z=0: $$\varepsilon_b D_L \frac{\partial C_i}{\partial Z}\Big|_{Z^+} = -u_s\left(C_i\Big|_{Z^-} - C_i\Big|_{Z^+}\right)$$

Z=L: $$\frac{\partial C_i}{\partial Z}\Big|_{Z^-} = 0$$

Z=0: $$\varepsilon_b \lambda_L \frac{\partial T_g}{\partial Z}\Big|_{Z^+} = -u_s CC_{p.g}\left(T_g\Big|_{Z^-} - T_g\Big|_{Z^+}\right)$$

Z=L: $$\frac{\partial T_g}{\partial Z}\Big|_{Z^-} = 0$$

Initial conditions are: [30,31]
C_i (Z, 0) = C_o

And: T (Z, 0) = T_{atm}

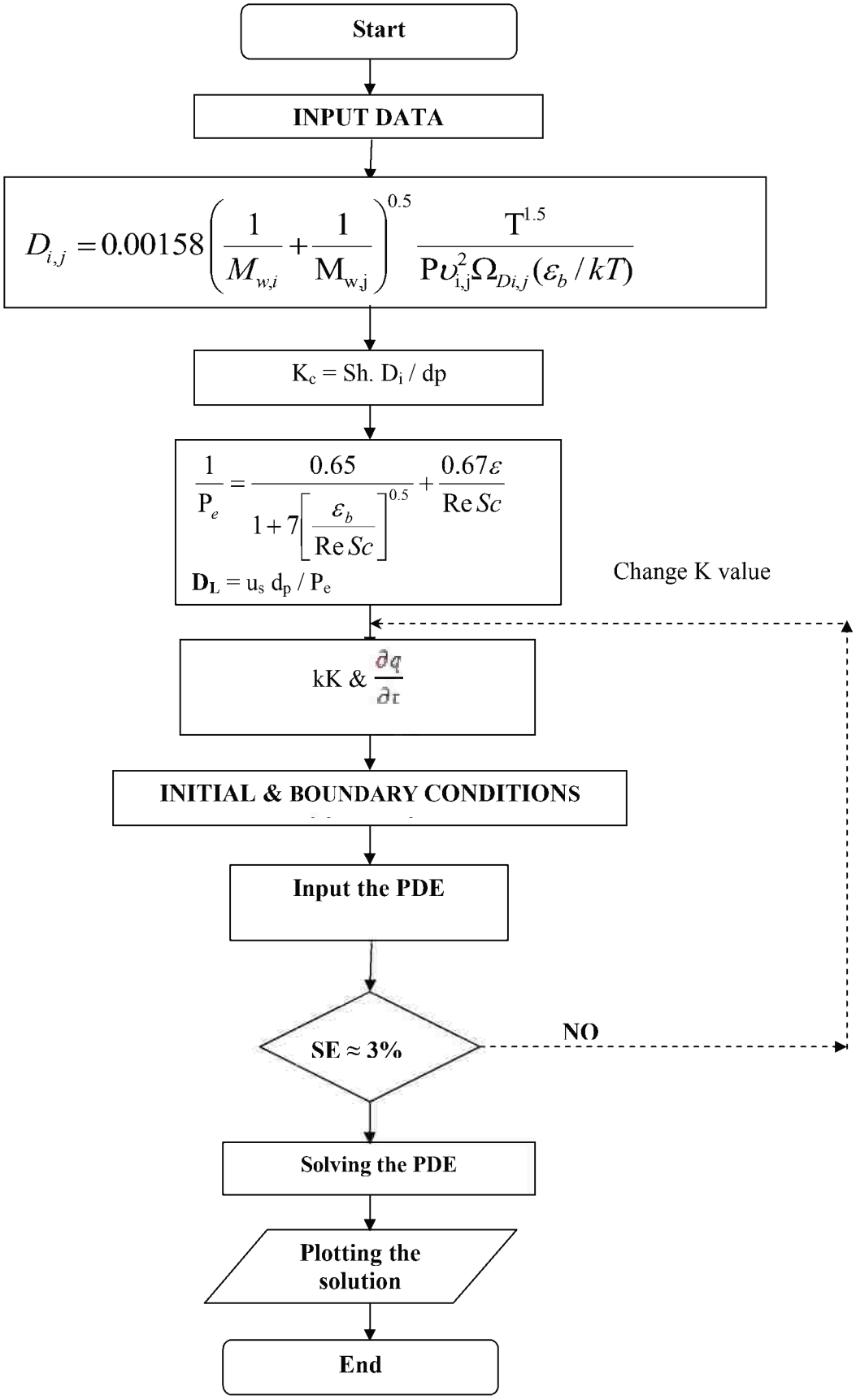

Figure 4.3 Block diagram of the nitrogen producing process calculation

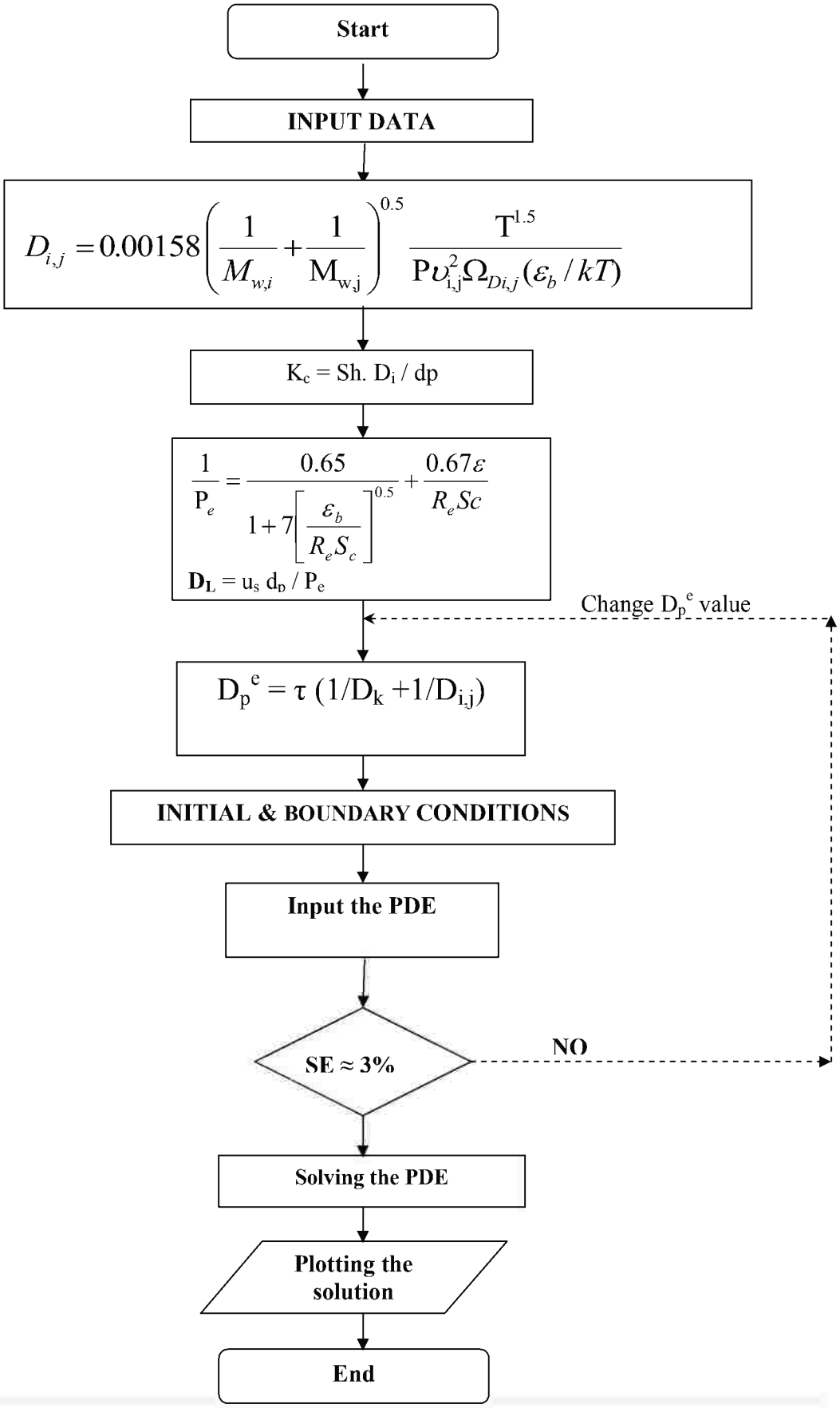

Figure 4.4 Block diagram of the Dehydration process calculation

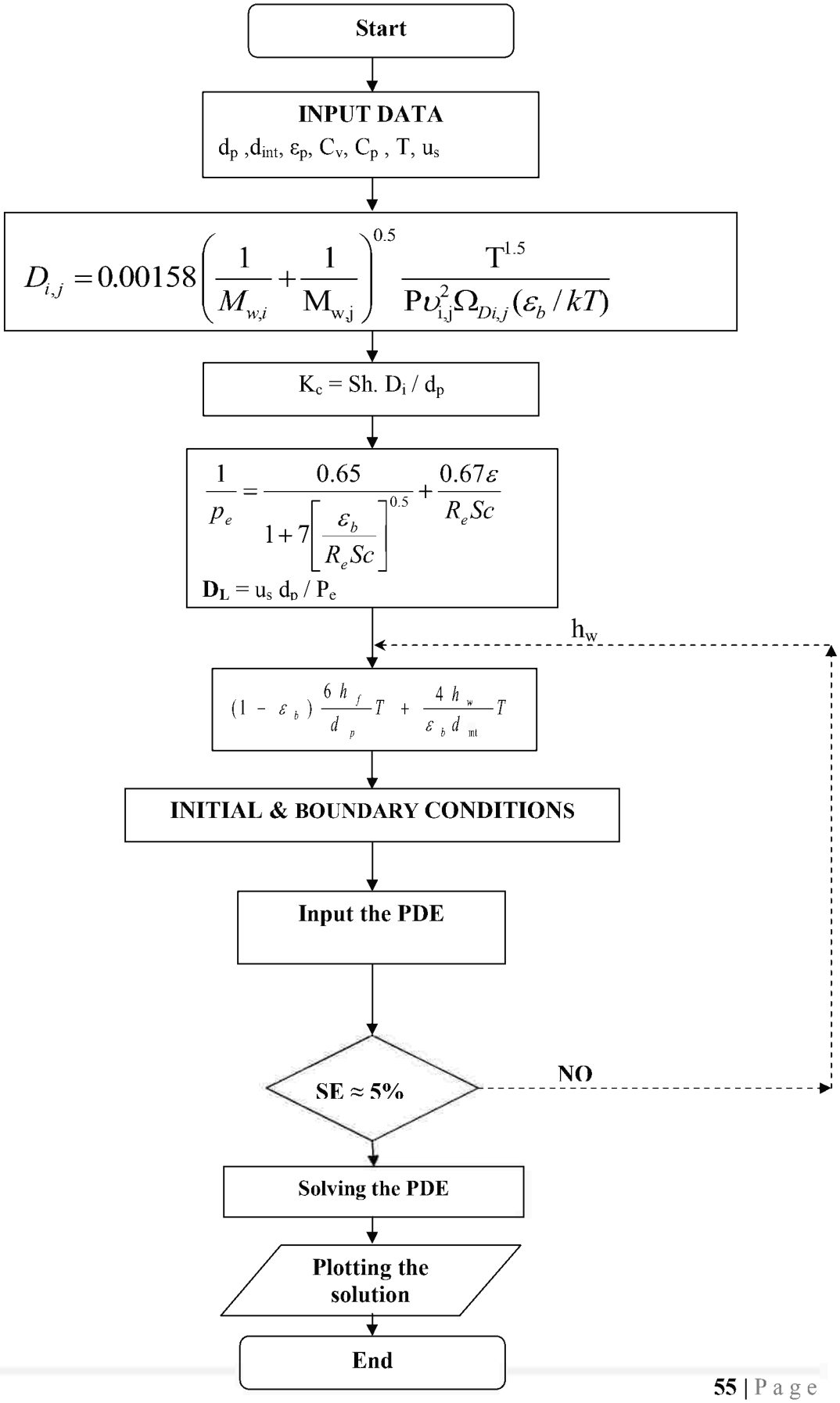

Figure 4.5 Block diagram of the temperature calculation